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Chiral alkaline earth metal complexes with M–Se direct bond (M = Mg, Ca, Sr, Ba): syntheses, structures and ϵ -caprolactone polymerisation†

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We report here a series of enantiomeric pure alkaline earth metal complexes, each with a metallic direct bond of selenium, with {HN(*R*-*CHMePh)(P(Se)Ph₂)} (**1a**) and {HN(*S*-*CHMePh)(P(Se)Ph₂)} (**1b**), synthesised using two routes. The first route involves a trans metalation reaction of enantiomeric pure potassium phosphinoselenoic amide [K{N(*R*-*CHMePh)(Ph₂P(Se))}(THF)_{*n*}] (**2a**) or [K{N(*S*-*CHMePh)(Ph₂P(Se))}(THF)_{*n*}] (**2b**) prepared from the reaction between either **1a** or **1b** and [KN(SiMe₃)₂], and the corresponding alkaline earth metal diiodides in THF at room temperature to afford the enantiomeric pure complexes of composition [M{N(*R*-*CHMePh)P(Se)Ph₂}(THF)_{*n*}] [M = Mg (**3a**), *n* = 1; M = Ca (**4a**), Sr (**5a**) and Ba (**6a**), *n* = 2] and [M{N(*S*-*CHMePh)P(Se)Ph₂}(THF)_{*n*}] [M = Mg (**3b**), *n* = 1; M = Ca (**4b**), Sr (**5b**) and Ba (**6b**), *n* = 2]. The same heavier alkaline earth metal complexes (**4a–6a** and **4b–6b**) can also be obtained through the silylamine elimination method using the corresponding metal bis(trimethylsilyl)amides [M{N(SiMe₃)₂}(THF)_{*n*}] (M = Ca, Sr, Ba) with phosphinoselenoic amine ligands **1a** and **1b** in ambient conditions. The solid-state structures of the metal complexes **4a–6a** and **4b–6b** were established using single-crystal X-ray diffraction analysis. In the solid state, all the metal complexes crystallise in the monoclinic *P*2₁ space group and each phosphinoselenoic amido ligand is ligated to the metal ion in a bidentate fashion. We also report the syntheses and structures of chiral amidophosphine-borane ligands {HN(*R*-*CHMePh)(P(BH₃)Ph₂)} (**7a**) and {HN(*S*-*CHMePh)(P(BH₃)Ph₂)} (**7b**) and the corresponding homoleptic barium complexes of composition [Ba{N(*R*-*CHMePh)P(BH₃)Ph₂}(THF)₂] (**8a**) and [Ba{N(*S*-*CHMePh)P(BH₃)Ph₂}(THF)₂] (**8b**). The molecular structures of **8a** and **8b** in the solid state confirm the attachment of chiral amidophosphine-borane ligands to the barium ions. The complexes **5** and **6** were tested as catalysts for the ring-opening polymerisation of ϵ -caprolactone. High activity in relation to the barium complexes **6a** and **6b** is observed, with moderate to narrow polydispersity index.

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Introduction

Efficient synthesis of optically active compounds is one of the most important tasks of synthetic organic chemistry. The most promising methodology is catalytic asymmetric synthesis using a chiral metal centre. Among many useful metal species, alkaline earth metals have long been recognised as belonging to a class of less toxic and less harmful metals.^{1,2} However, besides the potential high utility of the alkaline earth species as a homogeneous catalyst for ring-opening polymerisation of various cyclic esters,^{3,4} polymerisation of styrene and dienes,⁵ and hydroamination and hydrophosphination reactions of

alkenes and alkynes,⁶ its use in synthetic organic chemistry, especially in asymmetric synthesis as chiral catalyst, has been quite limited when compared to transition metal catalysts.^{1,2} Recently it was revealed that several catalytic asymmetric carbon–carbon bond-forming and related reactions proceeded smoothly in high enantioselectivities with the use of chiral Ca, Sr, and Ba catalysts.^{7–10} Their strong Brønsted basicity and mild Lewis acidity are promising and attractive characteristics and can influence their catalytic activity as well as their chiral modification capability in a positive manner.

A wide variety of chiral phosphorus ligands have been prepared over the years, and their coordination chemistry with various metal ions has been studied extensively.¹¹ In homogeneous catalyses, bidentate phosphine ligands, especially those having *C*₂ symmetry, have usually been employed. In most cases the stereogenic centres are chiral phosphorus atoms or phosphines with chiral hydrocarbon substituents as derivatives of the chiral pool.^{11a} The synthesis and limited use of heteroatom-substituted phosphines and their transition metal complexes

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have received some attention lately as a result of the search for new structural diversity.^{11b} However little has been published on the use of chiral amines as backbone for chiral phosphorus ligands. These chiral P, N ligands, which usually coordinate *via* the phosphorus atom to the centre metal, were basically used in transition metal and rare earth metal chemistry.¹²

Recently we introduced various amidophosphine chalcogenide and borane ligands with P, N, E (E = O, S, Se, BH₃) as donor atoms, into alkaline earth metal chemistry to study their coordination properties.¹³ These unique ligands are potentially capable of coordinating through the hard nitrogen and phosphorus donor atoms as well as the soft E donor atom. Bearing these characteristic features in mind, as well as our continuing interest in highly electropositive alkaline earth metals, catalytic activity and the vast potential of the field in asymmetric synthesis, we proposed to synthesise various novel chiral alkaline earth metal complexes stabilised by chiral amidophosphine selenoids and boranes, to explore the chemistry of alkaline earth metals in asymmetric synthesis. To achieve our target compounds with high-purity and good yield, we chose chiral phosphineamines HN(*R*-*CHMePh)(PPh₂) and HN(*S*-*CHMePh)(PPh₂), which were originally introduced by Brunner into coordination chemistry of the late transition metals.¹⁴ Roesky *et al.* introduced the same ligands into zirconium chemistry,¹⁵ group 3 and lanthanide chemistry.¹⁶ We synthesise the corresponding enantiomeric pure amidophosphine-selenoids [HN(*R*-*CHMePh)P(Se)Ph₂] (**1a**) and [HN(*S*-*CHMePh)P(Se)Ph₂] (**1b**) in order to introduce them into the alkaline earth metal chemistry. We envisage that these ligands potentially coordinate through the amido nitrogen and selenium atoms, thus forming a four-membered metallacycle with a centre metal ion.

In this context, detailed synthetic and coordination properties of homoleptic alkaline earth metal complexes of molecular composition [M{N(*R*-*CHMePh)-P(Se)Ph₂}₂(THF)₂] [M = Mg (**3a**), Ca (**4a**), Sr (**5a**) and Ba (**6a**)] and [M{N(*S*-*CHMePh)P(Se)Ph₂}₂(THF)₂] [M = Mg (**3b**), Ca (**4b**), Sr (**5b**) and Ba (**6b**)], were described with the chiral phosphinoselenoic amide ligands {HN(*R*-*CHMePh)P(Se)Ph₂} (**1a**) and {HN(*S*-*CHMePh)P(Se)Ph₂} (**1b**). In addition, we report the synthesis and structures of the chiral amidophosphine-borane ligands {HN(*R*-*CHMePh)P(BH₃)Ph₂} (**7a**) and {HN(*S*-*CHMePh)P(BH₃)Ph₂} (**7b**) and their corresponding homoleptic barium complexes of composition [Ba{N(*R*-*CHMePh)P(BH₃)Ph₂}₂(THF)₂] (**8a**) and [Ba{N(*S*-*CHMePh)P(BH₃)Ph₂}₂(THF)₂] (**8b**). The details of the ring-opening polymerisation of ϵ -caprolactone using complexes **5** and **6** are also presented.

Results and discussion

To introduce the chiral phosphinoselenoic amide ligands {HN(*R*-*CHMePh)P(Se)Ph₂}[−] and {HN(*S*-*CHMePh)P(Se)Ph₂}[−] into alkaline earth metal chemistry, we first synthesised the protio ligands {HN(*R*-*CHMePh)P(Se)Ph₂} (**1a**) and {HN(*S*-*CHMePh)P(Se)Ph₂} (**1b**) and their potassium salts [K{N(*R*-*CHMePh)(Ph₂P(Se))}(THF)_{*n*}] (**2a**) and [K{N(*S*-*CHMePh)(Ph₂P(Se))}(THF)_{*n*}] (**2b**). The potassium salts **2a** and **2b** were reacted with alkaline earth metal diiodide (MI₂) to obtain corresponding homoleptic complexes.

Chiral phosphinoselenoic amide ligands

The chiral phosphinoselenoic amides {HN(*R*-*CHMePh)(Ph₂P(Se))} (**1a**) and {HN(*S*-*CHMePh)(Ph₂P(Se))} (**1b**) were prepared in enantiomeric pure forms in a similar method as analogous [Ph₂P(Se)NHCHPh₂] and [Ph₂P(Se)NHCHPh₃] were prepared, that is, they were synthesised in quantitative yield by the treatment of pure 1,1-diphenyl-*N*-(1-phenylethyl)phosphinamines {HN(*R*-*CHMePh)(Ph₂P)} and {HN(*S*-*CHMePh)(Ph₂P)} with slight excess elemental selenium in 1 : 1.2 molar ratio at ambient temperature in THF solvent (see Scheme 1).^{13c,17} Both the enantiomeric pure compounds **1a** and **1b** were characterised using standard ¹H, ¹³C{¹H}, ³¹P{¹H} NMR spectra, combustion analysis and the solid-state structures were established using single-crystal X-ray diffraction analysis.

Both the enantiomeric pure compounds **1a** and **1b** show strong absorption at 559 cm^{−1} in their FT-IR spectrum and can be assigned to the characteristic P=Se bond stretching frequency and it is comparable with the previously observed values: 568 cm^{−1} for [Ph₂P(Se)NHCHPh₂], 599 cm^{−1} for [Ph₂P(Se)NHCHPh₃] and 535 cm^{−1} for [Ph₂P(Se)NHC(CH₃)₃], which were reported by our group.¹³ ¹H NMR spectrum of isomers **1a** and **1b** shows a doublet resonance signal at δ 1.42 ppm (*J*_{H-H} = 6.76 Hz) and a multiplet centred at 4.52 ppm respectively, corresponding to the methyl protons and CH proton attached to the α -position of amine nitrogen atom. A broad resonance signal at δ 2.57 ppm represents the amine (N-H) proton of the ligand moiety. These values are observed as slightly downfield shifted when compared to free chiral phosphineamine [Ph₂PNH{*R*-*CHMePh}] or [Ph₂PNH{*S*-*CHMePh}] due to the attachment of the selenium atom to the phosphorous atom.^{14a}

Fig. 1 Solid-state structures of ligands **1a** (left) and **1b** (right). Selected bond lengths (Å) and bond angles (°).

1a. P1–Se1 2.1219(15), P1–N1 1.671(5), P1–C9 1.818(6), P1–C15 1.815(6), C1–N1 1.454(7), C1–C2 1.551(10), C1–C3 1.517(9), N1–P1–Se1 116.4(2), C9–P1–C15 106.5(3), C9–P1–Se1 111.0(2), C15–P1–Se1 112.8(2), C9–P1–N1 105.7(3), C15–P1–N1

Scheme 1 Synthesis of chiral-phosphinoselenoic amide ligands.

103.6(3), P1–N1–C1 120.8(4), N1–C1–C2 110.7(6), N1–C1–C3 112.4(5), C2–C1–C3 109.7(5).

1b. P1–Se1 2.126(2), P1–N1 1.645(5), P1–C9 1.808(7), P1–C15 1.802(7), C1–N1 1.470(9), C1–C2 1.532(11), C1–C3 1.521(10), N1–P1–Se1 116.0(2), C9–P1–C15 106.5(3), C9–P1–Se1 110.5(3), C15–P1–Se1 112.9(3), C9–P1–N1 106.2(3), C15–P1–N1 104.1(3), P1–N1–C1 121.5(5), N1–C1–C2 110.4(7), N1–C1–C3 111.9(6), C2–C1–C3 110.2(6).

The solid-state structures of **1a** and **1b** were confirmed using single-crystal X-ray diffraction analysis. The details of the structural parameters are given in Table TS1 in ESI.† The solid-state structures of both enantiomers and selected bond lengths and bond angles are shown in Fig. 1. From the molecular structure of two compounds, it is clear that both enantiomers are non-super imposable mirror images and crystallise in the triclinic space group *P*1, with one molecule in the unit cell. The P=Se bond distances, 2.1219(15) Å (for **1a**) and 2.126(2) Å (for **1b**), are in good agreement with our previously reported values: 2.1019(8) Å for [Ph₂P(Se)NH(2,6-Me₂C₆H₄)],^{13a} 2.1086(12) Å for [Ph₂P(Se)NHCHPh₂],^{13c} 2.1166(8) Å for [Ph₂P(Se)NHCHPh₃]^{13c} and 2.1187(8) Å for [Ph₂P(Se)NHC(CH₃)₃].^{13g} P1–N1 distance [1.671(5) for **1a** and 1.645(5) Å for **1b**] and C1–N1 distance [1.454 (7) for **1a** and 1.470(9) Å for **1b**] are also similar to those of phosphinoselenoic amides [Ph₂P(Se)NHR]: P1–N1 1.656(3) Å, C1–N1 1.441(4) Å for R = 2,6-Me₂C₆H₄, P1–N1 1.642(4) Å, C1–N1 1.459 (6) Å for R = CHPh₂, P1–N1 1.664(2) Å, C1–N1 1.496(4) Å for R = CPh₃ and P1–N1 1.655(3) Å, C1–N1 1.494(4) Å.

Potassium complexes

The potassium salts of molecular composition [K{N(R-CHMePh)(Ph₂P(Se))}{THF}_n] (**2a**) and [K{N(S-CHMePh)(Ph₂P(Se))}{THF}_n] (**2b**) were readily prepared by the reaction of compound **1a** or **1b** with potassium precursor [K(N(SiMe₃)₂)] in THF *via* the elimination of volatile bis(trimethylsilyl)amine (see Scheme 2).¹⁷ The potassium complexes **2a** and **2b** were characterised using spectroscopic and analytical techniques. However, suitable crystals for X-ray diffraction analysis were not obtained due to high solubility of the compounds (**2a,b**) in the THF solvent. In FT-IR spectra, the compound (**2a,b**) showed a strong absorption band at 570 cm⁻¹ which can be best assigned to characteristic P=Se bond stretching and it is in good agreement with our previously described potassium salts of phosphinoselenoic amides: 569 cm⁻¹ for [{(THF)₂KPh₂P(Se)-N(CHPh₂)₂}] and 570 cm⁻¹ for [K(THF)₂{Ph₂P(Se)-N(CMe₃)₃}]_n.^{13c,g}

Scheme 2 Synthesis of potassium salts **2a** and **2b** of chiral phosphinoselenoic amides.

³¹P{¹H} NMR spectra of compound (**2a,b**) showed a sharp singlet resonance signal at δ 48.6 ppm, which is up-field shifted (56.1 ppm) compared to that of the free ligand (**1a,b**), indicating clear evidence of the formation of potassium salt. Two multiplet signals in the region of 3.50–3.53 ppm and 1.37–1.40 ppm in ¹H spectra also confirm the presence of coordinated THF molecules in the complex **2a,b** and using integration it was calculated that three THF molecules were coordinated. One set of signals was observed for the compound (**2a,b**) in the ¹H and ¹³C{¹H} NMR spectra, similar to the free ligand, indicating a dynamic behaviour of the complexes in the solution state.

Chiral alkaline earth metal complexes

The alkaline earth metal complexes of composition [K²-{Ph₂P(Se)N(R-CHMePh)}₂M(THF)₂] (M = Mg (**3a**), Ca (**4a**), Sr (**5a**) and Ba (**6a**)) and [K²-{Ph₂P(Se)N(S-CHMePh)}₂] [M = Mg (**3b**), Ca (**4b**), Sr (**5b**) and Ba (**6b**)] were prepared as pure enantiomers by two synthetic methods. In the first method, ligands **1a** or **1b** were treated with corresponding alkaline earth metal bis(trimethylsilyl)amides [M{N(SiMe₃)₂}(THF)_n] (M = Ca, Sr and Ba) in 2 : 1 molar ratio at ambient temperature in THF to afford the desired complexes **4–6** *via* the elimination of volatile trimethylsilylamine (see Scheme 3).¹⁷ In the second, a salt metathesis reaction was employed in which alkaline earth metal diiodides MI₂ (M = Mg, Ca, Sr and Ba) were charged with potassium salt [K{N(R-CHMePh)(Ph₂P(Se))}{THF}_n] (**2a**) or [K{N(S-CHMePh)(Ph₂P(Se))}{THF}_n] (**2b**) in 1 : 2 molar ratio at ambient temperature in THF (see Scheme 3) through the elimination of insoluble potassium iodide. Both methods were used to isolate calcium, strontium and barium complexes. However, the magnesium complexes **3a** and **3b** were obtained through the second method only. All the complexes are soluble in polar solvents such as THF and dioxan and insoluble in hydrocarbon solvents such as pentane and hexane. Complexes **3a,b–6a,b** were re-crystallised through slow evaporation from a THF/*n*-pentane solution (1 : 2) at –35 °C. All the complexes were fully characterised using standard analytical/spectroscopic techniques and the solid-state structures of **4a,b–6a,b** were confirmed using single-crystal X-ray diffraction analysis.

A strong absorption at 562 cm⁻¹ (for **3a,b**), 559 cm⁻¹ for (**4a,b**), 552 cm⁻¹ (for **5a,b**) and 553 cm⁻¹ (for **6a,b**) in FT-IR spectra indicates the presence of P=Se bond in each metal complex. In ¹H NMR spectra, the resonance of one methine proton (CH) α to amido nitrogen was observed as multiplets (δ 4.58–4.62 ppm for **3a,b**, 4.26–4.34 ppm for **4a,b**, 4.47–4.55

Scheme 3 Synthesis of alkaline earth metal complexes of chiral phosphinoselenoic amides.

ppm for **5a,b** and 4.21–4.29 ppm for **6a,b**), which are almost uninfluenced compared to those of free ligands **1a** and **1b** (4.52 ppm). Doublet signals centred at δ 1.86 (**3a,b**), 1.68 (**4a,b**), 1.20 (**5a,b**) and 1.48 ppm (**6a,b**) were noticed with coupling constants in the range $J_{H-H} = 6.20$ – 6.85 Hz, which can be assigned to methyl protons ($-CH_3$) group attached to the chiral carbon atom in each complex. In $^{31}P\{^1H\}$ NMR spectra, the magnesium complexes **3a,b** showed a sharp resonance signal at δ 45.1 ppm, which is upfield shifted compared to free ligands **1a** and **1b**. In contrast, the heavier alkaline earth metal complexes **4a,b–6a,b** displayed one singlet resonance signal at δ 68.9 ppm, which is significantly downfield shifted compared to that of free ligands **1a** and **1b** (56.1 ppm) upon coordination of calcium, strontium or barium ion onto the ligand fragment **1**. This difference can be attributed to the lower charge of heavier alkaline earth metals, which subsequently causes deshielding of the magnetic field in comparison with the magnesium ion. Similar observations were made in our previously reported complex $[(THF)_3M\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ [$M = Ca, Sr, Ba$] (δ 71–73 ppm) with respect to the magnesium complex $[(THF)_3Mg\{Ph_2P(Se)NCH_2CH_2NPPh_2(Se)\}]$ (43.7 ppm).^{13f} Both the phosphorus atoms present in the ligand moieties $\{Ph_2P(Se)N(*CHMePh)\}^-$ are chemically equivalent.

Fig. 2 Solid-state structures of calcium complexes **4a** and **4b**. Hydrogen atoms are omitted for clarity except methyl and methine hydrogen atoms. Selected bond lengths (Å) and bond angles ($^\circ$).

4a. P1–Se1 2.1444(10), P1–N1 1.603(3), P1–C9 1.829(4), P1–C15 1.831(4), C1–N1 1.489(5), C1–C2 1.536(6), C1–C3 1.523(5), P2–Se2 2.1389(10), P2–N2 1.607(3), P2–C35 1.840(4), C21–N2 1.488(4), C21–C22 1.527(5), C21–C23 1.531(6), Ca1–Se1 3.0303(9), Ca1–N1 2.441(3), Ca1–O1 2.400(3), Ca1–O2 2.444(3), Ca1–Se2 3.0794(9), Ca1–N2 2.426(3), N1–P1–Se1 108.33(12), C1–N1–P1 119.8(2), C2–C1–N1 111.9(3), C9–P1–C15 99.44(17), N1–Ca1–Se1 66.88(8), O1–Ca1–O2 79.03(13), N2–Ca1–Se2 66.15(7), N2–P2–Se2 108.42(12), C21–N2–P2 116.9(3), N1–Ca1–N2 104.74(11), Se1–Ca1–Se2 162.60(3).

4b. P1–Se1 2.1443(17), P1–N1 1.611(5), P1–C9 1.835(6), P1–C15 1.825(6), C1–N1 1.482(8), C1–C2 1.527(9), C1–C3 1.526(8), P2–Se2 2.1420(16), P2–N2 1.602(5), P2–C35 1.838(7),

C21–N2 1.498(7), C21–C22 1.533(8), C21–C23 1.510(10), Ca1–Se1 3.0327(15), Ca1–N1 2.444(5), Ca1–O1 2.440(5), Ca1–O2 2.394(5), Ca1–Se2 3.0817(14), Ca1–N2 2.430(5), N1–P1–Se1 108.3(2), C1–N1–P1 119.8(4), C2–C1–N1 111.9(5), C9–P1–C15 99.8(3), N1–Ca1–Se1 66.92(13), O1–Ca1–O2 78.8(2), N2–Ca1–Se2 66.19(11), N2–P2–Se2 108.7(2), C21–N2–P2 117.1(4), N1–Ca1–N2 104.37(18), Se1–Ca1–Se2 162.75(5).

The complexes **3a,b–6a,b** represent, to the best of our knowledge, the first alkaline earth metal complexes having chiral phosphinoseleno amides in the coordination sphere. Thus, molecular structure determinations of these complexes were performed by single-crystal X-ray diffraction techniques. The small crystals obtained from THF/pentane solution of complex **3a,b** were found weakly diffracting; however, the solid-state structures of other complexes **4a,b–6a,b** confirmed the bidentate coordination of the chiral ligand phosphinoseleno amide. The details of the structural parameters are given in Table TS1 in the ESI† As a result of the similar ionic radii of the alkaline earth metal ions, the solid-state structures of compounds **4a–6a** are isostructural, whereas **4b–6b** form the corresponding enantiomers. All the six compounds crystallise in the monoclinic space group $P2_1$, with two molecules in the unit cell. Fig. 2 and 3 display the molecular structures of the calcium and barium complexes respectively. Fig. S1 in the ESI† represents the corresponding strontium complexes. In the calcium complexes **4a** and **4b**, the central calcium atom in each case adopts a distorted octahedral geometry due to κ^2 -coordination from two ligand moieties and two THF molecules. Each chiral ligand fragment $\{N(R-*CHMePh)P(Se)Ph_2\}^-$ and $\{N(S-*CHMePh)P(Se)Ph_2\}^-$ is bonded through the amido nitrogen atom and one selenium atom. The Ca–N distances [2.441(3) and 2.426(3) Å] for **4a** and [2.444(5) and 2.430(5) Å] for **4b** are in good agreement with our structurally characterised calcium complexes: 2.479(5) Å for $[Ca\{Ph_2P(Se)NCHPh_2\}_2(THF)_2]$,^{13c} 2.4534(14) Å for $[Ca\{Ph_2P(BH_3)N-CHPh_2\}_2(THF)_2]$,^{13d} 2.386(8) Å for $[Ca\{C_2H_4(NPh_2P=Se)_2\}-(THF)_3]$ ^{13f} and 2.451(3) Å for $[Ca\{Ph_2P(Se)NC(CH_3)_3\}_2(THF)_2]$.^{13g} However, the observed calcium–nitrogen bond distances are slightly elongated compared to the calcium–nitrogen covalent bond [2.361(2) and 2.335(2) Å] reported for $[Ca(Dipp_2DAD)(THF)_4]$ ($Dipp_2DAD = N,N'$ -bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene in the literature.¹⁸ The observed Ca–Se bond distances of 3.0303(9) and 3.0794(9) Å for **4a** and 3.0327(15) and 3.0817(14) Å for **4b** are slightly elongated but within the range of the reported Ca–Se distance of 2.9889(8) Å for structurally characterised complex $[Ca\{Ph_2P(Se)NCHPh_2\}_2(THF)_2]$ ^{13c} and 2.9619(3) Å for the complex $[Ca\{Ph_2P(Se)NC(CH_3)_3\}_2(THF)_2]$ ^{13g} and 3.252(2) Å for the complex $[Ca\{C_2H_4(NPh_2P=Se)_2\}_2(THF)_3]$.^{13d} The literature reported 2.945(1) Å for $[(THF)_2Ca\{(PyCH)(Se)PPh_2\}_2]$,¹⁹ 2.93 Å to 3.00 Å reported for $[(THF)_4Ca(SeMeS')_2]$ and 2.958(2) Å to 3.001(2) Å reported for $[(THF)_2Ca(Se_2PPh_2)_2]$.^{20,21} The considerably elongated Ca–P distance of 3.2960(13), 3.3013(11) Å in **4a** and 3.295(2), 3.3069(19) Å in **4b**, was greater than the sum of the covalent radii of calcium and phosphorus (3.07 Å), indicating no interaction between calcium and phosphorus atoms. The P=Se distances [2.1444(10), 2.1389(10) Å for **4a** and 2.1443(17), 2.1420(16) Å for **4b**] are slightly elongated but within the same range as that of the free ligand **1a** [2.1219(15) Å]. The P–N

distances [1.603(3), 1.607(3) Å for **4a** and 1.611(5), 1.602(5) Å for **4b**] are slightly shortened compared to the free ligand **1a** [1.671(5) Å]. The central calcium atom is additionally ligated by two THF molecules with a Ca–O distance of 2.400(3), 2.444(3) Å for **4a** and 2.440(5), 2.394(5) Å for **4b** to adopt the calcium atom distorted octahedron geometry. Thus two four-membered metallacycles Ca1–Se1–P1–N1 and Ca1–Se2–P2–N2 are formed due to the ligation of two ligand moieties *via* selenium and amide nitrogen atoms. The plane containing N1, P1, Se1 and Ca1 makes a dihedral angle of 82.02° (for **4a**) and 82.38° (for **4b**) with the plane having N2, P2, Se2 and Ca1, indicating that two four-membered metallacycles are almost perpendicular to each other. The O1–Ca1–O2 bond angle is found to be 79.03(13)° for **4a** and 78.8(2)° for **4b**. Thus the enantiomeric pure compounds **4a** and **4b** are seen to be fully structurally characterised calcium complexes and, to the best of our knowledge, these are the first examples of chiral calcium complexes with a calcium–selenium direct bond.

The strontium complex **5a** is isostructural to calcium complex **4a** due to similar ionic radii of the metal centres ($\text{Ca}^{2+} = 1.00$ Å; $\text{Sr}^{2+} = 1.18$ Å for CN = 6)²² and the strontium complex **4b** forms the corresponding enantiomer (Fig. S1 in ESI†). In the enantiomeric pure strontium complexes **5a** and **5b** the strontium ion is six-fold coordinated by the two mono-anionic $\{\text{N}^*(\text{CHMePh})\text{P}(\text{Se})\text{Ph}_2\}^-$ ligands and two THF molecules. Each ligand $\{\text{N}^*(\text{CHMePh})\text{P}(\text{Se})\text{Ph}_2\}^-$ coordinates in κ^2 fashion *via* the amido nitrogen atom and one selenium atom to adopt a distorted octahedral geometry for the strontium ion. The Sr–N distances [(2.570(7) and 2.542(7) Å) for **5a** and (2.564(5) and 2.569(5) Å) for **5b**] fit well with our previously reported strontium–nitrogen bond distances: 2.609(3) Å for the complex $[\text{Sr}\{\text{Ph}_2\text{P}(\text{Se})\text{NCHPh}_2\}_2(\text{THF})_2]$ and 2.591(4) Å for $[\text{Sr}\{\text{Ph}_2\text{P}(\text{BH}_3)\text{NCHPh}_2\}_2(\text{THF})_2]$ and 2.540(5) Å for $[\text{Sr}\{\text{C}_2\text{H}_4(\text{NPh}_2\text{P}=\text{Se})_2\}(\text{THF})_3]$.¹³ The Sr–Se bond distances of 3.1726(10) and 3.2141(10) Å for **5a**, 3.2151(8) and 3.1722(9) Å for **5b** are observed, which are quite long, compared to the calcium analogue [3.0327(15) to 3.0817(14) Å] due to the larger ionic radius of the Sr^{2+} ion. The observed Sr–Se distances in compounds **5a** and **5b** are within the range of Sr–Se distances [3.138(7) to 3.196(9) Å] of structurally characterised complex $[(\text{THF})_3\text{Sr}(\text{Se}_2\text{PPh}_2)_2]$ published by Westerhausen and coworkers^{23b} and 3.066(1) Å for the complex $[\text{Sr}\{\text{Se}(2,4,6\text{-tBu}_3\text{C}_6\text{H}_2)_2\}_2(\text{THF})_4]$ ^{23a} and 3.1356(9) Å for the complex $[\text{Sr}\{\text{Ph}_2\text{P}(\text{Se})\text{NCHPh}_2\}_2(\text{THF})_2]$ and 3.2788(10) Å for the complex $[\text{Sr}\{\text{C}_2\text{H}_4(\text{NPh}_2\text{P}=\text{Se})_2\}(\text{THF})_3]$ reported by us.^{13cd} No interaction was observed between the strontium ion and phosphorus atom as the Sr–P distances of 3.449(2), 3.4586(19) Å in **5a** and 3.4520(17), 3.4539(15) Å in **5b** are greater than the sum of the covalent radii (3.25 Å). Two four-membered metallacycles Sr1–Se1–P1–N1 and Sr1–Se2–P2–N2 are formed due to the ligation of two ligand moieties *via* selenium and amido nitrogen atoms. The plane containing N1, P1, Se1 and Sr1 makes a dihedral angle of 81.13° (for **5a**) and 81.14° (for **5b**) against the plane with N2, P2, Se2 and Sr1, indicating that two four-membered metallacycles are almost perpendicular to each other as we observed in the case of calcium complexes (**4a** and **4b**). Thus the enantiomeric pure compounds **5a** and **5b** are, to the best of our knowledge, the first examples of chiral strontium complexes with a strontium–selenium direct bond.

Fig. 3 Solid-state structures of barium complexes **6a** and **6b**. Hydrogen atoms are omitted for clarity except methyl and methine hydrogen atoms. Selected bond lengths (Å) and bond angles (°).

6a. P1–Se1 2.1447(15), P1–N1 1.597(5), P1–C9 1.833(5), P1–C15 1.832(6), C1–N1 1.483(7), C1–C2 1.533(9), C1–C3 1.511(8), P2–Se2 2.1514(15), P2–N2 1.607(5), P2–C35 1.823(7), C21–N2 1.486(6), C21–C22 1.535(8), C21–C23 1.515(9), Ba1–Se1 3.3181(6), Ba1–N1 2.693(4), Ba1–O1 2.690(5), Ba1–O2 2.719(5), Ba1–Se2 3.3524(7), Ba1–N2 2.679(5), N1–P1–Se1 109.88(17), C1–N1–P1 120.0(4), C2–C1–N1 111.3(5), C9–P1–C15 103.1(2), N1–Ba1–Se1 60.56(10), O1–Ba1–O2 78.94(19), N2–Ba1–Se2 60.19(9), N2–P2–Se2 109.23(18), C21–N2–P2 120.6(4), N1–Ba1–N2 103.52(15), Se1–Ba1–Se2 168.708(19).

6b. P1–Se1 2.144(2), P1–N1 1.601(6), P1–C10 1.826(8), P1–C16 1.837(7), C1–N1 1.481(10), C1–C3 1.534(11), C1–C4 1.511(11), P2–Se2 2.150(2), P2–N2 1.612(7), P2–C35 1.826(9), C2–N2 1.486(9), C2–C22 1.530(11), C2–C23 1.523(12), Ba1–Se1 3.3172(9), Ba1–N1 2.693(6), Ba1–O1 2.729(7), Ba1–O2 2.696(7), Ba1–Se2 3.3537(9), Ba1–N2 2.672(7), N1–P1–Se1 109.9(2), C1–N1–P1 119.7(5), C3–C1–N1 110.8(6), C10–P1–C16 102.9(3), N1–Ba1–Se1 60.64(13), O1–Ba1–O2 79.2(3), N2–Ba1–Se2 60.23(14), N2–P2–Se2 109.1(3), C2–N2–P2 120.0(6), N1–Ba1–N2 103.4(2), Se1–Ba1–Se2 168.72(3).

Similar to calcium and strontium complexes (**4a,b–5a,b**), the analogous chiral barium complexes **6a** and **6b** were also crystallised in the monoclinic space group $P2_1$ with two molecules in the unit cell. The coordination sphere of the central barium ion of each enantiomer was occupied by two monoanionic $\{\text{N}^*(\text{CHMePh})\text{P}(\text{Se})\text{Ph}_2\}^-$ ligand moieties where each ligand bonded *via* amido nitrogen and one selenium atom and two THF molecules through oxygen atoms. Therefore, the central Ba^{2+} ion in the each enantiomer is six-fold coordinated and adopts distorted octahedral geometry. The Ba–N bond distances of 2.693(4) and 2.679(5) Å for **6a** and 2.693(6) and 2.672(7) Å for **6b** were observed, which are quite long when compared to analogous calcium [2.441(3) to 2.430(5) Å] and strontium [2.542(7) to 2.570(7) Å] complexes. The observed Ba–N distances are similar to our previously reported values, 2.777(6) and 2.778(6) Å for $[\text{Ba}\{\text{Ph}_2\text{P}(\text{Se})\text{NCHPh}_2\}_2(\text{THF})_2]$, 2.733(6) Å for $[\text{Ba}\{\text{Ph}_2\text{P}(\text{BH}_3)\text{NCHPh}_2\}_2(\text{THF})_2]$, (2.657(5) and 2.654(6) Å) for $[\text{Ba}\{\text{C}_2\text{H}_4(\text{NPh}_2\text{P}=\text{Se})_2\}(\text{THF})_3]$, and 2.774(5) Å, 2.790(5) and 2.789(5) Å for polymeric ‘ate’ complex of $[\text{K}(\text{THF})\text{Ba}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)_3\}_n]$ reported by us¹³ and 2.706(4) Å for

[Ba((Dip)₂DAD)(μ-I)(THF)₂]₂ reported in the literature.¹⁸ The Ba–Se bond distances of 3.3181(6) and 3.3524(7) Å for **6a** and 3.3172(9) and 3.3537(9) Å for **6b** were observed and these are within the range of the Ba–Se distances [3.366(1) Å and 3.324(1) Å] for the complex [Ba{4,5-(P(Se)Ph₂)₂tz}₂(THF)₇] reported by Raymundo Cea-Olivares *et al.*,^{24a} 3.2787(11) Å for [Ba(THF)₄(–SeMes*)₂] (Mes* = 2,4,6-^tBu₃C₆H₂) and 3.2973(3) Å for [Ba(Py)₃(THF)(SeTrip)₂]₂ (Trip = 2,4,6-ⁱPr₃C₆H₂) reported by Ruhlandt-Senge *et al.*,^{24b} [3.3553(10) and 3.3314(10) Å] for [Ba{Ph₂P(Se)NCHPh₂}(THF)₂]₂, 3.3842(8) Å for [η²-N(PPh₂Se)₂]₂-Ba(THF)₃] and [3.3274(7) Å, 3.3203(7) Å and 3.3518(7) Å] for [K(THF)Ba{Ph₂P(Se)N(CMe₃)₃}]₃ previously reported by us.¹³ The much elongated Ba–P distances of 3.5838(13), 3.5959(15) Å in **6a** and 3.5837(18), 3.595(2) Å in **6b** indicate no ligation through phosphorus atom to the barium ion. Similar to the calcium and strontium complexes, in **6a** and **6b**, two four-membered metallacycles Ba1–Se1–P1–N1–Ba1 and Ba1–Se2–P2–N2–Ba1 are formed due to κ²-ligation of two ligand moieties *via* selenium and amide nitrogen atoms. The plane containing N1, P1, Se1 and Ba1 makes a dihedral angle of 81.37° (for **6a**) and 81.29° (for **6b**) with the plane having N2, P2, Se2 and Ba1, indicating that the two four-membered metallacycles are almost perpendicular to each other as we observed in the case of the calcium (**4a** and **4b**) and strontium (**5a** and **5b**) complexes. Thus, the enantiomeric pure compounds **6a** and **6b** are seen to be new class of alkaline earth metal molecules and to the best of our knowledge; these are the first examples of chiral barium complexes with a barium–selenium direct bond.

Chiral amidophosphine-borane ligands

In our previous studies on phosphine-borane adducts in alkali and alkaline earth metal chemistry, we introduced a mono-anionic amidophosphine-borane {Ph₂P(BH₃)NR}[–] (R = CHPh₂ and CPh₃) and dianionic bis(amidodiphenylphosphine-borane) {Ph₂P(BH₃)NCH₂CH₂NP(BH₃)Ph₂}^{2–} as chelating ligands and exploited their chelating behaviour in alkali metal and alkaline earth metal chemistry.^{13d,f} The monoanionic amidophosphine-borane {Ph₂P(BH₃)NR}[–] acts as bi-dentate ligand and coordinates to the metal ions through amido nitrogen and borane hydrogens, whereas bis(amido-diphenylphosphine-borane) would form a dianion and acts as a tetra-dentate ligand towards metal ions. To extend our research on amidophosphine-boranes and demonstrate the versatility of the amidophosphine-boranes mainly in alkaline earth metal chemistry, we intended to develop chiral amidophosphine-borane ligands [HN(R*-CHMePh)(P(BH₃)Ph₂)] (**7a**) and [HN(S*-CHMePh)(P(BH₃)Ph₂)] (**7b**) and their homoleptic barium complexes [Ba{N(R*-CHMePh)P(BH₃)Ph₂}(THF)₂] (**8a**) and [Ba{N(S*-CHMePh)P(BH₃)Ph₂}(THF)₂] (**8b**). The amido-phosphineborane (**7a**) and (**7b**) were isolated as pure enantiomers from a single-step reaction involving corresponding chiral phosphineamines [HN(R*-CHMePh)(PPh₂)] and [HN(S*-CHMePh)(PPh₂)] and borane adduct [H₃B·SMe₂] at room temperature in a 1:1 molar ratio in toluene (see Scheme 4).¹⁷

The formation of the chiral amidophosphine-borane ligands **7a** and **7b** from [HN(R*-CHMePh)(PPh₂)] and [HN(S*-CHMePh)(PPh₂)]

Scheme 4 Synthesis of chiral amidophosphine-borane ligands **7a** and **7b**.

can easily be followed by ¹H NMR spectroscopy measured in CDCl₃, since additional resonances for the two chemically equivalent borane (BH₃) groups attached to the phosphorus atoms appear as a broad signal centered at δ 0.96 ppm. In the ¹H NMR spectra, the resonance signals of ligands **7a,b** are marginally shifted in comparison to the starting material with those reported for the phosphineamines.^{14a} The multiplet signals at δ 4.47–4.37 ppm can be assigned to the methine proton (–CH) α to amino nitrogen of ligand **7a,b**. A broad signal centered at δ 2.48 ppm corresponding to the –NH proton of ligand **7a,b** was observed and also downfield shifted (3.24 ppm) compared to that in **1a,b** (2.57 ppm). Ligands **7a,b** show a doublet signal at δ 1.40 ppm with coupling constant of J_{H–H} = 6.76 Hz, corresponding to the methyl (–CH₃) protons of the ligand **7a,b**. In the ³¹P{¹H} NMR spectra, the doublet resonance signal at δ 54.9 ppm with a coupling constant of J_{P–B} = 80.95 Hz can be attributed to the coupling of the phosphorus atom with the adjacent boron atom. In the ¹¹B{¹H} NMR spectrum, the broad signal at –37.9 ppm can be assigned to the BH₃ group attached to the phosphorus atom. This observation is in agreement with our previously reported values.^{13d} In the FT-IR spectra, a characteristic signal for P–B bond stretching at 608 cm^{–1} was observed along with another characteristic signal at 2379 cm^{–1} assigned to the B–H stretching frequency. These values are in agreement with those reported in literature.

Fig. 4 Solid-state structures of two enantiomers **7a** (left) and **7b** (right). Selected bond lengths (Å) and bond angles (°).

7a. P1–B1 1.915(5), P1–N1 1.638(3), P1–C9 1.817(3), P1–C15 1.818(4), C1–N1 1.466(4), C1–C2 1.531(5), C1–C3 1.530(4), B1–H1A 0.9600, B1–H1B 0.9600, B1–H1C 0.9600, N1–P1–B1 113.73(19), C9–P1–C15 104.54(14), C9–P1–B1 110.97(19), C15–P1–B1 112.8(2), C9–P1–N1 109.58(16), C15–P1–N1 104.62(16), P1–N1–C1 125.8(3), N1–C1–C2 109.3(3), N1–C1–C3 109.8(3), C2–C1–C3 114.3(3), H1A–B1–H1B 109.5.

7b. P1–B1 1.892(3), P1–N1 1.653(2), P1–C9 1.802(3), P1–C20 1.816(2), C1–N1 1.478(3), C1–C2 1.528(4), C1–C3 1.502(4), B1–H1B 0.9600, B1–H1C 0.9600, B1–H1D 0.9600, N1–P1–B1 116.4(2), C9–P1–C20 104.94(12), C9–P1–B1 111.89(15), C20–P1–

B1 112.13(13), C9–P1–N1 105.00(12), C20–P1–N1 109.45(12), N1–C1–C2 110.2(3), N1–C1–C3 110.8(2), C2–C1–C3 113.0(3).

The molecular structures of enantiomers **7a** and **7b** were established using single-crystal X-ray diffraction analysis. *R*-isomer (**7a**) crystallises in the monoclinic space group $P2_1$, with two independent molecules in the unit cell, whereas the corresponding *S*-isomer (**7b**) crystallises in the orthorhombic space group $P2_12_12_1$ with eight independent molecules in the unit cell. The details of the structural parameters are given in Table TS1 in ESI.† Fig. 4 represents the molecular structure of **7a** and **7b**. The P1–B1 bond distances [1.915(5) Å (**7a**) and 1.892(3) Å (**7b**)] are almost similar and in full agreement with reported values, 1.918(6) Å for $[\text{Ph}_2\text{P}(\text{BH}_3)\text{-NH}(\text{CHPh}_2)]$, 1.9091(2) and 1.916(1) Å for $[\{\text{Ph}_2\text{P}(\text{BH}_3)\text{NH-CH}_2\text{-CH}_2\text{-NHP}(\text{BH}_3)\text{-Ph}_2\}]$ and 2.1019(8) Å for $[\{\text{Ph}_2\text{P}(\text{BH}_3)\}_2\text{CH}_2]$ and 1.921(3) Å for $[(\text{CH}_2\text{-}o\text{-CF}_3\text{C}_6\text{H}_4)\text{-(Ph)P}(\text{BH}_3)\text{C}_4\text{H}_8\text{P}(\text{BH}_3)\text{(Ph)}\text{-(CH}_2\text{-}o\text{-CF}_3\text{C}_6\text{H}_4)]$, so they may be considered as the phosphorus–boron dative bond reported by us and others.²⁵ The P1–N1 bond ranges from 1.638(3) Å to 1.653(2) Å and C1–N1 bond distances of 1.466(4) Å and 1.478(3) are also similar to those reported by us previously:¹³ P1–N1 1.673(6) Å and C1–N1 1.453(8) Å for $[\text{Ph}_2\text{PNH}(\text{CHPh}_2)]$ and P1–N1 1.638(3) Å and C1–N1 1.468(5) Å for $[\text{Ph}_2\text{P}(\text{BH}_3)\text{-NH}(\text{CHPh}_2)]$.

Barium complexes

In a single pot-reaction, chiral ligands **7a** or **7b** was made to react with $[\text{K}\{\text{N}(\text{SiMe}_3)_2\}]$ in THF at an ambient temperature in a 1 : 1 molar ratio followed by the addition of barium diiodide to afford the barium complexes $[(\text{THF})_2\text{Ba}\{\text{N}(\text{R}^*\text{-CHMePh})\}(\text{P}(\text{BH}_3)\text{-Ph}_2)_2]$ (**8a**) and $[(\text{THF})_2\text{Ba}\{\text{N}(\text{S}^*\text{-CHMePh})\}(\text{P}(\text{BH}_3)\text{-Ph}_2)_2]$ (**8b**) through the elimination of KI and volatile $[\text{HN}(\text{SiMe}_3)_2]$ (see Scheme 5).¹⁷

In FT-IR spectra, a strong absorption band at 602 cm^{-1} is assigned to the P–B bond of complexes **8a,b** which is in the range similar to that of ligand **7a** or **7b** (608 cm^{-1}). The ^1H NMR spectra of complex **8a,b** measured in C_6D_6 are very similar to the spectra recorded for ligand **7a** or **7b** and reveal time-averaged C_s -symmetry in solution. Methyl protons in the ligand backbone appear as a doublet at δ 1.40 ppm with a coupling constant of 6.76 Hz. The resonances of the three protons attached to the boron atom appear as multiplets centered at δ 1.22 ppm in the ^1H NMR spectra. Methine proton of the anionic ligand in the barium complexes **8a,b** observed as multiplet signals in the region of δ 4.39–4.48 in the ^1H NMR spectra. In the proton decoupled ^{31}P NMR spectra, complexes **8a,b** show only one doublet signal at δ 46.9 ppm and this value is significantly up-

field shifted compared to the value obtained for compound **7a** or **7b** (54.9 ppm) upon the coordination of barium ion to the ligand **7a** or **7b**. The phosphorus atoms present in the $[\text{N}^*(\text{CHMePh})\text{-P}(\text{BH}_3)\text{Ph}_2]^-$ moieties are chemically equivalent. A broad signal centered at δ –34.9 ppm was observed in the ^{11}B $\{^1\text{H}\}$ NMR spectra of complexes **8a,b**.

Fig. 5 Solid-state structures of barium complexes **8a** and **8b**. Hydrogen atoms are omitted for clarity except for methyl, methine as well as for borane hydrogen atoms. Selected bond lengths (Å) and bond angles ($^\circ$).

8a. P1–B1 1.929(6), P1–N1 1.610(4), P1–C9 1.826(5), P1–C15 1.826(5), C1–N1 1.482(6), C1–C2 1.527(7), C1–C3 1.523(7), P2–B2 1.924(6), P2–N2 1.604(4), P2–C29 1.839(5), C21–N2 1.486(6), C21–C22 1.534(7), C21–C23 1.514(6), Ba1–B1 3.221(6), Ba1–N1 2.674(4), Ba1–O1 2.759(4), Ba1–O2 2.697(4), Ba1–B2 3.155(6), Ba1–N2 2.684(4), Ba1–H1b 2.68(6), Ba2–H1d 2.87(6), B1–H1b 1.03(6), B2–H1d 1.14(6), N1–P1–B1 110.8(2), C1–N1–P1 119.3(3), C2–C1–N1 108.9(4), C9–P1–C15 103.8(2), N1–Ba1–B1 58.48(13), O1–Ba1–O2 82.20(14), N2–Ba1–B2 58.90(13), N2–P2–B2 110.2(2), C21–N2–P2 121.4(3), N1–Ba1–N2 104.51(12), B1–Ba1–B2 167.87(15), H1b–Ba1–H1d 162.4(17), P1–Ba1–H1b 44.3(13), P2–Ba1–H1d 45.8(12), N1–Ba1–H1b 70.0(13), N2–Ba1–H1d 69.1(12).

8b. P1–B1 1.920(5), P1–N1 1.608(4), P1–C9 1.823(4), P1–C15 1.835(5), C1–N1 1.477(5), C1–C2 1.534(6), C1–C3 1.520(6), P2–B2 1.920(5), P2–N2 1.607(4), P2–C29 1.819(4), C21–N2 1.475(5), C21–C22 1.537(6), C21–C23 1.521(6), Ba1–B1 3.228(5), Ba1–N1 2.677(3), Ba1–O1 2.694(3), Ba1–O2 2.778(4), Ba1–B2 3.153(5), Ba1–N2 2.683(3), Ba1–H1b 2.69(5), Ba2–H1d 2.90(5), B1–H1b 1.12(5), B2–H1d 1.01(6), N1–P1–B1 111.0(2), C1–N1–P1 119.5(3), C2–C1–N1 108.4(4), C9–P1–C15 103.5(2), N1–Ba1–B1 58.22(12), O1–Ba1–O2 81.96(12), N2–Ba1–B2 58.96(12), N2–P2–B2 110.4(2), C21–N2–P2 121.2(3), N1–Ba1–N2 104.66(11), B1–Ba1–B2 167.70(14), H1b–Ba1–H1d 156.8(13), P1–Ba1–H1b 44.8(10), P2–Ba1–H1d 46.4(11), N1–Ba1–H1b 70.3(10), N2–Ba1–H1d 70.4(11).

Scheme 5 Synthesis of barium complexes **8a** and **8b** of chiral amine-phosphine-borane ligands.

Although there is ongoing interest in alkaline earth organometallics²⁶ and particularly in the cyclopentadienyl chemistry of these elements,²⁷ complexes **8a,b** represent, to the best of our knowledge, the first barium complexes containing a chiral amidophosphine-borane ligand in its coordination sphere. Therefore, the molecular structure in the solid state was determined using X-ray diffraction analysis. Compounds **8a** and **8b** were re-crystallised by slow evaporation from THF and *n*-pentane mixture (1 : 2) and was found to crystallise in the monoclinic space group *P*₂₁ with two molecules in the unit cell. The solid-state structures of complexes **8a,b** confirmed the attachment of chiral amidophosphine-borane ligand onto the barium ion. Fig. 5 shows the non-super imposable mirror images of barium complexes **8a** and **8b**. The details of the structural parameters are given in Table TS1 in the ESI.† The enantiomeric pure barium compounds **8a,b** are non-centrosymmetric and each barium ion in **8a** and **8b** is coordinated by two amido nitrogen atoms and two BH₃ groups of two ligand fragments. One of the borane (BH₃) groups coordinates through the hydrogen atoms in a η^1 fashion and has a Ba1–B1 distance of 3.221(6) Å. The second borane (BH₃) group coordinates in η^2 fashion and has Ba1–B2 distance of 3.155(6) Å. Thus, ligand **7a** or **7b** can be considered a pseudo bi-dentate ligand, similar to {Ph₂P(BH₃)N(CHPh₂)} which was previously introduced into alkaline earth metal chemistry by us.^{13c} Additionally, two THF molecules are coordinated to each barium ion and the geometry around each barium ion is best described as a distorted octahedral. It must be noted that the P–B distances [1.929(6) and 1.924(6) Å] are in the same range as that of the ligands **7a** [1.915(5) Å] and **7b** [1.892(3) Å] even after the ligation of the BH₃ group to the barium centre. The Ba–N [2.674(4), 2.684(4) Å] and Ba1–O1 [2.759(4) and 2.697(4) Å] distances are in agreement with those of the reported complexes.²⁸

Ring-opening polymerisation study

Catalytic activities of the chiral strontium and barium complexes **5a** or **5b** and **6a** or **6b** were performed (see Scheme 6). Polymerisation studies were typically conducted in toluene, with various monomer/catalyst ratios at 25 °C. Selected data obtained with respect to complexes **5** and **6** are given in Table 1.

The catalytic ability of the newly synthesised enantiomeric pure mono-nuclear strontium complexes **5a** or **5b** to promote the ROP of ϵ -CL was first evaluated (Table 1, entries 1–5). Indeed, the moderate reactivity of the strontium complexes is very similar to that observed in previously reported studies using other strontium complexes for ROP of ϵ -caprolactone.²⁹ Since the larger ion radius barium complexes have been reported to be more active than the calcium and strontium

congeners in ROP,^{30,31} we tested compound **6a** or **6b** as a catalyst and observed an enhanced rate of polymerisation (Table 1, entries 6–10). In the case of strontium, higher reactivity was observed for conversion of ϵ -caprolactone to poly-caprolactone and up to 500 ϵ -CL units were successfully converted in high yields (75–90 per cent), within 15 and 10 minutes respectively, at 25 °C. The control over the ROP process was rather good, affording PCLs, featuring a considerable match between the observed (as determined by GPC) and calculated molar mass values, as well as moderate dispersity data ($PDI = M_w/M_n < 1.94$). However, the overall efficiency of the strontium initiator **5a,b** towards the ROP of ϵ -CL was weaker than that of the barium analogue **6a,b**. Being the largest ionic radius of the barium atom, it was anticipated that complex **6a,b** would show the highest reactivity among all the three alkaline earth metal complexes.^{32,33} In reality we observed that up to 500 ϵ -CL units were successfully converted in good yields (80–98 per cent) within 10 minutes at 25 °C (Table 1, entries 6–10). The poly-caprolactone produced by the use of the barium catalyst was a considerable match between the observed and calculated molar mass values, and we observed a relatively narrow poly-dispersity data (PDI up to 1.55, entry 9 in Table 1). Thus, among strontium and barium metal complexes, the barium complexes **6a,b** showed the highest activity for ROP of ϵ -caprolactone.

Experimental

General consideration

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} Torr) line, or in an argon-filled M. Braun glove box. THF was pre-dried over Na wire and distilled under nitrogen from sodium and benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from LiAlH₄ and stored in the glove box. ¹H NMR (400 MHz), ¹³C{¹H} and ³¹P{¹H} NMR (161.9 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Alkaline earth metal diiodides (MgI₂, CaI₂, SrI₂ and BaI₂), KN(SiMe₃)₂, selenium and Me₂S·BH₃ were purchased from Sigma Aldrich and used as such. The chiral-aminophosphines [HN(*R*·CHMePh)(PPh₂)], [HN(*S*·CHMePh)(PPh₂)] were prepared according to procedure prescribed in the literature.^{14a} The NMR solvent C₆D₆ and CDCl₃ were purchased from Sigma Aldrich and dried under Na/K alloy (for C₆D₆) or molecular sieves (for CDCl₃) prior to use.

Preparation of [Ph₂P(Se)HN(*R*·CHMePh)] (**1a**) and [Ph₂P(Se)HN(*S*·CHMePh)] (**1b**)

In a 25 ml round-bottomed flask, chiral-aminophosphines [HN(*R*·CHMePh)(PPh₂)] or [HN(*S*·CHMePh)(PPh₂)] (1.0 g, 3.27 mmol) and elemental selenium (392 mg, 4.91 mmol) were heated to 60 °C in THF (10 ml) solvent for 12 hours. Excess

Scheme 6 Ring-opening polymerisation of ϵ -CL with strontium and barium complexes **5** and **6**.

Table 1 Polymerization of ϵ -caprolactone initiated by alkaline earth metal complexes of type $[(\text{THF})_2\text{M}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{R}/\text{S}-^*\text{CHMePh})\}_2]$ (where $\text{M} = \text{Sr}, \text{Ba}$)^a

Entry	[M]	$[\epsilon\text{-CL}]_0/[\text{M}]_0$	Reac. time ^b [min]	Conv. ^c [%]	M_n (theo) ^d [g mol ⁻¹]	M_n (GPC) ^e [g mol ⁻¹]	M_w (GPC) ^e [g mol ⁻¹]	M_w/M_n (PDI) ^f
1	Sr	100	15	90	9001	8797	17 108	1.94
2	Sr	200	15	80	16 603	10 515	17 153	1.63
3	Sr	300	15	73	21 904	12 717	19 707	1.54
4	Sr	400	15	82	32 807	20 492	32 065	1.56
5	Sr	500	15	75	37 508	22 261	24 295	1.09
6	Ba	100	10	98	9802	8829	11 512	1.30
7	Ba	200	10	90	18 003	10 351	14 450	1.39
8	Ba	300	10	85	25 505	11 735	17 467	1.48
9	Ba	400	10	80	32 007	12 620	19 581	1.55
10	Ba	500	10	83	43 509	32 338	37 336	1.15

^a Results are representative of at least two experiments. ^b Reaction times were not necessarily optimized. ^c Monomer conversions were determined by ¹H NMR spectroscopy. ^d Theoretical molar mass values calculated from the relation: $[\text{monomer}]_0/[\text{M}]_0 \times \text{monomer conversion}$ where $[\text{M}]_0 = 8.76 \times 10^{-3}$ mmol and monomer weight of $\epsilon\text{-CL} = 114$ g mol⁻¹. ^e Experimental molar masses were determined by GPC *versus* polyethylene glycol standards. ^f Molar mass distributions were calculated from GPC.

selenium metal was filtered through a G4 frit to collect the yellow-coloured filtrate. After evaporation of the solvent from filtrate *in vacuo*, a light-yellow solid residue was obtained, which was further purified by washing with *n*-hexane. Compound **1a** was re-crystallised from THF at room temperature.

Yield: 1.24 g (98%) (**1a**) and 1.25 g (99%) (**1b**). ¹H NMR (400 MHz, CDCl₃): δ 7.88–7.94 (m, 2H, ArH), 7.71–7.77 (m, 2H, ArH), 7.30–7.39 (m, 4H, ArH), 7.12–7.25 (m, 7H, ArH), 4.43–4.52 (m, 1H, CH), 2.57 (br, 1H, NH), 1.42 (d, $J_{\text{H-H}} = 6.76$ Hz, 3H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.7 (ArC), 132.0 (P-ArC), 131.8 (P attached *o*-ArC), 131.6 (*o*-ArC), 128.5 (P attached *m*-ArC), 128.3 (*m*-ArC), 127.1 (*p*-ArC), 126.3 (P attached *p*-ArC), 52.7 (CH), 25.2 (CH₃) ppm. ³¹P{¹H} NMR (161.9 MHz, CDCl₃): δ 56.1 ppm. FT-IR (selected frequencies): $\nu = 3501$ (N-H), 1434 (P-C), 954 (P-N), 556 (P=Se) cm⁻¹. Elemental analysis: C₂₀H₂₀NPSe (385.05): calcd C 62.50, H 5.25, N 3.64. Found C 62.28, H 5.13, N 3.42.

Preparation of $[\text{K}\{\text{N}(\text{R}-^*\text{CHMePh})(\text{Ph}_2\text{P}(\text{Se}))\}(\text{THF})_n]$ (**2a**) and $[\text{K}\{\text{N}(\text{S}-^*\text{CHMePh})(\text{Ph}_2\text{P}(\text{Se}))\}(\text{THF})_n]$ (**2b**)

In a 50 ml pre-dried Schlenk flask, one equivalent (1.00 g, 2.60 mmol) of ligand **1a** and one equivalent of potassium bis(trimethylsilyl)amide (520 mg, 2.60 mmol) were mixed together with 10 ml of dry THF. After 6 hours of stirring, the THF solvent was evaporated *in vacuo* and the dry compound was further purified by washing with *n*-pentane (5 ml) twice. The title compound **2a** was obtained as a light orange powder. Compound **2b** was also obtained by similar procedure.

Yield: 1.24 g, (90%) (**2a**) and yield: 1.20 g (86%) (**2b**). ¹H NMR (400 MHz, C₆D₆): δ 7.92–8.08 (m, 4H, ArH), 7.34 (bs, 2H, ArH), 7.01–7.19 (m, 9H, ArH), 4.31–4.37 (m, 1H, CH), 3.50–3.53 (m, THF), 1.37–1.40 (m, THF), 1.30 (d, $J_{\text{H-H}} = 6.20$ Hz, 3H, CH₃) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 144.7 (ArC), 132.0 (P-ArC), 131.8 (P attached *o*-ArC), 131.6 (*o*-ArC), 128.7 (P attached *m*-ArC), 128.4 (*m*-ArC), 127.7 (*p*-ArC), 126.7 (P attached *p*-ArC), 67.6 (THF), 52.7 (CH), 26.1 (CH₃), 25.6 (THF) ppm. ³¹P{¹H} NMR (161.9 MHz, C₆D₆): δ 42.7 ppm. FT-IR

(selected frequencies): $\nu = 1435$ (P-C), 955 (P-N), 550 (P=Se) cm⁻¹. Elemental analysis: C₂₈H₃₅NKNO₂PSe (567.12): calcd C 59.35, H 6.23, N 2.47. Found C 58.84, H 5.99, N 2.23.

Preparation of $[\{(\text{THF})_2\text{Mg}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{R}-^*\text{CHMePh})\}_2]$ (**3a**) and $[\{(\text{THF})_2\text{Mg}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{S}-^*\text{CHMePh})\}_2]$ (**3b**)

In a 25 ml pre-dried Schlenk flask, potassium salt of ligand **1a** (304 mg, 0.72 mmol) (**1b** for **3b**) was mixed with MgI₂ (100 mg, 0.36 mmol) in 10 ml THF solvent at ambient temperature and stirring continued for 12 hours. The white precipitate of KI was filtered off and the filtrate was evaporated *in vacuo*. The resulting white residue was further purified by washing with *n*-pentane and crystals suitable for X-ray analysis were grown from THF/*n*-pentane (1 : 2) mixture at –35 °C.

Yield: 154.0 mg, (90%) (**3a**) and 125 mg (80%) (**3b**). ¹H NMR (400 MHz, C₆D₆): δ 8.06–8.12 (m, 1H, ArH), 7.91–7.98 (m, 2H, ArH), 7.76–7.82 (m, 1H, ArH), 7.40–7.42 (m, 1H, ArH), 6.89–7.11 (m, 10H, ArH), 4.58–4.62 (m, 1H, CH), 3.68–3.74 (m, THF), 1.86 (d, $J_{\text{H-H}} = 6.72$ Hz, 3H, CH₃), 1.42–1.44 (m, THF) ppm. ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 144.7 (ArC), 132.0 (P-ArC), 131.8 (P attached *o*-ArC), 131.6 (*o*-ArC), 128.5 (P attached *m*-ArC), 128.3 (*m*-ArC), 127.1 (*p*-ArC), 126.3 (P attached *p*-ArC), 52.7 (CH), 25.2 (CH₃) ppm. ³¹P{¹H} NMR (161.9 MHz, C₆D₆): δ 45.1 ppm. FT-IR (selected frequencies): $\nu = 1435$ (P-C), 955 (P-N), 562 (P=Se) cm⁻¹. Elemental analysis: C₃₈H₄₈MgN₂O₃P₂Se₂ (826.13): calcd C 55.32, H 5.86, N 3.40. Found C 54.93, H 5.62, N 3.13.

Preparation of $[\{(\text{THF})_2\text{Ca}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{R}-^*\text{CHMePh})\}_2]$ (**4a**) and $[\{(\text{THF})_2\text{Ca}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{S}-^*\text{CHMePh})\}_2]$ (**4b**)

Route 1. In a 10 ml sample vial, two equivalents (200 mg, 0.52 mmol) of ligand **1** and one equivalent of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2 \cdot (\text{THF})_2]$ (130.8 mg, 0.26 mmol) were mixed together with 5 ml of THF. After 6 hours of stirring, 2 ml of *n*-pentane (2 ml) was added to it and kept at –35 °C in a freezer. After one day, colourless crystals suitable for X-ray diffraction analysis were obtained.

Route 2. In a 25 ml pre-dried Schlenk flask, compound 2 (288 mg, 0.68 mmol) was mixed with CaI_2 (100 mg, 0.34 mmol) in 10 ml THF solvent at ambient temperature and stirring continued for 12 hours. The white precipitate of KI was filtered off and filtrate was evaporated *in vacuo*. The resulting white residue was further purified by washing with *n*-pentane and crystals suitable for X-ray analysis were grown from THF/*n*-pentane (1 : 2) mixture at -35°C .

Yield: 154.0 mg, (90%) (**4a**) and 149 mg (86%) (**4b**). ^1H NMR (400 MHz, C_6D_6): δ 7.95–8.00 (m, 2H, ArH), 7.63–7.94 (m, 2H, ArH), 7.43–7.45 (m, 2H, ArH), 6.85–7.06 (m, 9H, ArH), 4.26–4.34 (d, 1H, CH), 3.63 (m, THF), 1.68 (d, $J_{\text{H-H}} = 6.56$ Hz, 3H, CH_3), 1.21 (m, THF) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 150.2 (ArC), 150.1 (ArC), 132.6 (P-ArC), 132.4 (P attached *o*-ArC), 130.2 (*o*-ArC), 129.9 (P attached *m*-ArC), 128.6 (*m*-ArC), 126.6 (*p*-ArC), 125.9 (P attached *p*-ArC), 69.0 (THF), 58.7 (CH), 30.0 (CH_3), 25.5 (THF) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, C_6D_6): δ 69.8 ppm. FT-IR (selected frequencies): $\nu = 1435$ (P–C), 954 (P–N), 559 (P=Se) cm^{-1} . Elemental analysis: $\text{C}_{48}\text{H}_{54}\text{CaN}_2\text{O}_2\text{P}_2\text{Se}_2$ (950.87): calcd C 60.63, H 5.72, N 2.95. Found C 60.41, H 5.66, N 2.86.

Preparation of $\{[(\text{THF})_2\text{Sr}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{R}^*\text{CHMePh})\}_2]\}$ (**5a**) and $\{[(\text{THF})_2\text{Sr}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{S}^*\text{CHMePh})\}_2]\}$ (**5b**)

Route 1. In a 10 ml sample vial, two equivalents (200 mg, 0.52 mmol) of ligand 1 and one equivalent of $[\text{Sr}\{\text{N}(\text{SiMe}_3)_2\}_2\text{-(THF)}_2]$ (143.6 mg, 0.26 mmol) were mixed together with 5 ml of THF. After 6 hours of stirring, 2 ml of *n*-pentane was added to it and kept at -35°C in a freezer. After 24 hours, colourless crystals suitable for X-ray diffraction analysis were obtained.

Route 2. In a 25 ml pre-dried Schlenk flask, compound 2 (245 mg, 0.58 mmol) was mixed with SrI_2 (100 mg, 0.29 mmol) in 10 ml THF solvent at ambient temperature and stirring continued for 12 hours. The white precipitate of KI was filtered off and filtrate was evaporated *in vacuo*. The resulting white residue was further purified by washing with *n*-pentane (3 ml) and crystals suitable for X-ray analysis were grown from THF/*n*-pentane (1 : 2) mixture at -35°C .

Yield: 154.0 mg, (90%) (**5a**) and 145 mg (85%) (**5b**). ^1H NMR (400 MHz, C_6D_6): δ 7.98–8.03 (m, 2H, ArH), 7.78–7.84 (m, 4H, ArH), 6.90–6.97 (m, 2H, ArH), 6.78–6.87 (m, 7H, ArH), 4.47–4.55 (m, 1H, CH), 3.45–3.48 (m, THF), 1.29–1.32 (m, THF), 1.20 (d, $J_{\text{H-H}} = 6.80$ Hz, 3H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 145.4 (ArC), 145.3 (ArC), 135.4 (P-ArC), 134.5 (P-ArC), 132.3 (P attached *o*-ArC), 131.2 (*o*-ArC), 128.1 (P attached *m*-ArC), 127.9 (*m*-ArC), 127.7 (*p*-ArC), 126.4 (P attached *p*-ArC), 67.6 (THF), 52.5 (CH), 25.6 (THF), 25.1 (CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, C_6D_6): δ 69.8 ppm. FT-IR (selected frequencies): $\nu = 1434$ (P–C), 955 (P–N), 552 (P=Se) cm^{-1} . Elemental analysis: $\text{C}_{48}\text{H}_{54}\text{N}_2\text{O}_2\text{P}_2\text{Se}_2\text{Sr}$ (998.41): calcd C 57.74, H 5.45, N 2.81. Found C 57.50, H 5.29, N 2.61.

Preparation of $\{[(\text{THF})_2\text{Ba}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{R}^*\text{CHMePh})\}_2]\}$ (**6a**) and $\{[(\text{THF})_2\text{Ba}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{S}^*\text{CHMePh})\}_2]\}$ (**6b**)

Route 1. In a 10 ml sample vial, two equivalents (200 mg, 0.52 mmol) of ligand 1a and one equivalent of $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2\text{-(THF)}_3]$ (156.7 mg, 0.26 mmol) were mixed together with 5 ml of

THF. After 6 hours of stirring, 2 ml of *n*-pentane was added to it and kept at -35°C in a freezer. After 24 hours, colourless crystals suitable for X-ray diffraction analysis were obtained.

Route 2. In a 25 ml pre-dried Schlenk flask, compound 2a (216 mg, 0.52 mmol) was mixed with BaI_2 (100 mg, 0.26 mmol) in 10 ml THF solvent at ambient temperature and stirring continued for 12 hours. The white precipitate of KI was filtered off and filtrate was evaporated *in vacuo*. The resulting white residue was further purified by washing with *n*-pentane and crystals suitable for X-ray analysis were grown from THF/*n*-pentane (1 : 2) mixture at -35°C .

Yield: 154.0 mg, (90%) (**6a**) and 156 g, (91%) (**6b**). ^1H NMR (400 MHz, C_6D_6): δ 7.96–7.99 (m, 2H, ArH), 7.62–7.66 (m, 2H, ArH), 7.19–7.29 (m, 4H, ArH), 6.90–7.06 (m, 7H, ArH), 4.21–4.29 (m, 1H, CH), 3.54–3.57 (m, THF), 1.48 (d, $J_{\text{H-H}} = 6.20$ Hz, 3H, CH_3), 1.35–1.38 (m, THF) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 144.7 (ArC), 132.1 (P-ArC), 130.2 (P attached *o*-ArC), 129.5 (*o*-ArC), 127.8 (P attached *m*-ArC), 126.8 (*m*-ArC), 126.4 (*p*-ArC), 126.3 (P attached *p*-ArC), 68.0 (THF), 52.7 (CH), 25.2 (CH_3), 25.6 (THF) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, C_6D_6): δ 69.8 ppm. FT-IR (selected frequencies): $\nu = 1435$ (P–C), 956 (P–N), 553 (P=Se) cm^{-1} . Elemental analysis: $\text{C}_{48}\text{H}_{54}\text{BaN}_2\text{O}_2\text{P}_2\text{Se}_2$ (1048.12): calcd C 55.00, H 5.19, N 2.67. Found C 54.81, H 4.91, N 2.42.

Preparation of $[\text{Ph}_2\text{P}(\text{BH}_3)\text{HN}(\text{R}^*\text{CHMePh})]$ (**7a**) and $[\text{Ph}_2\text{P}(\text{BH}_3)\text{HN}(\text{S}^*\text{CHMePh})]$ (**7b**)

In a pre-dried Schlenk flask 1.0 g (3.27 mmol) of chiral-aminophosphines $[\text{HN}(\text{R}^*\text{CHMePh})(\text{PPh}_2)]$ or $[\text{HN}(\text{S}^*\text{CHMePh})(\text{PPh}_2)]$ was placed in 10 ml of toluene, and to this solution, borane-dimethyl sulfide (0.30 ml, 3.27 mmol) in 5 ml of toluene was added drop wise with constant stirring at room temperature. The reaction mixture was then stirred for another 12 hours. A white precipitate was formed and was filtered through a G4 frit and dried *in vacuo*. The pure compound was obtained after washing with *n*-pentane.

Yield: 1.20 g (100%) (**7a**) and 1.20 g (100%) (**7b**). Compound 7a was soluble in CDCl_3 , CH_2Cl_2 , THF, and hot toluene. It was re-crystallised from hot toluene. ^1H NMR (400 MHz, CDCl_3): δ 7.60–7.54 (m, 4H, ArH), 7.45–7.30 (m, 6H, ArH), 7.24–7.15 (m, 5H, ArH), 4.47–4.37 (m, 1H, CH), 2.48 (br, 1H, NH), 1.40 (d, $J_{\text{H-H}} = 6.76$ Hz, 3H, CH_3), 1.17–0.75 (br, 3H, BH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 145.1 (ArC), 132.4 (P-ArC), 131.9 (P attached *o*-ArC), 131.1 (*o*-ArC), 128.5 (P attached *m*-ArC), 128.3 (*m*-ArC), 127.0 (*p*-ArC), 125.8 (P attached *p*-ArC), 53.1 (CH), 25.9 (CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, CDCl_3): δ 54.9 (d, $J_{\text{P-B}} = 80.95$ Hz) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128.4 MHz, CDCl_3): δ –37.9 (br) ppm. FT-IR (selected frequencies): ν 3438 (N–H), 1436 (P–C), 909 (P–N), 2379 (B–H), 608 (P–B) cm^{-1} . Elemental analysis: $\text{C}_{20}\text{H}_{23}\text{BNP}$ (319.17): calcd C 75.26, H 7.26, N 4.39. Found C 74.82, H 6.91, N 4.22.

Preparation of $\{[(\text{THF})_2\text{Ba}\{\text{Ph}_2\text{P}(\text{BH}_3)\text{N}(\text{R}^*\text{CHMePh})\}_2]\}$ (**8a**) and $\{[(\text{THF})_2\text{Ba}\{\text{Ph}_2\text{P}(\text{BH}_3)\text{N}(\text{S}^*\text{CHMePh})\}_2]\}$ (**8b**)

In a 25 ml pre-dried Schlenk flask, ligand 7, potassium bis(trimethylsilyl)amide and BaI_2 (100 mg, 0.26 mmol) were mixed in 10 ml THF solvent at ambient temperature and stirring

continued for 12 hours. The white precipitate of KI was filtered off and filtrate was evaporated *in vacuo*. The resulting white residue was further purified by washing with *n*-pentane and crystals suitable for X-ray analysis were grown from THF/*n*-pentane (1 : 2) mixture at -35°C .

Yield: 154.0 mg, (90%) (**8a**) and 156 g, (91%) (**8b**). ^1H NMR (400 MHz, C_6D_6): δ 7.60–7.54 (m, 4H, ArH), 7.45–7.30 (m, 6H, ArH), 7.247.15 (m, 5H, ArH), 4.48–4.39 (m, 1H, CH), 2.48 (br, 1H, NH), 1.40 (d, $J_{\text{H-H}} = 6.76$ Hz, 3H, CH_3), 1.49–0.94 (br, 3H, BH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 144.7 (ArC), 132.0 (P-ArC), 131.8 (P attached *o*-ArC), 131.6 (*o*-ArC), 128.5 (P attached *m*-ArC), 128.3 (*m*-ArC), 127.1 (*p*-ArC), 126.3 (P attached *p*-ArC), 52.7 (CH), 25.2 (CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.9 MHz, C_6D_6): δ 46.9 ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (128.4 MHz, C_6D_6): δ -34.9 (d) ppm. FT-IR (selected frequencies): $\nu = 1434$ (P-C), 999 (P-N), 2383 (B-H), 602 (P-B) cm^{-1} . Elemental analysis: $\text{C}_{48}\text{H}_{60}\text{B}_2\text{BaN}_2\text{O}_2\text{P}_2$ (917.87): calcd C 62.81, H 6.59, N 3.05. Found C 61.94, H 6.20, N 2.83.

Typical polymerisation experiment

In a glove box under argon atmosphere, the catalyst was dissolved in the appropriate amount (1.0 ml) of dry toluene. ϵ -Caprolactone in 1.0 ml of toluene was then added along with vigorous stirring. The reaction mixture was stirred at room temperature for 5–20 minutes, after which the reaction mixture was quenched by the addition of a small amount of (1.0 ml) methanol. Later, a small quantity of excess acidified methanol was added. The polymer was precipitated in excess methanol and it was filtered and dried under vacuum. The final polymer was then analysed by NMR and GPC.

X-ray crystallographic studies of 1, 4–8

Single crystals of compounds **1a,b** were grown from a concentrated solution of THF at room temperature. However, the single crystals of **4a,b–8a,b** suitable for X-ray measurement were grown at -35°C under inert atmosphere. For compounds **4a,b–8a,b**, (except **7a,b**) a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. However for compounds **1a,b** and **7a,b**, the data were collected at 293 K. All measurements were made on an agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic Cu-K α (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarised in Table TS1 in the ESI.† The structures were solved by direct methods (SIR92)³⁴ and refined on F^2 by full-matrix least-squares methods; using SHELXL-97.³⁵ Non-hydrogen atoms were anisotropically refined. H atoms were included in the refinement in calculated positions riding on their carrier atoms. No restraint was made with respect to any of the compounds. The function minimised was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\max(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The function R1 and wR2 were $(\sum ||F_o| - |F_c||)/\sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum (wF_o^4)]^{1/2}$, respectively. The Diamond-3 program was used to draw the molecule.†

Conclusion

We have demonstrated a series of alkaline earth metal complexes obtained in enantiomeric pure form with chiral phosphinoselenoic amides ligand through two routes of synthesis. In the solid-state structures of Ca–Ba complexes, the monoanionic ligand attached to the metal centre in κ^2 fashion *via* the coordination of amido nitrogen and selenium atoms, confirming the bidentate chelation of chiral phosphinoselenoic amide. Thus, the enantiomeric pure compounds **4–6** are known to be a new class of alkaline earth metal complexes, and to the best of our knowledge, these are the first examples of chiral alkaline earth metal complexes with a metal-selenium direct bond. We have also described the synthetic and structural features of chiral amidophosphine-borane ligands and the corresponding barium complex. It was found that the amidophosphine-borane ligand is coordinated through the amido nitrogen and BH_3 hydrogens (η^1 and η^2) to the barium ion. We have tested complexes **5–6** as catalysts for the ROP of ϵ -caprolactone and observed that the barium complex, having the largest ionic radius, acts as the best catalyst between the two analogous complexes.

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