

# Synthesis of monomeric and polymeric alkali and alkaline earth metal complexes using a phosphinoselenoic amide ligand in metal coordination sphere

JAYEETA BHATTACHARJEE, RAVI K KOTTALANKA, HARINATH ADIMULAM and TARUN K PANDA\*

Department of Chemistry, Indian Institute of Technology Hyderabad, Ordnance Factory Estate, Yeddumailaram 502 205, Telangana, India  
e-mail: tpanda@iith.ac.in

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**Abstract.** We report the monomeric complexes of magnesium and calcium of composition  $[M(\text{THF})_n\{\eta^2\text{-Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)_2\}]$  [ $M = \text{Mg}$  (**3**),  $n = 1$  and  $M = \text{Ca}$  (**4**),  $n = 2$ ] and polymeric complexes of potassium and barium of composition  $[\text{K}(\text{THF})_2\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)\}]_n$  (**2**) and  $[\text{K}(\text{THF})\text{Ba}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)\}_3]_n$  (**5**) respectively. The potassium complex **2** was readily prepared by the reaction of potassium bis(trimethylsilyl)amide with phosphinoselenoic amide ligand (**1**) at ambient temperature. The calcium complex **4** was prepared by two synthetic routes: in the first method, commonly known as salt metathesis reaction, the potassium complex **2** was made to react with alkaline earth metal diiodide at room temperature to afford the corresponding calcium complex. The metal bis(trimethylsilyl)amides were made to react with protic ligand **1** in the second method to eliminate the volatile bis(trimethylsilyl)amine. The magnesium complex **3** and barium complex **5** were prepared only through the first method. Solid-state structures of all the new complexes were established by single crystal X-ray diffraction analysis. The smaller ionic radii of  $\text{Mg}^{2+}$  (0.72 Å) and  $\text{Ca}^{2+}$  (0.99 Å) ions form the monomeric complex, whereas the larger ions  $\text{K}^+$  (1.38 Å) and  $\text{Ba}^{2+}$  (1.35 Å) were found to form one-dimensional polymeric complexes with monoanionic ligand **1**. Compound **2** serves an example of magnesium complex with a Mg–Se direct bond.

**Keywords.** Magnesium; calcium; barium; potassium; phosphorus; selenium.

## 1. Introduction

To date, the chemistry of alkaline earth metals is less developed when compared to magnesium chemistry, and the former are often termed ‘sleeping beauties’.<sup>1,2</sup> Among the alkaline earth metals (Mg, Ca, Sr and Ba), magnesium is exceptional; it was studied extensively by Grignard, who established that the organomagnesium reagent plays a significant role in synthetic inorganic and organic chemistry.<sup>3,4</sup> In recent years, the chemistry of heavier alkaline earth metals has been well established and complexes of the alkaline earth metals are employed in various catalytic applications such as ring-opening polymerisation of various cyclic esters,<sup>5,6</sup> polymerisation of styrene and dienes,<sup>7–9</sup> and hydroamination and hydrophosphination reactions of alkenes and alkynes.<sup>10</sup> Exploration of the structure and reactivity of alkaline earth metal species is one of the most important steps towards the design and development of efficient homogeneous catalysts. However, full realisation of

the catalytic potential of these elements still requires substantial advances in understanding their basic coordination and organometallic chemistry. To stabilise these extremely oxophilic and electropositive metals, a wide variety of nitrogen-based ancillary ligands, such as tris(pyrazolyl)borates,<sup>1</sup> aminotroponimines,<sup>11</sup>  $\beta$ -diketiminates,<sup>12–14</sup> iminopyrroles<sup>15–17</sup> and 1,4-diaza-1,3-butadiene<sup>18,19</sup> have been introduced to prepare well-defined alkaline earth metal complexes, revealing that the catalytic activity and selectivity of the alkaline earth metal complexes can be controlled via the well-defined nitrogen-based ligand architecture. Another important application of alkaline earth metal chalcogenolates is in high temperature superconductors and ferroelectrics. In particular, alkaline earth metal oxide compounds are used as suitable precursors.<sup>20</sup> Much less attention has been paid to the alkaline earth metal thiolates and selenates, although many heavier chalcogenates are known as potential dopants for chalcogen-based semiconductors.<sup>21</sup> Chelating ligands with selenium as the donor atom to stabilise heavier alkaline earth metal complexes are rare. Over the

\*For correspondence

last few years very few alkaline earth selenium-based complexes have been reported and structurally characterised. Among these are  $[\text{Mg}(\text{SeMes}^*)_2(\text{THF})_2]$  ( $\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$ ),<sup>22</sup>  $[\text{M}(\text{SeMes})_2(\text{THF})_4]$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ),<sup>23–25</sup>  $[\text{Ca}\{\text{CH}(\text{Py})(\text{Se})\text{PPh}_2\}_2(\text{THF})_2]$  ( $\text{Py} = \text{pyridine}$ )<sup>26</sup> and  $[(\text{TMEDA})_2\text{Ca}(\text{SeSi}(\text{SiMe}_3)_3)]$ .<sup>27</sup> Full structural characterisation of strontium selenides is even more scarce.<sup>23,28</sup> A complex with a barium–selenium bond is limited as structurally authenticated examples are mostly restricted to various sulphur derivatives:  $[\{(\text{H}_2\text{O})_2\text{Ba}(\text{tmtH}_2)_2\}_n]$  ( $\text{tmt} = 2,4,6\text{-trimarcaptotriazine}, \text{S}_3\text{C}_3\text{N}_3$ ),<sup>29</sup>  $[(\text{[18]crown-6})\text{Ba}(\text{hmpa})\text{SMes}^*][\text{SMes}^*](\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2)$ ,<sup>30</sup>  $[\text{Ba}(\text{hmpa})_3\{\text{Na-PhNNN}(\text{C}(\text{S}))_2\}_2]$ ,<sup>31</sup>  $[\text{Ba}(\text{hmpa})_3(\text{C}(\text{=S})\text{NOPh}_2)]$ <sup>32</sup> and  $[\text{Ba}(\text{SCMe}_3)_2]$ ,<sup>33</sup>  $[\text{Ba}(\text{tmeda})_2(\text{SeSi}(\text{SiMe}_3)_3)_2]$ ,<sup>27</sup> with only a few more examples being reported. Ruhlandt-Senge and colleagues reported barium selenoates like  $[\text{Ba}(\text{THF})_4(\text{SeMes}^*)_2]$ ,  $[(\text{[27]crown-6})\text{Ba}(\text{hmpa})_2(\text{SMes}^*)_2]$ ,  $[\text{Ba}(\text{Py})_3(\text{THF})(\text{SeTrip})_2]_2$  ( $\text{Trip} = 2,4,6\text{-iPr}_3\text{C}_6\text{H}_2$ ), and  $[\text{Ba}(\text{[18]crown-6})(\text{SeTrip})_2]$ ;<sup>34</sup> however the vast potential of this field of chemistry is yet to be developed. Recently, we reported heavier alkaline earth metal selenium containing complexes  $[\text{M}(\text{THF})_2\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CHPh}_2)\}_2]$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ) to enrich the field of heavier group 2 metal seleno complexes.<sup>35</sup> In that work we showed that phosphinoseleonic amide ligands are capable of stabilising heavier alkaline earth metals through the formation of a selenium metal bond. In continuation of our focus on alkaline earth metal selenide complexes, we now explore the ligand's role in the nuclearity of metal complexes. Other research groups also reported various main group chemistry with phosphonic diamides  $^t\text{BuP}(\text{O})(\text{NHR})_2$  and phosphonic triamides  $(\text{C}_5\text{H}_9\text{NH})_3\text{PO}$ .<sup>36,37</sup>

In this context, detailed synthetic and structural features of the phosphinoseleonic amide ligand  $[\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)]$  (**1**), the corresponding monomeric magnesium and calcium complexes of molecular composition  $[\text{M}(\text{THF})_n\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)\}_2]$  [ $\text{M} = \text{Mg}$  (**3**),  $n = 1$  and  $\text{M} = \text{Ca}$  (**4**),  $n = 2$ ] and polymeric potassium and barium complexes  $[\text{K}(\text{THF})_2\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)\}]_n$  (**2**) and  $[\text{K}(\text{THF})\text{Ba}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)\}_3]_n$  (**5**) respectively are presented.

## 2. Experimental

### 2.1 General information

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 a sodium wire and distilled under nitrogen from sodium and benzophenoneketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from  $\text{LiAlH}_4$  and stored in the glove box.  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (100 MHz) and  $^{31}\text{P}\{^1\text{H}\}$  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.  $[\text{KN}(\text{SiMe}_3)_2]$ ,<sup>38</sup>  $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$ <sup>39,40</sup> and *N-tert*-butyl-1,1-diphenylphosphinamine  $[\text{Ph}_2\text{PNHCMe}_3]$ <sup>41</sup> were prepared according to published procedures.  $\text{MI}_2$  ( $\text{M} = \text{Mg}, \text{Ca}, \text{Ba}$ ), were purchased from Sigma Aldrich and used without further purification.

### 2.2 Synthesis of $[\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)](\text{I})$

*N-tert*-butyl-1,1-diphenylphosphinamine (1.50 g, 5.82 mol) and elemental selenium (900 mg, 12.0 mol) were heated to  $60^\circ\text{C}$  in THF (10 mL) for 12 hours. Excess selenium metal was filtered through a G4 frit to collect the yellow colour filtrate. After evaporation of solvent from filtrate in *vacuo*, a light yellow solid residue was obtained. Compound **1** was re-crystallised from THF at room temperature.

Yield: 1.85 g, 94%.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02–8.08 (m, 4H, *ArH*), 7.40–7.45 (m, 6H, *ArH*), 1.36 (s, 9H,  $\text{CH}_3$ ), 2.22 (br, 1H, *NH*) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  136.3 (P attached *ArC*), 135.4 (P attached *ArC*), 131.8 (P attached *o-ArC*), 131.7 (P attached *o-ArC*), 131.4 (P attached *p-ArC*), 128.3 (P attached *m-ArC*), 128.1 (P attached *m-ArC*), 54.7 ( $\text{CMe}_3$ ), 31.5 ( $\text{CH}_3$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  46.33 ppm. FT-IR (selected data):  $\nu = 3216$  (N–H), 1433 (P–C), 993 (P–N), 535 (P=Se)  $\text{cm}^{-1}$ . Elemental analysis:  $\text{C}_{16}\text{H}_{20}\text{NPSe}$  (336.26); Calculated: C 57.15 H 5.99 N 4.17, Found: C 56.89 H 5.39 N 3.81.

### 2.3 Synthesis of $[\text{K}(\text{THF})_2[\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)]]_n$ (**2**)

In a 10 mL sample vial, ligand **1** (100 mg, 0.296 mmol) and  $[\text{K}\{\text{N}(\text{SiMe}_3)_2\}]$  (59.144 mg, 0.296 mmol) were mixed together with 5 mL of THF. After 6 hours of stirring, a small amount of THF (2 mL) and *n*-pentane (2 mL) were added to it and kept at  $-40^\circ\text{C}$ . After 24 hours, colourless crystals of compound **2** were obtained.

Yield: 140 mg, 90%.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  8.08–8.13(m, 4H, ArH), 6.90–7.09 (m, 6H, ArH), 1.29 (s, 9H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  133.8 (P attached ArC), 133.7 (P attached ArC), 132.2 (P attached o-ArC), 131.2 (P attached o-ArC), 130.1 (P attached p-ArC), 124.1 (P attached m-ArC), 123.4 (P attached m-ArC), 77.1 (THF), 60.4 ( $\text{CMe}_3$ ), 14.2 ( $\text{CH}_3$ ), 25.6 (THF) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.9 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  46.3 ppm. FT-IR (selected data):  $\nu = 1433$  (P–C), 992 (P–N), 576 (P=Se)  $\text{cm}^{-1}$ . Elemental analysis:  $\text{C}_{24}\text{H}_{32}\text{KNO}_2\text{PSe}$  (515.54); Calculated: C 55.91 H 6.26 N 2.72, Found: C 55.36 H 5.92 N 2.43.

#### 2.4 Synthesis of $[\text{Mg}(\text{THF})_n\{\eta^2\text{-Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)_2\}]$ (3)

In a 25 mL pre-dried Schlenk flask, compound **2** (186 mg, 0.36 mmol) was mixed with  $\text{MgI}_2$  (50 mg, 0.18 mmol) in 10 mL THF solvent at ambient temperature and stirred for 12 hours. The white precipitate of KI was filtered and the filtrate was evaporated in *vacuo*. The resulting white residue was further purified by washing with pentane (3 mL) and crystals suitable for X-ray analysis were grown from THF/pentane (1: 2 ratio) mixture at  $-40^\circ\text{C}$ .

Yield: 118 mg, 85%.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  8.17–8.23 (m, 8H, ArH), 6.98–7.15 (m, 12H, ArH), 1.20 (s, 18H,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  132.4 (P-ArC), 132.3 (P-ArC), 131.3 (P attached o-ArC), 130.8 (P attached o-ArC), 128.3 (P attached p-ArC), 128 (P attached m-ArC), 127.8 (P attached m-ArC), 55.0 ( $\text{CMe}_3$ ), 31.4 ( $\text{CH}_3$ ), ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.9 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  59.5 ppm. FT-IR (selected data):  $\nu = 1436$  (P–C), 930 (P–N), 570 (P=Se)  $\text{cm}^{-1}$ . Elemental analysis:  $\text{C}_{40}\text{H}_{54}\text{MgN}_2\text{O}_2\text{P}_2\text{Se}_2$  (839.02); Calculated: C 57.26 H 6.49 N 3.34, Found: C 56.83 H 5.97 N 3.01.

#### 2.5 Synthesis of $[(\text{THF})_n\text{Ca}\{\eta^2\text{-Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)_2\}]$ (4)

**Route 1:** In a 10 mL sample vial, two equivalents (100 mg, 0.296 mmol) of ligand **1** and one equivalent of  $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2]$  were mixed together with 5 mL of THF. After 6 hours of stirring, another 2 mL of THF and *n*-pentane (2 mL) were added to it and kept at  $-40^\circ\text{C}$ . After 24 hours, colourless crystals were obtained.

Yield: 115.0 mg, 90%.

**Route 2:** In a 25 mL pre-dried Schlenk flask, compound **2** (320 mg, 0.68 mmol) was mixed with  $\text{CaI}_2$  (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 pentane and crystals suitable for X-ray analysis were grown from THF/pentane (1: 2 ratio) mixture at  $-40^\circ\text{C}$ .

Yield: 270 mg, 92%.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  8.12–8.17 (m, 8H, ArH), 7.09–7.16 (m, 12H, ArH), 3.76 (m, THF), 1.49 (s, 18H,  $\text{CH}_3$ ), 1.37 (m, THF) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  142.5 (P-ArC), 141.8 (P-ArC), 132.7 (P attached o-ArC), 132.6 (P attached o-ArC), 129.7 (P attached p-ArC), 127.5 (P attached m-ArC), 127.4 (P attached m-ArC), 68.7 (THF), 55.0 ( $\text{CMe}_3$ ), 35.9 ( $\text{CH}_3$ ), 25.6 (THF) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.9 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  37.1 ppm. FT-IR (selected data):  $\nu = 1433$  (P–C), 995 (P–N), 581 (P=Se)  $\text{cm}^{-1}$ . Elemental analysis:  $\text{C}_{44}\text{H}_{62}\text{CaN}_2\text{O}_4\text{P}_2\text{Se}_2$  (942.90); Calculated: C 56.05 H 6.63 N 2.97, Found: C 55.77 H 6.32 N 2.58.

#### 2.6 Synthesis of $[\text{K}(\text{THF})\text{Ba}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)_2\}]_n$ (5)

In a 25 mL pre-dried Schlenk flask, potassium complex **2** (264 mg, 0.52 mmol) was mixed with  $\text{BaI}_2$  (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 and filtrate was evaporated in *vacuo*. The resulting white compound was further purified by washing with pentane and crystals suitable for X-ray analysis were grown from THF/pentane (1:2 ratio) mixture at  $-40^\circ\text{C}$ .

Yield: 285 mg, 90%.

$^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  8.27–8.33 (m, 12H, ArH), 7.08–7.15 (m, 18H, ArH), 1.27 (s, 27H,  $\text{CH}_3$ ) ppm, 3.67 (m, THF), 1.51 (m, THF) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  132.3 (P attached ArC), 132.2 (P attached o-ArC), 132.1 (P attached o-ArC), 128.3 (P attached p-ArC), 128 (P attached m-ArC), 127.8 (P attached m-ArC), 68.7 (THF), 58.9 ( $\text{CMe}_3$ ), 31.5( $\text{CH}_3$ ), 25.6 (THF) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR(161.9 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  46.3 ppm. FT-IR (selected data):  $\nu = 1433$  (P–C), 996 (P–N), 576 (P=Se)  $\text{cm}^{-1}$ . Elemental analysis:  $\text{C}_{56}\text{H}_{73}\text{BaKN}_3\text{O}_2\text{P}_3\text{Se}_3$  (1326.39); Calculated: C 50.71 H 5.55 N 3.17, Found: C 50.23 H 5.11 N 2.74.

## 2.7 Single-crystal x-ray structure determinations

Single crystals of compound **1** were grown from THF at room temperature and complexes **2–5** were grown from a solution of THF/pentane mixture (1:2) under inert atmosphere at a temperature of  $-40^{\circ}\text{C}$ . In each case 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. All measurements were made on an Agilent Supernova X-calibur Eos CCD detector with graphite-monochromatic MoK $\alpha$  (0.71073 Å) (for **1**) and Cu K $\alpha$

(1.54184 Å) (for **2**, **3**, **4** and **5**) radiation. Crystal data and structure refinement parameters are summarised in table 1. The structures were solved by direct methods (SIR92)<sup>42</sup> and refined on  $F^2$  by full-matrix least-squares methods; using SHELXL-97.<sup>43</sup> Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimised was  $[\sum w(F_o^2 - F_c^2)^2]$  ( $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ ), where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$  with  $\sigma^2(F_o^2)$  from counting statistics. The function  $R_1$  and  $wR_2$  were  $(\sum \|F_o\| - |F_c|) / \sum |F_o|$  and  $[\sum w(F_o^2 -$

**Table 1.** Structural parameters for complexes **1–5**.

Crystal Parameters	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
CCDC No.	991038	991040	991042	991041	991039
Formula weight	336.26	515.54	839.02	942.90	1326.39
$T(\text{K})$	150(2)	150(2)	150(2)	150(2)	150(2)
$\lambda(\text{Å})$	0.71073	1.54184	1.54184	1.54184	1.54184
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P 21 21 21$	$P 21/c$	$P 21/c$	$P-1$	$P-1$
$a(\text{Å})$	9.5205(3)	11.2088(5)	10.5224(4)	9.0371(8)	11.1136(6)
$b(\text{Å})$	9.5544(3)	24.0100(11)	10.0241(3)	10.3328(8)	11.6984(7)
$c(\text{Å})$	17.5037(6)	10.8149(5)	39.048(2)	13.0838(8)	24.9355(14)
$\alpha(^{\circ})$	90	90	90	88.7	87
$\beta(^{\circ})$	90	11	93	75	82
$\gamma(^{\circ})$	90	90	90	69	67
$V(\text{Å}^3)$	1592.18(9)	2573.9(2)	4110.2(3)	1104.36(15)	2969.8(3)
$Z$	4	4	4	1	2
$D_{\text{calc}} \text{ g cm}^{-3}$	1.403	1.330	1.356	1.418	1.483
$\mu(\text{mm}^{-1})$	2.446	4.155	3.402	4.131	9.007
$F(000)$	688	1068	1736	490	1336
Theta range for data collection	2.43 to 25.77 deg.	3.68 to 70.91 deg.	4.21 to 70.74 deg.	4.59 to 70.91 deg.	4.09 to 70.59 deg.
Limiting indices	$-11 \leq h \leq 6$ $-11 \leq k \leq 10$ $-20 \leq l \leq 12$	$-13 \leq h \leq 13$ $-29 \leq k \leq 29$ $-8 \leq l \leq 13$	$-12 \leq h \leq 12$ $-12 \leq k \leq 11$ $-47 \leq l \leq 35$	$-11 \leq h \leq 10$ $-12 \leq k \leq 11$ $-15 \leq l \leq 14$	$-13 \leq h \leq 13$ $-8 \leq k \leq 14$ $-30 \leq l \leq 30$
Reflections collected / unique	3347 / 2379	10691 / 4852	16320 / 7738	7548 / 4145	22614 / 11197
Completeness to theta	[R(int)=0.0206] 87.7 % (25.77)	[R(int)=0.0377] 97.6 % (70.91)	[R(int)=0.0369] 97.9 %	[R(int)=0.0339] 97.5 %	[R(int)=0.0570] 98.2 %
Absorption correction	Å	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan
Max. and min. transmission	1.000 and 0.705	1.00000 and 0.65812	1.00000 and 0.61950	1.00000 and 0.65234	1.00000 and 0.12772
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data / restraints / parameters	2379 / 0 / 176	4852 / 0 / 273	7738 / 0 / 448	4145 / 0 / 253	11197 / 0 / 581
Goodness-of-fit on $F^2$	1.080	1.061	1.057	1.067	1.031
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0296$ , $wR_2 = 0.0797$	$R_1 = 0.0566$ , $wR_2 = 0.1559$	$R_1 = 0.0404$ , $wR_2 = 0.1019$	$R_1 = 0.0449$ , $wR_2 = 0.1249$	$R_1 = 0.0663$ , $wR_2 = 0.1766$
R indices (all data)	$R_1 = 0.0298$ , $wR_2 = 0.0801$	$R_1 = 0.0712$ , $wR_2 = 0.1762$	$R_1 = 0.0515$ , $wR_2 = 0.1071$	$R_1 = 0.0494$ , $wR_2 = 0.1296$	$R_1 = 0.0726$ , $wR_2 = 0.1881$
Absolute structure parameter	0.645(10)				
Largest diff. peak and hole	0.336 and $-0.570 \text{ e.Å}^{-3}$	0.966 and $-1.174 \text{ e.Å}^{-3}$	0.483 and $-0.920 \text{ e.Å}^{-3}$	1.151 and $-0.710 \text{ e.Å}^{-3}$	2.988 and $-2.197 \text{ e.Å}^{-3}$

$F_c^2/\Sigma(wFo^4)]^{1/2}$  respectively. The ORTEP-3 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication, Nos. CCDC 991038 (1), 991040 (2), 991042 (3), 991041 (4), 991039 (5). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + (44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

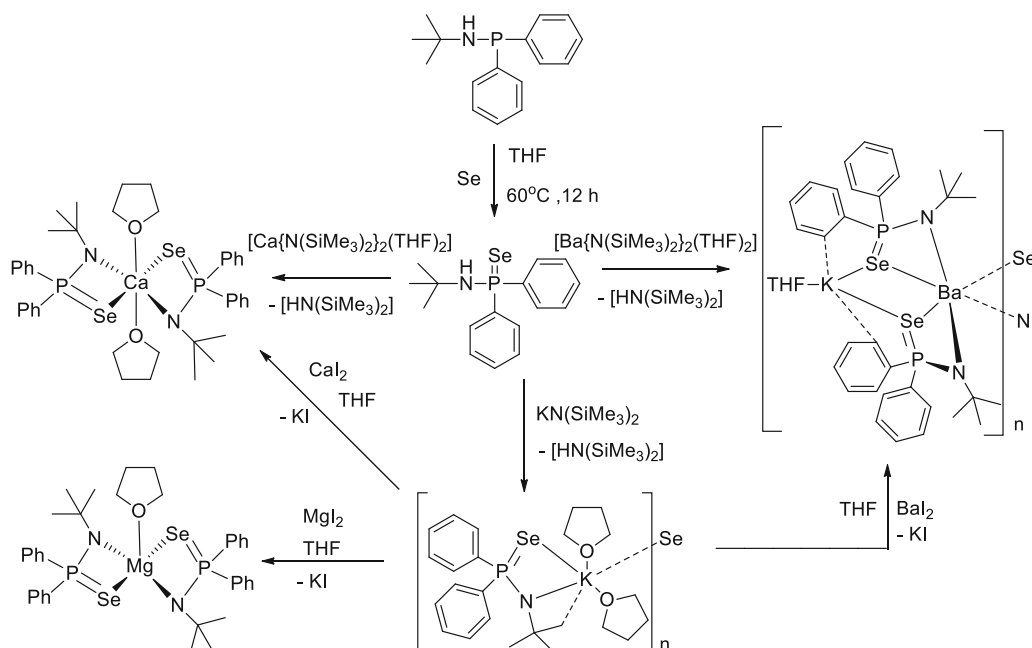
### 3. Results and Discussion

The bulky phosphinoselenoic amine [ $\text{Ph}_2\text{P}(\text{Se})\text{NHC}(\text{CH}_3)_3$ ] (**1**) was prepared in a similar fashion as [ $\text{Ph}_2\text{P}(\text{Se})\text{NH}-2,6\text{-Me}_2\text{C}_6\text{H}_4$ ]. [ $\text{Ph}_2\text{P}(\text{Se})\text{NHCHPh}_2$ ] and [ $\text{Ph}_2\text{P}(\text{Se})\text{NHCPh}_3$ ] were synthesised in quantitative yield by the treatment of [ $\text{Ph}_2\text{PNHC}(\text{CH}_3)_3$ ] with elemental selenium in 1:2 molar ratio at ambient temperature in THF solvent (scheme 1).<sup>35,42</sup> Compound **1** was characterised using standard analytical/spectroscopic techniques and its solid-state structure was established by single crystal X-ray diffraction analysis.

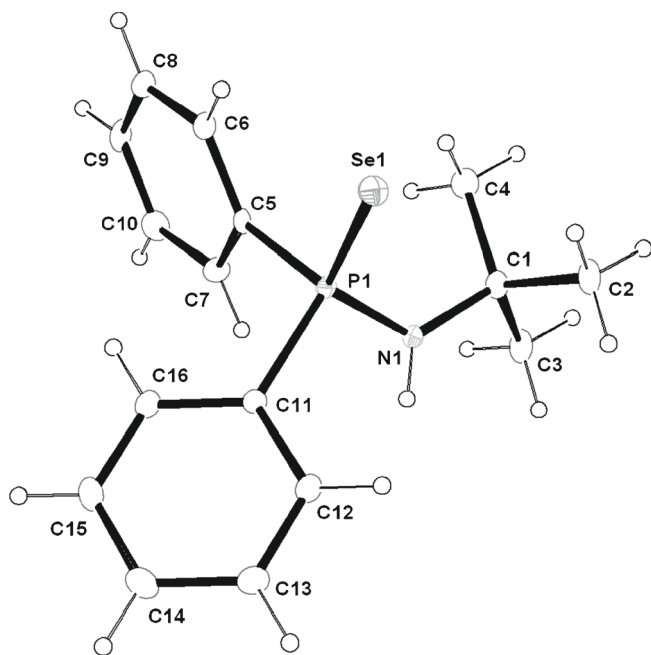
FT-IR spectrum of compound **1** shows strong absorption bands at  $535\text{ cm}^{-1}$  and  $993\text{ cm}^{-1}$  which can be assigned to the characteristic  $\text{P}=\text{Se}$  and  $\text{P}-\text{N}$  bond stretching frequencies respectively and these values are comparable with reported values  $568\text{ cm}^{-1}$  and

$901\text{ cm}^{-1}$ .<sup>42</sup> In the  $^1\text{H}$  NMR spectra, resonance signal at 1.36 ppm corresponds to the nine methyl protons of the *t*-butyl group and signal at 2.22 ppm represents the amine N-H proton of ligand **1**. Both the values are slightly downfield shifted with respect to the free phosphine amine [ $\text{Ph}_2\text{PNHC}(\text{CH}_3)_3$ ]. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **1**, signals at 54.7 and 31.5 ppm can be best assigned to tertiary carbon atom and methyl carbon atom, respectively. Proton decoupled  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra is more informative as compound **1** shows a signal at 46.3 ppm which is slightly downfield shifted from the phosphine amine [ $\text{Ph}_2\text{PNHC}(\text{CH}_3)_3$ ] (28.6 ppm) due to addition of the selenium atom to the phosphorus atom.

In the solid-state structure, compound **1** crystallises in the orthorhombic  $P2_12_1$  space group, having four molecules in the unit cell. The solid-state structure of compound **1** is shown in figure 1. The details of the structural parameters are given in table 1. The  $\text{P}=\text{Se}$  bond distance is found to be  $2.1187(8)\text{ \AA}$ , which is in good agreement with values we reported previously:  $2.1019(8)\text{ \AA}$  for [ $\text{Ph}_2\text{P}(\text{Se})\text{NH}(2,6\text{-Me}_2\text{C}_6\text{H}_4)$ ],  $2.1086(12)\text{ \AA}$  for [ $\text{Ph}_2\text{P}(\text{Se})\text{NHCHPh}_2$ ] and  $2.1166(8)\text{ \AA}$  for [ $\text{Ph}_2\text{P}(\text{Se})\text{NHCPh}_3$ ].  $\text{P1}-\text{N1}$  distance [ $1.655(3)\text{ \AA}$ ] and  $\text{C1}-\text{N1}$  distance [ $1.494(4)\text{ \AA}$ ] are also similar to those of phosphinoselenoic amides [ $\text{Ph}_2\text{P}(\text{Se})\text{NHR}$ ], which we previously reported:  $\text{P1}-\text{N1}$   $1.656(3)\text{ \AA}$ ,  $\text{C1}-\text{N1}$   $1.441(4)\text{ \AA}$  for  $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_4$ ,  $\text{P1}-\text{N1}$   $1.642(4)\text{ \AA}$ ,  $\text{C1}-\text{N1}$   $1.459(6)\text{ \AA}$  for  $\text{R} = \text{CHPh}_2$ , and  $\text{P1}-\text{N1}$   $1.664(2)\text{ \AA}$ ,  $\text{C1}-\text{N1}$   $1.496(4)\text{ \AA}$  for  $\text{R} = \text{CPh}_3$ .<sup>35,44</sup>



**Scheme 1.** Synthesis of alkali and alkaline earth metal complexes of phosphinoselenoic amide ligand (**1**).



**Figure 1.** ORTEP diagram of **1** with thermal displacement parameters drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]. P1–N1 1.655(3), P1–Se1 2.1187(8), P1–C5 1.815(3), P1–C11 1.816(3), N1–C1 1.494(4), C1–C2 1.533(5), C1–C3 1.526(5), C1–C4 1.529(5), N1–P1–Se1 119.41(10), Se1–P1–C5 112.48(10), Se1–P1–C11 110.70(10), N1–P1–C11 102.22(13), C5–P1–C11 105.15(14), P1–N1–C1 127.6(2), N1–C1–C4 109.9(3), N1–C1–C3 106.1(3), C2–C1–C3 109.9(3), C2–C1–C4 110.4(3), N1–C1–C2 110.4(3), C3–C1–C4 110.1(3).

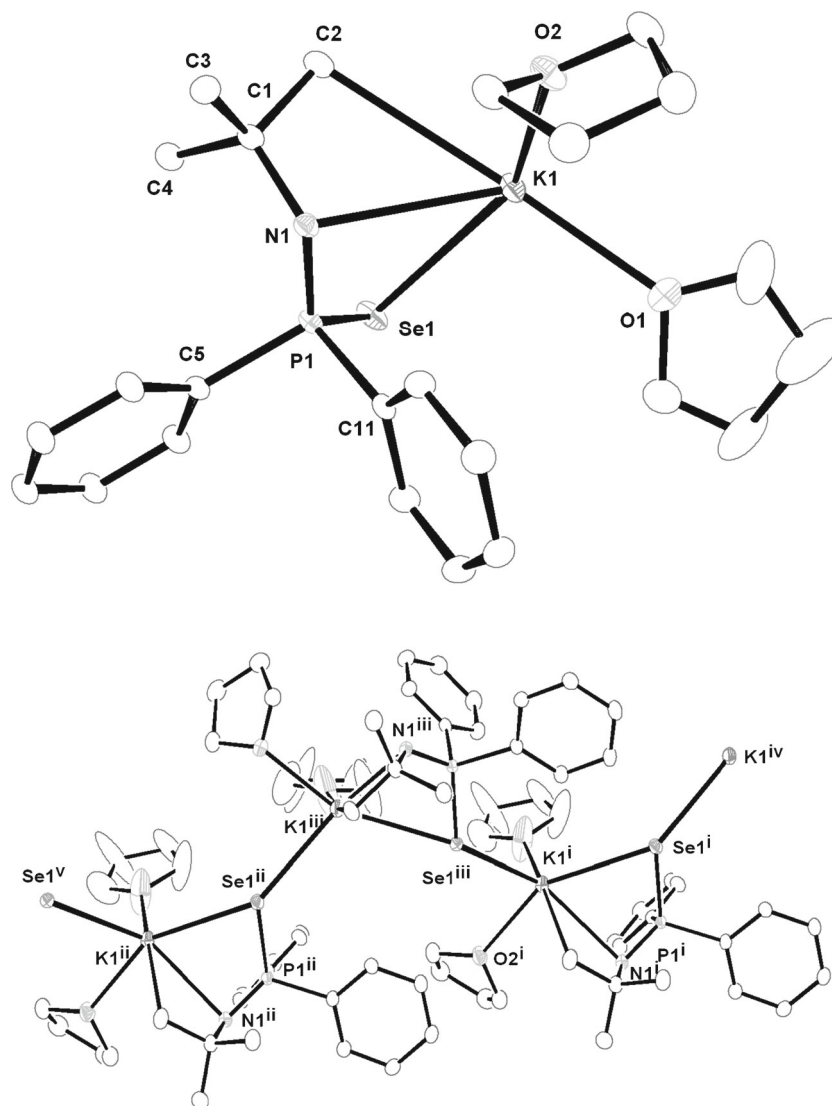
### 3.1 Potassium complex

The potassium complex of composition  $[\text{K}(\text{THF})_2\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)\}]_n$  (**2**) can be readily prepared by the reaction of compound **1** and potassium bis(trimethylsilyl)amide in THF through the elimination of volatile bis(trimethylsilyl)amine (scheme 1). Compound **2** was re-crystallised from a mixture of THF/pentane. Air and moisture sensitive compound **2** crystallises in the monoclinic  $P2_1/c$  space group, with four molecules in the unit cell. The details of the structural and refinement parameters are given in table 1. The asymmetric unit as well as the polymeric form of compound **2** in the solid state is shown in figure 2. In the asymmetric unit, the central potassium atom is surrounded by one monoanionic ligand **1** coordinating through the selenium and amido nitrogen atoms to form a four-membered metallacycle K1–Se1–P1–N1 with angles N1–K1–Se1 of 61.33(6)° and N1–P1–Se1 of 119.10(13)°. The K1–Se1 bond distance is 3.3125(10) Å which is in good agreement with the value we previously reported for the potassium salt of ligand

$[\text{Ph}_2\text{P}(\text{Se})\text{NCHPh}_2]^-$  (K–Se 3.3090(10) Å).<sup>35</sup> The K1–N1 bond distance is 3.047(3) Å which is slightly elongated compared to the previously reported value of K–N 2.725(3) Å.<sup>35</sup> The P1–K1 distance is 3.3806(13) Å and this is slightly shorter than the corresponding distances 3.5579(12) Å in  $[\{(\text{THF})_2\text{KPh}_2\text{P}(\text{Se})\text{N}(\text{CHPh}_2)\}_2]$ ,<sup>35</sup> 3.5354(14) Å in  $[\{(\text{THF})_2\text{KPh}_2\text{P}(\text{S})\text{N}(\text{CHPh}_2)\}_2]$ <sup>45</sup> and 3.5148(10) Å in  $[\{(\text{Ph}_2\text{CHNP}(\text{BH}_3)\text{Ph}_2)\text{K}(\text{THF})_2\}_2]$ ,<sup>46</sup> which we reported. The P1–K1 distance is within the sum of the covalent radii (3.45 Å) of potassium and phosphorous atoms, indicating a covalent interaction between them.<sup>47</sup> The potassium atom also has a weak interaction with one of the methyl carbon atoms of the tertiary butyl group [the K1...C2 distance is 3.210(5) Å]. The one-dimensional polymeric network for complex **2** is formed by the extended coordination of the selenium atom with the potassium atom of the neighbouring molecule. The K–Se distance of 3.2859(11) Å is within the range of the values mentioned above. Two additional THF molecules are chelated to the potassium atom, with K1–O1 and K1–O2 bond distances of 2.606(5) Å and 2.654(3) Å respectively. Therefore, the geometry of each potassium centre in the polymeric unit is best described as distorted octahedral. It is noteworthy that the polymeric structure for complex **2** was observed, due to the bulky *t*-butyl group on the amido nitrogen, as in contrast only dimeric polymetallacyclic structure for the potassium salt  $[(\text{THF})_2\text{K}\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CHPh}_2)\}]_2$  potassium structure was found by using diphenylmethyl (CHPh<sub>2</sub>) group on the same nitrogen atom, keeping other groups identical in our previous report.<sup>35</sup> Thus, the presence of the more bulky *t*-butyl group at nitrogen plays an important role in determining the nuclearity of complex **2**. In the solution state, complex **2** shows only one set of signals similar to the free ligand **1** in the <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra, which indicates the dynamic behaviour of complex **2** in the solution state. <sup>31</sup>P{<sup>1</sup>H} NMR spectra of complex **2** shows single peak at 46.33 ppm which is very similar to ligand **1** (46.30 ppm), indicating that there is no influence of the potassium atom on the phosphorous centre of ligand **1** upon complex formation.

### 3.2 Alkaline earth metal complexes

The magnesium, calcium and barium complexes **3**, **4** and **5** respectively, were prepared in good yield and high purity using two synthetic routes. In the first method, complexes **3–5** were prepared by the reaction of respective alkaline earth metal diiodides  $\text{MI}_2$  (where M = Mg, Ca and Ba) with potassium salt of phosphinoselenoic amide  $[\text{K}(\text{THF})_2\{\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)\}]_n$



**Figure 2.** ORTEP diagram of **2** with thermal displacement parameters drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]. K1-N1 3.047(3), K1-Se1 3.3125(10), K1-O1 2.606(5), K1-O2 2.654(3), K1-C2 3.210(5), P1-N1 1.576(3), P1-Se1 2.1792(11), P1-C5 1.842(4), P1-C11 1.825(4), N1-C1 1.476(5), C1-C2 1.534(6), C1-C3 1.528(6), C1-C4 1.542(6), P1-N1-K1 87.97(14), C1-N1-K1 106.2(2), P1-Se1-K1 72.70(3), N1-K1-Se1 61.33(6), Se1-K1-O1 105.06(18), O1-K1-O2 93.6(2), N1-K1-O2 88.29(10), O1-K1-N1 126.8(2), Se1-K1-O2 149.61(8), N1-P1-C5 114.69(18), C5-P1-C11 100.89(17), C11-P1-Se1 108.10(13), N1-P1-Se1 119.10(13), C11-P1-N1 103.72(18), C5-P1-Se1 108.42(13), P1-N1-C1 126.3(3), C2-C1-N1 109.8(3), N1-C1-C3 107.0(3), C2-C1-C3 108.5(4), C2-C1-C4 108.3(4), C3-C1-C4 108.4(4).

(**2**), which was prepared according to the procedure in the literature involving ligand **1** and potassium bis(trimethylsilyl)amide.<sup>48</sup> The second method involved treating the phosphinoselenoic amide (**1**) directly with calcium bis(trimethylsilyl)amide  $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2\{\text{THF}\}_n]$  in THF at ambient temperature to afford the calcium complex of molecular formula  $[(\text{THF})_2\text{Ca}\{\eta^2-$

$\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)_2$ ]**2**) (**4**) (scheme 1). The first route was followed for the three metal complexes **3–5**, while the second was followed only for complex **4**. The novel alkaline earth metal complexes **3–5** were characterised using analytical/spectroscopic techniques and the molecular structures of complexes **3–5** were determined by single crystal X-ray diffraction analyses.

The strong absorption at  $570\text{ cm}^{-1}$  (for **3**),  $581\text{ cm}^{-1}$  (for **4**) and  $576\text{ cm}^{-1}$  (for **5**) in FT-IR spectra indicates the evidence of P=Se bond in each complex and the values are very similar to that of the neutral ligand **1** ( $535\text{ cm}^{-1}$ ) due to the slight elongation of P=Se bond bound to the metal centre. In  $^1\text{H}$  NMR spectra, the amino proton of ligand **1**, which was present at 2.22 ppm, is absent. Two multiplet signals for each complex at 3.76 and 1.37 ppm (for **4**), 3.67 and 1.51 ppm (for **5**) can be assigned to the solvated THF molecules coordinated to the metal centre. One set of signals for the phenyl protons are also observed, which is in the same range as that of ligand **1**, indicating no significant effect of metal atoms on the phenyl groups due to complex formation. In  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, in complexes **3–5**, all the phosphorus atoms present in the phosphinoselenoic amide ligand (**1**) moieties are chemically equivalent and show only one signal at 59.5 ppm (for **3**), 37.1 ppm (for **4**) and 46.3 ppm (for **5**). For compound **3** this value is shifted to downfield and for compound **4**, shifted up field in comparison to potassium salt **2** (46.3 ppm) and neutral ligand **1** (46.3 ppm). Unlike the magnesium and calcium complexes (**3** and **4**), the barium complex **5** shows  $^{31}\text{P}\{^1\text{H}\}$  NMR signal at 46.3 ppm which is the same as that of potassium salt **2** as well as neutral ligand **1** (46.3 ppm). This observation is quite different from our previous studies where we noticed a high downfield shift for the resonance of phosphorus atoms (71.9 ppm for Ca, 71.8 ppm for Sr and 71.9 for Ba) bound to heavier alkaline earth metals compared to the free phosphinoselenoic amido ligand  $[\text{Ph}_2\text{P}(\text{Se})\text{NCHPh}_2]^-$  (58.0 ppm).<sup>35</sup>

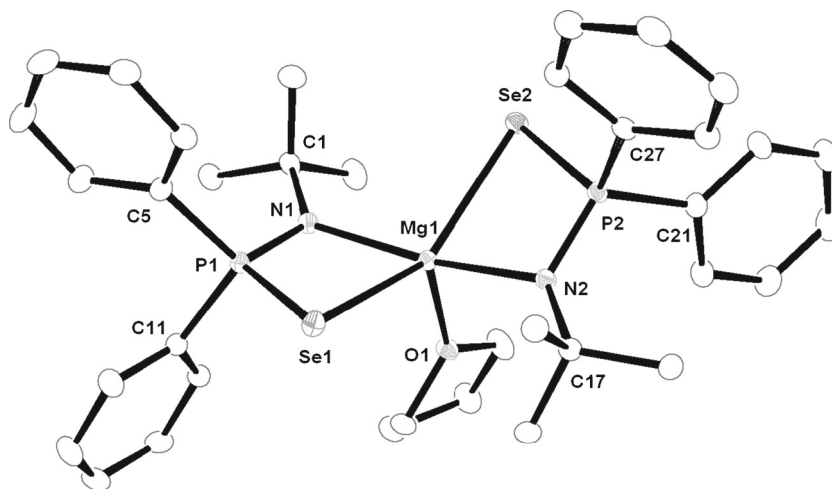
In the solid state, the magnesium complex **3** crystallises in the monoclinic  $P2_1/c$  space group, with four molecules in the unit cell. The details of the structural parameters for compound **3** are given in table 1. The molecular structure of compound **3** is shown in figure 3. In magnesium complex **3**, the coordination polyhedron is formed by two monoanionic  $[\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)]^-$  ligands, and one THF molecule. Each  $[\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)]^-$  ligand coordinates to the magnesium atom through the chelation of one selenium atom and one amido nitrogen atom. The P–Mg distance of  $2.9963(14)\text{ \AA}$  and  $2.9987(14)\text{ \AA}$  is slightly greater than the average Mg–P coordination bond ( $2.667\text{ \AA}$ ) and thus a weak interaction between them was observed.<sup>49</sup> Thus the  $[\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)]^-$  group can be considered a bi-dentate ligand. The geometry around the central magnesium atom can be best described as a distorted square pyramidal, having two amido nitrogen and two selenium atoms of two  $[\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)]^-$  moieties in the basal plane and the oxygen atom from the THF molecule at the

axial position. Two four-membered metallacycles N1–P1–Se1–Mg1 and N2–P2–Se2–Mg1 are formed and a dihedral angle of  $40.6^\circ$  is observed between the two mean planes, having N1, P1, Se1 and Mg1, and N2, P2, Se2 and Mg1 atoms respectively.

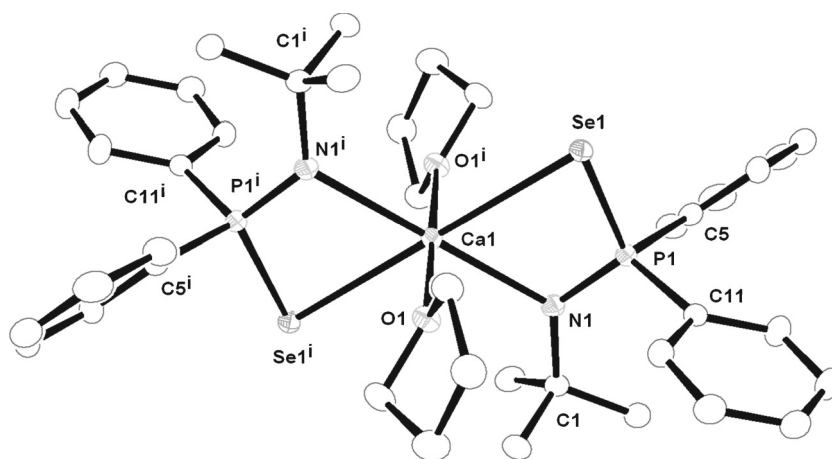
The most interesting thing is that the magnesium–selenium bond distances [Mg1–Se1  $2.6964(12)\text{ \AA}$  and Mg1–Se2  $2.7056(12)\text{ \AA}$ ] are slightly elongated in comparison to previously reported value of  $2.536(3)\text{ \AA}$  for the compound  $[\text{Mg}(\text{SeMes}^*)_2(\text{THF})_2]$  (where  $\text{Mes}^* = 2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2$ ).<sup>27</sup> This is mainly due to the steric bulk on the backbone of the phosphineamido ligand moiety. The magnesium–nitrogen distances [Mg1–N1  $2.169(3)\text{ \AA}$  and Mg1–N2  $2.145(3)\text{ \AA}$ ] were observed for compound **3**; these are slightly longer when compared to the Mg–N bond reported in the literature. For example, the Mg–N bond distance was reported as  $1.970(3)\text{ \AA}$  for  $[\{(\text{L}^{\text{iPr}})_2\text{Mg}(\text{THF})_2\} \cdot (\text{THF})]$ ,  $2.094(3)\text{ \AA}$  for  $[\{(\text{L}^{\text{iPr}})_2\text{Mg}\} \cdot (\text{THF})]$  (where  $\text{L}^{\text{iPr}} = [(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})_2]$ ) and  $2.051(2)\text{ \AA}$  for  $[(\text{L}^{\text{Mes}})_2\text{Mg}(\text{THF})_3]$  and  $2.070(2)\text{ \AA}$  for  $[(\text{L}^{\text{Mes}})_2\text{Mg}]$  (where  $\text{L}^{\text{Mes}} = [(2,4,6\text{-}Me_3\text{C}_6\text{H}_2)\text{NC}(\text{Me})_2]$ ).<sup>50</sup> Recently, we also synthesised magnesium complex of the type  $[\text{Mg}\{\text{C}_2\text{H}_4(\text{NPh}_2\text{P}(\text{Se}))_2\}\{\text{THF}\}_3]$  in which we observed Mg–N distances of  $2.066(3)\text{ \AA}$  and  $2.083(3)\text{ \AA}$ , which is well in agreement with the reported values, but slightly shorter than the observed values  $2.169(3)\text{ \AA}$  and  $2.145(3)\text{ \AA}$  for complex **3**. The P–Se bond distances [ $2.1567(9)\text{ \AA}$  and  $2.1581(9)\text{ \AA}$ ] and P–N bond distances [ $1.606(3)\text{ \AA}$  and  $1.602(3)\text{ \AA}$ ] are within the range for alkaline earth metal complexes that we previously reported: P–Se distance  $2.1449(18)\text{ \AA}$  for Ca,  $2.1477(12)\text{ \AA}$  for Sr and  $2.152(2)\text{ \AA}$  for Ba, and P–N distance  $1.631(6)\text{ \AA}$  for Ca,  $1.610(3)\text{ \AA}$  for Sr and  $1.609(7)\text{ \AA}$  for Ba.<sup>35</sup>

In contrast to the magnesium complex **3** the homoleptic calcium complex **4** crystallises in the triclinic space group  $P-1$ , with one molecule in the unit cell. The details of the structural parameters are given in table 1. The solid state structure of complex **4** is shown in figure 4. In accordance with alkaline earth metal complexes, we previously reported  $[\text{M}\{\text{Ph}_2\text{P}(\text{Se})\text{NCHPh}_2\}_2(\text{THF})_2]$  (where  $\text{M} = \text{Ca}$  and  $\text{Sr}$ ), in the calcium complex **4**, the coordination polyhedron is formed by two  $[\text{Ph}_2\text{P}(\text{Se})\text{N}(\text{CMe}_3)]^-$  ligands, and two THF molecules which are *trans* to each other. Therefore, the calcium atom adopts a distorted octahedral geometry. The structural differences between the magnesium and calcium complexes can be explained by the larger ionic radius of  $\text{Ca}^{2+}$  ( $0.99\text{ \AA}$ ) compared to that of  $\text{Mg}^{2+}$  ( $0.72\text{ \AA}$ ).<sup>51</sup> The Ca–Se bond distance of  $2.9619(3)\text{ \AA}$  observed in complex **4** is quite long, compared to the magnesium analogue [ $2.6964(12)\text{ \AA}$

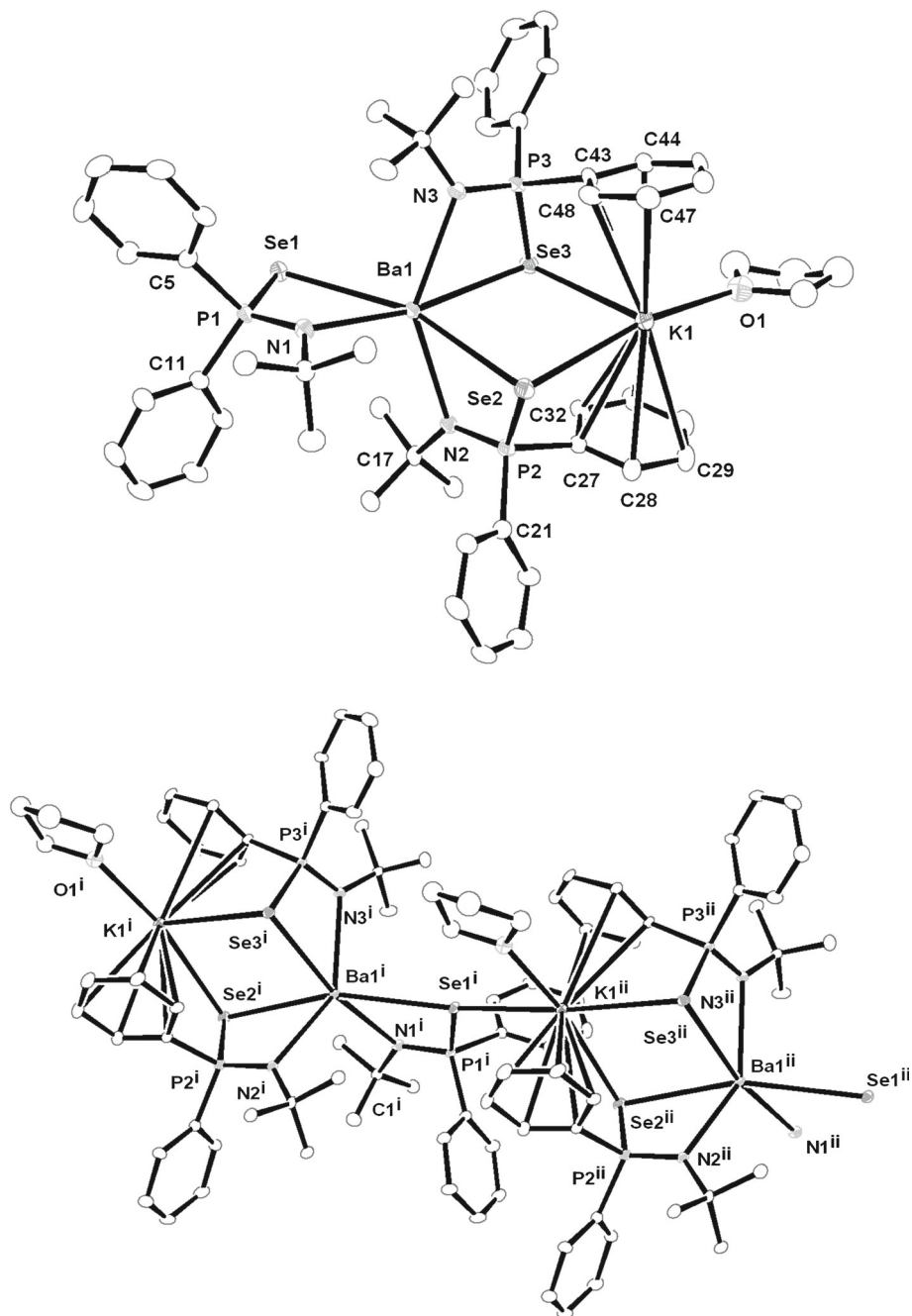




**Figure 3.** ORTEP diagram of **4** with thermal displacement parameters drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]. Mg1-N2 2.145(3), Mg1-Se2 2.7056(12), Mg1-O1 2.067(3), Mg1-N1 2.169(3), Mg1-Se1 2.6964(12), P1-Se1 2.1567(9), P1-N1 1.606(3), N1-C1 1.496(4), P1-C5 1.828(4), P1-C11 1.827(4), P2-N2 1.602(3), P2-Se2 2.1581(9), P2-C21 1.825(4), P2-C27 1.834(4), N2-C17 1.497(4), Mg1-Se2-P2 75.19(3), Mg1-N2-P2 105.39(14), N2-Mg1-Se2 74.99(8), N2-Mg1-O1 95.95(11), O1-Mg1-Se1 107.81(8), Se2-Mg1-N1 100.90(8), Se1-Mg1-N1 75.40(8), Mg1-Se1-P1 75.34(3), Mg1-N1-P1 104.11(14), Mg1-N1-C1 129.4(2), N1-P1-Se1 105.03(10), P1-N1-C1 129.4(2), Se1-P1-C11 105.55(12), N1-P1-C5 116.52(16), C5-P1-C11 103.97(17), Se1-P1-C5 109.51(12), N1-P1-C11 115.73(16), C21-P2-C27 105.86(17), N2-P2-C21 115.08(16), Se2-P2-C27 110.60(11), N2-P2-Se2 104.18(10), N2-P2-C27 114.30(15), Se2-P2-C21 106.61(12).



**Figure 4.** ORTEP diagram of **4** with thermal displacement parameters drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]. Ca1-N1 2.451(3), Ca1-Se1 2.9619(3), Ca1-O1 2.465(2), Ca1-O1<sup>i</sup> 2.465(2), Ca1-Se1<sup>i</sup> 2.9619(3), Ca1-N1<sup>i</sup> 2.451(3), P1-N1 1.591(3), P1-Se1 2.1706(8), N1-C1 1.495(4), P1-C5 1.835(3), P1-C11 1.835(3). Ca1-N1-C1 126.33(19), P1-N1-Ca1 105.15(13), P1-Se1-Ca1 76.91(2), N1-Ca1-Se1 68.73(6), N1-Ca1-O1 92.66(8), O1-Ca1-Se1<sup>i</sup> 92.66(8), Se1<sup>i</sup>-Ca1-N1<sup>i</sup> 68.73(6), N1<sup>i</sup>-Ca1-O1<sup>i</sup> 92.66(8), C11-P1-C5 104.56(15), C11-P1-N1 112.89(14), N1-P1-Se1 109.19(10), C5-P1-N1 115.73(16), C11-P1-Se1 107.43(10), P1-N1-C1 126.9(2).



**Figure 5.** ORTEP diagram of **5** with thermal displacement parameters drawn at the 30% probability level; hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and bond angles [°]. Ba1-Se2 3.3203(7), Ba1-Se3 3.3518(7), Ba1-N2 2.790(5), Ba1-N3 2.789(5), Ba1-Se1 3.3274(7), Ba1-N1 2.774(5), O1-K1 2.731(6), K1-Se3 3.4175(15), K1-Se2 3.3627(15), P1-N1 1.603(5), P1-Se1 2.1681(16), N1-C1 1.491(8), P1-C11 1.825(6), P1-C5 1.826(6), P2-Se2 2.1681(15), P2-C27 1.835(6), P2-C21 1.852(6), P2-N2 1.577(5), N2-C17 1.488(7), P3-Se3 2.1692(15), P3-N3 1.593(5), N3-C33 1.490(8), P3-C37 1.829(6), P3-C43 1.838(6), N3-C33 1.490(8). K1-Se3-Ba1 96.20(3), K1-Se2-Ba1 97.86(3), Se2-Ba1-Se3 82.865(18), P2-Se2-Ba1 79.80(4), P2-N2-Ba1 109.3(2), N2-Ba1-Se2 59.95(10), Se3-Ba1-N3 59.78(10), N3-Ba1-Se1 95.75(10), N1-Ba1-Se1 59.68(11), N1-Ba1-N2 106.15(15), Ba1-Se1-P1 80.57(4), Ba1-N1-P1 110.7(2), Ba1-N1-C1 119.3(4), Ba1-N3-P3 109.9(2), Ba1-N3-C33 122.5(3), O1-K1-Se3 101.11(13), O1-K1-Se2 168.59(14), Se2-K1-Se3 81.26(3), N1-P1-Se1 108.26(19), P1-N1-C1 126.5(4), Se1-P1-C5 105.8(2), N1-P1-C11 114.1(3), C5-P1-C11 103.6(3), N1-P1-C5 115.8(3).

and 2.7056(12) Å] due to the larger ionic radius of the Ca<sup>2+</sup> ion. The observed Ca–Se bond distance [2.9619(3) Å] is within the range of Ca–Se distances [2.9889(8) Å] of the structurally characterised complex [Ca{Ph<sub>2</sub>P(Se)NCHPh<sub>2</sub>}<sub>2</sub>(THF)<sub>2</sub>] reported by us.<sup>35</sup> In the literature, we find 2.945(1) Å reported for [(THF)<sub>2</sub>Ca{(PyCH)(Se)PPh<sub>2</sub>}<sub>2</sub>],<sup>26</sup> 2.93 Å to 3.00 Å reported for [(THF)<sub>4</sub>Ca(SeMes')<sub>2</sub>] and 2.958(2) Å to 3.001(2) Å reported for [(THF)<sub>2</sub>Ca(Se<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>].<sup>16,23</sup> The Ca–N distance [2.451(3) Å] is slightly longer compared to the calcium–nitrogen covalent bond reported in the literature [2.361(2) Å and 2.335(2) Å] reported for [Ca(Dipp<sub>2</sub>DAD)(THF)<sub>4</sub>] (Dipp<sub>2</sub>DAD = N,N'-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene).<sup>19</sup> The P–Ca distance [3.2516(8) Å] is too long to consider any interaction between them.

Unlike the magnesium and calcium complexes **3** and **4**, barium metal forms an 'ate' complex of molecular formula [K(THF)Ba{Ph<sub>2</sub>P(Se)N(CMe<sub>3</sub>)<sub>3</sub>}<sub>3</sub>]<sub>n</sub> (**5**). This is mainly due to the larger ionic radius of the Ba<sup>2+</sup> ion and *t*-butyl group on the nitrogen atom of ligand **1** allows the third anionic ligand to coordinate to the barium centre. Complex **5** crystallises in the triclinic space group *P*–1, with two molecules in the unit cell. The details of the structural parameters are given in table 1. The solid state structure of complex **5** is shown in figure 5. In the asymmetric unit of complex **5**, the central Ba<sup>2+</sup> ion is surrounded by three anionic ligand **1** moieties, which coordinate with Ba<sup>2+</sup> ion through the amide nitrogen and selenium atoms. There is one potassium ion (K1) in complex **5**, which is η<sup>3</sup>-attachment by two flanking phenyl rings from each of the phosphinoselenoic amide ligand moiety and one THF molecule also coordinated to potassium. In addition, two selenium atoms of the two anionic ligands are coordinated to the potassium ion in the bridging fashion. The geometry of the barium in complex **5** is therefore best described as distorted octahedral geometry. The Ba–Se bond distances [3.3274(7) Å, 3.3203(7) Å and 3.3518(7) Å] in complex **5** are within the range of the Ba–Se distances [3.366(1) Å and 3.324(1) Å] for the complex [{BaI(4,5-(P(Se)Ph<sub>2</sub>)<sub>2</sub>tz)}<sub>2</sub>(thf)<sub>7</sub>] reported by Raymundo Cea-Olivares *et al.*<sup>52</sup> 3.2787(11) Å for [Ba(THF)<sub>4</sub>(SeMes\*)<sub>2</sub>] (Mes\* = 2,4,6-*t*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and 3.2973(3) Å for [{Ba(Py)<sub>3</sub>(THF)(SeTrip)<sub>2</sub>}<sub>2</sub>] (Trip = 2,4,6-<sup>1</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) reported by Ruhlandt-Senge *et al.*,<sup>34</sup> 3.3553(10) Å and 3.3314(10) Å for [Ba{Ph<sub>2</sub>P(Se)NCHPh<sub>2</sub>}<sub>2</sub>(THF)<sub>2</sub>], and 3.3842(8) Å for [{η<sup>2</sup>-N(PPh<sub>2</sub>Se)<sub>2</sub>}<sub>2</sub>Ba(THF)<sub>3</sub>] previously reported by us.<sup>34,53</sup> The K–Se distances 3.3627(15) Å and 3.4175(15) Å are also within the range [3.3090(10) Å] for the complex [{(THF)<sub>2</sub>KPh<sub>2</sub>P(Se)N(CHPh<sub>2</sub>)<sub>2</sub>}<sub>2</sub>] reported by our

group.<sup>35</sup> The K–C distances vary between 3.333(6) Å and 3.336(6) Å, which are comparable with the K–C bond lengths found in [(L<sup>Mes</sup>)<sub>2</sub><sup>2-</sup>Mg(η<sup>6</sup>:η<sup>6</sup>-K(THF)<sub>2</sub>)] [K(THF)<sub>6</sub>·(THF)<sub>2</sub>] where L<sup>Mes</sup> = [(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)NC(Me)]<sub>2</sub> (3.127 Å and 3.259 Å)<sup>50</sup> and [{(THF)<sub>2</sub>K(μ-N(Ph)<sup>i</sup>Pr)<sub>2</sub>}<sub>2</sub>Ca] (3.156(2)–3.259(2) Å) with the slipped η<sup>6</sup>-coordination.<sup>54–60</sup> The average distance of K···phenyl ring is about 3.127 Å and Ba···K separation is about 5.039 Å which allows the potassium ion to interact with the selenium atom [K1–Se1<sup>#</sup> 3.3259(15) Å] of the neighbouring unit to grow the one dimensional polymer. Thus we observed that larger ion radii (K<sup>+</sup> and Ba<sup>2+</sup>) form polymeric complexes with ligand **1**. The P–Se bond [2.1681(16) Å, 2.1681(15) Å and 2.1692(15) Å] is slightly longer [2.1187(8) Å for ligand **1**] upon coordination of the selenium and barium atoms. A weak interaction between barium and phosphorus [Ba1–P1 3.6617(15), Ba1–P2 3.6299(15) and Ba1–P3 3.6520(14)] was also observed. The Ba–N distances [2.774(5) Å, 2.790(5) Å and 2.789(5) Å] are similar to the values [2.777(6) Å and 2.778(6) Å] for [Ba(Ph<sub>2</sub>P(Se)NCHPh<sub>2</sub>)<sub>2</sub>(THF)<sub>2</sub>], 2.733(6) Å for [Ba(Ph<sub>2</sub>P(BH<sub>3</sub>)NCHPh<sub>2</sub>)<sub>2</sub>(THF)<sub>2</sub>] reported by us<sup>35</sup> and 2.720(4) Å and 2.706(4) Å for [Ba((Dip)<sub>2</sub>DAD)(μ-I)(THF)<sub>2</sub>]<sub>2</sub> reported in the literature.<sup>18</sup>

#### 4. Conclusion

We have demonstrated the monomeric and polymeric alkali metal and alkaline earth metal complexes with phosphinoselenoic amide ligand **1**, and in each complex direct metal selenium is observed. In the solid state, due to differences in the ionic radii of the metal centres, the magnesium complex adopts a square pyramidal geometry, whereas the calcium complex adopts a distorted octahedral geometry with the phosphinoselenoic amide ligand. Since the barium atom is the largest in terms of ionic radii amongst Mg, Ca and Ba, a polymeric ate-complex of molecular formula [K(THF)Ba{Ph<sub>2</sub>P(Se)N(CMe<sub>3</sub>)<sub>3</sub>}<sub>3</sub>]<sub>n</sub> is obtained. The unique feature of ligand **1**, with three potential donor atoms, nitrogen, phosphorus and selenium, makes a clear distinction in molecular structure among the alkali and alkaline earth metal complexes. Further reactivity studies on these complexes are underway in our laboratory.

#### Supplementary Information (SI)

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of compounds **1**–**5** are given in supplementary information available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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