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## Introduction

Homoleptic and heteroleptic alkaline earth metal complexes are attractive to organometallic chemists because of their oxophilic and electropositive nature compare to those of early d-transition metals.1 The alkaline earth metal compounds have recently been employed in various catalytic applications for ring-opening polymerization of various cyclic esters,<sup>2,3</sup> polymerization of styrene and dienes,<sup>4</sup> and hydroamination and hydrophosphination reactions of alkenes and alkynes.<sup>5</sup> Determining the structure and reactivity of alkaline earth metal species is an important step toward the design and development of efficient catalysts; however, full realization of the catalytic potential of these elements still requires substantial advances in understanding their basic coordination and organometallic chemistry. To stabilize these extremely oxophilic and electropositive metals, a wide variety of nitrogen-based ancillary ligands, such as tris(pyrazolyl)borates,<sup>6</sup>

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## Heavier alkaline earth metal complexes with phosphinoselenoic amides: evidence of direct M–Se contact (M = Ca, Sr, Ba)†

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We report here a series of heavier alkaline earth metal complexes with a phosphinoselenoic amide ligand using two synthetic routes. In the first route, the heavier alkaline earth metal bis(trimethylsilyl)-amides  $[M\{N(SiMe_3)_2\}_2(THF)_n]$  (M = Ca, Sr, Ba) were treated with phosphinoselenoic amine  $[Ph_2P(Se)NH-(CHPh_2)]$  (**3**), prepared by the treatment of bulky phosphinamines  $[Ph_2PNH(CHPh_2)]$  (**1**) with elemental selenium in THF, and afforded homoleptic alkaline earth metal complexes of composition  $[M(THF)_2\{Ph_2P-(Se)N(CHPh_2)\}_2]$  (M = Ca (**7**), Sr (**8**), Ba (**9**)). The metal complexes **7–9** can also be obtained *via* salt meta-thesis route where the alkali metal phosphinoselenoic amides of composition  $[\{(THF)_2M'Ph_2P(Se)N-(CHPh_2)\}_2]$  (M' = Na (**5**) and K (**6**)) were reacted with respective metal diiodides in THF at ambient temperature. The solid state structures of the alkali metal complexes **5–6** and alkaline earth metal complexes **7–9** were established by single crystal X-ray diffraction analysis. In the solid state, alkali metal complexes **5** and **6** are dimeric and form a poly-metallacyclic structural motif. In contrast, complexes **7–9** are monomeric and a direct metal–selenium bond is observed in each case.

aminotroponiminates,<sup>7</sup>  $\beta$ -diketiminates,<sup>8</sup> iminopyrroles,<sup>9</sup> and 1,4-diaza-1,3-butadiene,<sup>10</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 nitrogenbased 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>11</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>12</sup> Chelating ligands having selenium as the donor atom to stabilize the heavier alkaline earth metal complexes are rare. Over the last few years very few calcium selenides have been reported, such as [(TMEDA)<sub>2</sub>Ca(SeSi(SiMe<sub>3</sub>)<sub>3</sub>)],<sup>13</sup> but to date only the solidstate structure of [(THF)<sub>4</sub>Ca(SeMes')<sub>2</sub>]<sup>14</sup> and [(THF)<sub>2</sub>Ca{(PyCH)-(Se)PPh<sub>2</sub><sup>2</sup><sup>15</sup> have been reported. Full structural characterization of strontium selenides is even scarcer.<sup>16</sup> Complexes having a barium-selenium bond are limited as the structurally authenticated examples are mostly restricted for the various sulfur derivatives  $[{(H_2O)_2Ba(tmtH_2)_2}_n]$  (tmt = 2,4,6-trimercaptotriazine, S<sub>3</sub>C<sub>3</sub>N<sub>3</sub>),<sup>17</sup> [([18]crown-6)Ba(hmpa)SMes\*][SMes\*]  $(Mes^* = 2,4,6-tBu_3C_6H_2)$ ,<sup>18</sup>  $[Ba(hmpa)_3\{NaPhNNNNC(S)\}_2]$ ,<sup>19</sup>  $[Ba(hmpa)_3(C(=S)NOPh_2)]^{20}$  and a few more examples

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including  $[Ba(SCMe_3)_2]$ ,<sup>21</sup>  $[Ba(tmeda)_2-(SeSi(SiMe_3)_3)_2]^{22}$  are reported but no structural data are available. Ruhlandt-Senge and coworkers reported barium selenoates like  $[Ba(THF)_4-(SeMes^*)_2]$ ,  $[([18]crown-6)Ba(hmpa)_2(SMes^*)_2]$ ,  $[{Ba(Py)_3(THF)-(SeTrip)_2}_2]$  (Trip = 2,4,6-iPr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), and  $[Ba([18]-crown-6)-(SeTrip)_2]$ ,<sup>23</sup> however the vast potential of this field of chemistry is still to be developed.

Our work is focused towards the exploration of synthetic methodologies allowing for a facile, clean, and high-yield production of the required molecules and determination of the molecular structure and function. In our on-going project we have synthesized N-(diphenylphosphino)-2,6-dimethylaniline  $[Ph_2PNH(2,6-Me_2C_6H_3)]$  and their chalcogenides  $[Ph_2P(O)NH (2,6-Me_2C_6H_3)$ ] and  $[Ph_2P(S)NH(2,6-Me_2C_6H_3)]^{24}$  and their complexes with alkali metals. Recently we also reported a number of alkali metal poly-cyclic compounds using various phosphinamine chalcogenide ligands.<sup>25</sup> Now we want to introduce new bulky seleno-phosphinamines [Ph2P(Se)NH(CHPh2)] (3) and [Ph<sub>2</sub>P(Se)NH(CPh<sub>3</sub>)] (4) derived from the bulky phosphinamines [Ph<sub>2</sub>PNH(CHPh<sub>2</sub>)] (1) and [Ph<sub>2</sub>PNH(CPh<sub>3</sub>)] (2) respectively with elemental selenium, having (Se,P,N)-chelating coordination sites, into alkaline earth metal chemistry. This unique ligand is potentially capable of coordinating through hard nitrogen and phosphorus donor atoms along with the soft selenium donor atom. Thus, by deprotonation reactions of the amine group present in these ligands, the neutral ligands can be converted to monoanionic ligands which can potentially form complexes with heavier alkaline earth metals via coordination of three donor atoms (N, P and Se). The work will enable us to better understand alkaline-earth-metalselenium bond strengths and characteristics, and provide important information on the association and aggregation behaviour depending on selenium atoms, ligands and donors.

In this context, the selenium-containing heavier alkaline earth metal complexes  $[M(THF)_2{Ph_2P(Se)N(CHPh_2)}_2]$ (M = Ca (7), Sr (8), Ba (9)) are presented, which can be prepared in good yield and high purity by two synthetic routes. Thus, the heavier alkaline earth metal complexes reported herein,  $[M(THF)_2{Ph_2P(Se)N(CHPh_2)}_2]$  (M = Ca (7), Sr (8), Ba (9)), are examples of a rare class of complexes with a direct seleniumalkaline earth metal contact. The full accounts of two synthetic routes and the solid state structures of all the complexes will be presented.

## **Results and discussion**

#### Ligands

The phosphinoselenoic amines  $[Ph_2P(Se)NH(CHPh_2)]$  (3) and  $[Ph_2P(Se)NH(CPh_3)]$  (4) were prepared in quantitative yield by the treatment of the respective phosphinamines,  $[Ph_2PNH-(CHPh_2)]$  (1) and  $[Ph_2PNH(CPh_3)]$  (2), respectively, with excess elemental selenium in 1 : 1.2 molar ratio at ambient temperature in THF solvent (Scheme 1). Both compounds 3 and 4 have been characterized by standard analytical/spectroscopic





Scheme 1 Synthesis of phosphinoselenoic amines 3 and 4.



Fig. 1 Solid-state structure of compound 3 (a) and 4 (b); ellipsoids are drawn to encompass 30% probability. Selected bond lengths [Å] and bond angles [°]: 3: P1–Se1 2.1086(12), P1–N1 1.642(4), P1–C14 1.804(4), P1–C20 1.812(4), N1–C1 1.459(6), C1–C2 1.543(5), C1–C8 1.541(6), Se1–P1–N1 113.75(14), P1–N1–C1 124.1(3), C14–P1–C20 104.16(19), C20–P1–Se1 111.19(14), C14–P1–Se1 114.48(14); 4: P1–N1 1.664(2), P1–Se1(1) 2.1166(8), P1–C20 1.826(3), P1–C26 1.825(3), N1–C1 1.496(4), C1–C2 1.541(4), C1–C14 1.540(4), C1–C8 1.547(4), P1–N1–C1 129.4(2), N1–P1–Se1 119.90(10), Se1–P1–C20 111.13(11), Se1–P1–C26 112.96(11).

techniques and the solid-state structures were established by single crystal X-ray diffraction analysis.

In the FT-IR spectrum of compounds **3** and **4**, strong absorptions at 568 cm<sup>-1</sup> and 599 cm<sup>-1</sup>, respectively, are observed that can be assigned as characteristic P—Se bond stretchings and are comparable with the reported values 555 cm<sup>-1.26</sup> The characteristic signal of the methine proton ( $\delta$  5.62–5.68 ppm) in the <sup>1</sup>H NMR spectrum of compound **3** is slightly downfield shifted compare to free phosphinamine **1** ( $\delta$  = 5.26–5.37 ppm). <sup>31</sup>P{<sup>1</sup>H} NMR spectra is more informative as the compound **3** shows a signal at 58.0 ppm and compound **4** shows a signal at 60.3 ppm, which are slightly downfield shifted from those of compounds **1** (35.2 ppm) and **2** (26.3 ppm) upon addition of selenium atom to phosphorus atom.

In the solid state structures, both compounds 3 and 4 crystallize in the monoclinic space group  $P2_1/c$ , having four independent molecules along with one THF molecule in the unit cell (Fig. 1). The details of the structural parameters are given in Table 1. The P–Se bond distances (2.1086(12) Å for 3 and 2.1166(8) Å for 4) are almost the same and in good agreement with our previously reported<sup>14</sup> values 2.1019(8) Å for [Ph<sub>2</sub>P(Se)-NH(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)], and can be considered as phosphorus– selenium double bond. P1–N1 bond distances (1.642(4) Å for 3 and 1.664(2) Å for 4) and C1–N1 distances (1.459(6) for 3 and 1.496(4) for 4) are also similar to those of phosphinamine 3.THF

t on 27/10/2014 (	Thi	Table 1         Crystallographic data a
ctoria	s jour	Compound
ublished on 20 December 2012. Downloaded by University of Vi	nal is © The Royal Society of Chemistry 2013	CCDC No. Empirical formula Formula weight T (K) $\lambda$ (Å) Crystal system Space group a (Å) b (Å) c (Å) a (°) $\beta$ (°) $\gamma$ (°) $\gamma$ (°) $\gamma$ (°) $\gamma$ (Å) Z $D_{cale}$ (g cm <sup>-3</sup> ) $\mu$ (mm <sup>-1</sup> ) F (000) Theta range for data collection Limiting indices
Ъ		Reflections collected/unique

CCDC No.	903851	903856	903853	903855
Empirical formula	C <sub>20</sub> H <sub>30</sub> NOPSe	C <sub>35</sub> H <sub>34</sub> NOPSe	C <sub>66</sub> H <sub>74</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>4</sub> P <sub>2</sub> Se <sub>2</sub>	C66H72K2N2O4P2Se2
Formula weight	518 47	594 56	1225 11	1257 33
T(K)	150(2)	150(2)	150(2)	150(2)
$1 (\mathbf{R})$	1 54194	1 54194	1 54194	1 54194
λ (A)	1.54184	1.54184	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P1	P1
$a(\mathbf{A})$	9.4326(8)	12.2406(3)	10.392(17)	10.4891(10)
b (Å)	14.8835(14)	13.6069(4)	12.981(2)	13.1334(10)
c (Å)	20.239(2)	20.4841(6)	13.463(17)	13.4628(8)
$\alpha$ (°)	90	90	109.103(13)	67.483(6)
$\beta(0)$	116.921	121.334(2)	107,189(13)	84.963(6)
$\gamma(0)$	90	90	104 478(14)	66 685(8)
$V(\Lambda^3)$	2522.4(4)	$2014 \ 16(14)$	1512 9(4)	1568 0(2)
V(A)	2555.4(4)	2914.10(14)	1515.0(4)	1308.9(2)
$\sum_{n=1}^{\infty}$	4	4	1	1
$D_{\text{calc}} \left( g \operatorname{cm}^{-1} \right)$	1.359	1.355	1.344	1.331
$\mu (\mathrm{mm}^{-1})$	2.760	2.474	2.549	3.512
F(000)	1072	1232	636	652
Theta range for data collection	3.85 to 70.86°	4.12 to 70.78°	3.81 to 70.74°	3.56 to 70.72°
Limiting indices	$-10 \le h \le 11$ ,	$-14 \le h \le 11$ ,	$-11 \le h \le 12$ ,	$-12 \le h \le 12$ ,
0	$-18 \le k \le 17$ .	$-16 \le k \le 16$ .	$-14 \le k \le 15$ .	$-16 \le k \le 14$ .
	-19 < l < 24	$-21 \le l \le 24$	-16 < l < 11	$-16 \le l \le 15$
Peflections collected/unique	10046/4807	12004/5405	11164/5691	11/72/5901
Reflections confected/unique	[D(int) = 0.0510]	[D(int) = 0.0254]	[D(int) = 0.0202]	[D(int) = 0.0445]
General strength that a 74.05	[R(IIII) = 0.0516]	[R(IIII) = 0.0354]	[R(IIII) = 0.0303]	[R(IIII) = 0.0445]
Completeness to theta = $/1.25$	98.2%	98.1%	97.5%	97.9%
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.79 and 0.578	0.660 and 0.560	0.660 and 0.560	0.685 and 0.585
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 $F^2$
Data/restraints/parameters	4807/0/298	5495/0/352	5681/6/362	5891/6/382
Goodness-of-fit on $F^2$	1.028	0.757	1.036	1.063
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0595$ , $wR_2 = 0.1534$	$R_1 = 0.0426$ , w $R_2 = 0.1209$	$R_1 = 0.0379$ , w $R_2 = 0.0987$	$R_1 = 0.0470, wR_2 = 0.1155$
R indices (all data)	$R_1 = 0.0761 \text{ w}R_2 = 0.1675$	$R_1 = 0.0562 \text{ w}R_2 = 0.1386$	$R_1 = 0.0452$ w $R_2 = 0.1065$	$R_1 = 0.0635 \text{ w}R_2 = 0.1270$
Absolute structure parameter	M 0.0701, MM 0.1075	$n_1 = 0.0302, m_2 = 0.1300$	R1 0.0432, WR2 0.1003	R1 0.0033, WR2 0.1270
Absolute structure parameter	1 = (0, -1, -1, -1, -1, -1, -1, -1, -1, -1, -1	$1.741$ and $0.724 = \lambda^{-3}$	$0.227 \text{ and } 0.452 \text{ s}^{3}$	$0.500 \text{ and } 0.741 \text{ s}^{3}$
Largest diff. peak and hole	1.569 and -0.746 e A	1.741 and -0.734 e A	0.337 and -0.452 e A	0.586 and -0.741 e A
Compound	7-2THF	8·2THF		9
CCDC No	903852	903854		903850
Empirical formula	CHCaN-O-P-Se-	C. H. N.	O.P.Se.Sr	CHBaN-O-P-Se-
Empirical formula	1215 19	1066.75	2041 200201	1170.06
$T(\mathbf{r})$	1213.10	1200.75		11/2.20
$I(\mathbf{K})$	150(2)	150(2)		150(2)
$\lambda$ (A)	4 = 14 0 4			1.54184
('mucho) auctore	1.54184	0./1069		
Crystal system	1.54184 Triclinic	0./1069 Triclinic		Monoclinic
Space group	1.54184 Triclinic <i>P</i> 1	0./1069 Triclinic <i>P</i> 1		Monoclinic P2 <sub>1</sub>
Space group a (Å)	1.54184 Triclinic $P\hat{1}$ 10.2981(9)	0.71069 Triclinic $P\bar{1}$ 10.191(5)		Monoclinic $P2_1$ 15.7828(7)
Space group <i>a</i> (Å) <i>b</i> (Å)	1.54184 Triclinic $P\hat{1}$ 10.2981(9) 10.9898(9)	$\begin{array}{c} 0.71069 \\ \text{Triclinic} \\ P\bar{1} \\ 10.191(5) \\ 10.912(5) \end{array}$		Monoclinic $P2_1$ 15.7828(7) 11.0357(3)
Space group a (Å) b (Å) c (Å)	$1.54184 \\ \text{Triclinic} \\ P\bar{1} \\ 10.2981(9) \\ 10.9898(9) \\ 14.4141(13) \\ \end{array}$	$\begin{array}{c} 0.71069\\ \text{Triclinic}\\ P\bar{1}\\ 10.191(5)\\ 10.912(5)\\ 14.641(5)\end{array}$		Monoclinic $P2_1$ 15.7828(7) 11.0357(3) 16.9825(7)
Space group a (Å) b (Å) c (Å) a (°)	$\begin{array}{c} 1.54184 \\ \text{Triclinic} \\ P\bar{1} \\ 10.2981(9) \\ 10.9898(9) \\ 14.4141(13) \\ 99.955(7) \end{array}$	$\begin{array}{c} 0.71069\\ \text{Triclinic}\\ P\bar{1}\\ 10.191(5)\\ 10.912(5)\\ 14.641(5)\\ 99.369(5) \end{array}$		Monoclinic $P2_1$ 15.7828(7) 11.0357(3) 16.9825(7) 90
Space group a (Å) b (Å) c (Å) $\alpha$ (°) $\beta$ (°)	$\begin{array}{c} 1.54184 \\ \text{Triclinic} \\ P\bar{1} \\ 10.2981(9) \\ 10.9898(9) \\ 14.4141(13) \\ 99.955(7) \\ 101.789(8) \end{array}$	$\begin{array}{c} 0.71069 \\ \text{Triclinic} \\ P\bar{1} \\ 10.191(5) \\ 10.912(5) \\ 14.641(5) \\ 99.369(5) \\ 101.195(5) \end{array}$	5)	Monoclinic $P2_1$ 15.7828(7) 11.0357(3) 16.9825(7) 90 117.366(5)
Space group $a ( \hat{A} )$ $b ( \hat{A} )$ $c ( \hat{A} )$ $a ( ^{\circ} )$ $\beta ( ^{\circ} )$ $\gamma ( ^{\circ} )$	$\begin{array}{c} 1.54184 \\ \mathrm{Triclinic} \\ P\bar{\mathrm{I}} \\ 10.2981(9) \\ 10.9898(9) \\ 14.4141(13) \\ 99.955(7) \\ 101.789(8) \\ 103.034(7) \end{array}$	$\begin{array}{c} 0.71069 \\ \text{Triclinic} \\ P\bar{1} \\ 10.191(5) \\ 10.912(5) \\ 14.641(5) \\ 99.369(5) \\ 101.195(5) \\ 103.621(5) \end{array}$	5)	Monoclinic $P2_1$ 15.7828(7) 11.0357(3) 16.9825(7) 90 117.366(5) 90
Space group a (Å) b (Å) c (Å) $\alpha$ (°) $\beta$ (°) $\gamma$ (°) $\gamma$ (°) $\gamma$ (Å)	1.54184 Triclinic $P\bar{1}$ 10.2981(9) 10.9898(9) 14.4141(13) 99.955(7) 101.789(8) 103.034(7) 1514.2(2)	$\begin{array}{c} 0.71069\\ \text{Triclinic}\\ P\bar{1}\\ 10.191(5)\\ 10.912(5)\\ 14.641(5)\\ 99.369(5)\\ 101.195(5)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5)\\ 1514.7(11)\\ 103.621(5$	5)	Monoclinic $P2_1$ 15.7828(7) 11.0357(3) 16.9825(7) 90 117.366(5) 90 2626.9(2)
Space group a (Å) b (Å) c (Å) $\alpha$ (°) $\beta$ (°) $\gamma$ (°) V (Å <sup>3</sup> )	$\begin{array}{c} 1.54184 \\ \mathrm{Triclinic} \\ P\bar{\mathrm{I}} \\ 10.2981(9) \\ 10.9898(9) \\ 14.4141(13) \\ 99.955(7) \\ 101.789(8) \\ 103.034(7) \\ 1514.2(2) \end{array}$	$\begin{array}{c} 0.71069\\ \text{Triclinic}\\ P\bar{1}\\ 10.191(5)\\ 10.912(5)\\ 14.641(5)\\ 99.369(5)\\ 101.195(5)\\ 103.621(5)\\ 1514.7(11)\end{array}$	5) 5) 1)	Monoclinic $P2_1$ 15.7828(7) 11.0357(3) 16.9825(7) 90 117.366(5) 90 2626.9(2)

4-THF

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Table 1 (Contd.)

Compound	7-2THF	8.2THF	6
Z	1	1	6
$D_{\rm calc}~({ m g~cm^{-3}})$	1.333	1.389	1.482
$u (\overline{\mathrm{mm}}^{-1})$	3.144	2.193	8.372
F(000)	630	652	1180
Theta range for data collection	3.22 to 70.99°	1.45 to 25.79°	$2.93 \text{ to } 70.78^{\circ}$
Limiting indices	$-12 \le h \le 12$	$-10 \le h \le 12$	$-19 \le h \le 19$
1	$-13 \le k \le 12$	$-11 \le k \le 13$	$-13 \le k \le 10$
	$-17 \leq l \leq 17$	$-17 \le l \le 13$	$-20 \le l \le 20$
Reflections collected/unique	11585/5710	10504/5692	10905/7106
4	[R(int) = 0.0553]	[R(int) = 0.0312]	[R(int) = 0.0451]
Completeness to theta $= 71.25$	97.6%	97.8%	98.4%
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Max. and min. transmission	0.590 and 0.460	0.760 and 0.610	0.245 and 0.115
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	5710/0/349	5692/0/349	7106/1/604
Goodness-of-fit on $F^2$	1.186	1.063	1.026
Final R indices $[I > 2\sigma(I)]$	$R_1^{-a} = 0.0762, WR_2^{-b} = 0.1998$	$R_1^{-a} = 0.0444, WR_2^{-b} = 0.1149$	$R_1^{\ a} = 0.0545, WR_2^{\ b} = 0.1354$
R indices (all data)	$R_1^{-a} = 0.0897, WR_2^{-b} = 0.2068$	$R_1^{-a} = 0.0503, WR_2^{-b} = 0.1201$	$R_1^{-a} = 0.0583, WR_2^{-b} = 0.1396$
Absolute structure parameter			0.114(5)
Largest diff. peak and hole	$1.321 \text{ and } -0.546 \text{ e} \text{ \AA}^{-3}$	0.818 and $-0.625 \text{ e} \text{ \AA}^{-3}$	<b>1.801</b> and $-1.495 \text{ e} \text{ Å}^{-3}$
${}^{a}R_{1}(F) = \sum   F_{0}  -  F_{0}  /\sum  F_{0} , {}^{b}WR_{2}(F^{2}) = [\sum W(F_{0})^{2}]$	$-F_{ m c}{}^2)^2/\sum (wF_{ m o}{}^4)]^{1/2}.$		

compounds 1 (P1–N1 1.673(6) Å and C1–N1 1.453(8) Å) and 2 (P1–N1 1.691(2) Å and C1–N1 1.494(2) Å) previously observed by us.  $^{24,25}$ 

#### Alkali metal complexes

The dimeric sodium and potassium complexes of molecular formula  $[{(THF)_2M'Ph_2P(Se)N(CHPh_2)}_2]$  (M' = Na (5) and K (6)) were prepared by the reaction of compound 3 and sodium bis (trimethyl)silylamide (or potassium bis(trimethylsilyl)amide in case of 6) in toluene through the elimination of volatile bis(trimethylsilyl)amine (Scheme 2).<sup>27</sup>

Complex 5 crystallizes in triclinic space group  $P\bar{1}$  having one molecule in the unit cell. The solid state structure of complex 5 is given in Fig. 2. The details of the structural



**Scheme 2** Synthesis of alkali metal and alkaline earth metal phosphinoselenoic amide complexes.



**Fig. 2** Solid-state structure of compound **5**; ellipsoids are drawn to encompass 30% probability, omitting hydrogen atoms. Selected bond lengths [Å] and bond angles [°]: Na1–N1<sup>i</sup> 2.380(2), Na1–Se1 2.9956(12), Na1–Se1<sup>i</sup> 3.0694(11), Na1–O1 2.426(2), Na1–O2 2.399(2), Na1–P1<sup>i</sup> 3.2214(13), N1–P1 1.594(2), P1–Se1 2.1519(8), Se1–Na1–Se1<sup>i</sup> 99.14(3), Se1–Na1–N1<sup>i</sup> 115.92(6), Se1<sup>i</sup>–Na1–P1<sup>i</sup> 39.915(19), Se1–Na1–P1<sup>i</sup> 114.01(4), Se1<sup>i</sup>–Na1–O1 83.95(6), Se1<sup>i</sup>–Na1–O2 171.24(6), N1<sup>i</sup>–Na1–P1<sup>i</sup> 28.30(5), N1<sup>i</sup>–Na1–O1 108.79(8), N1<sup>i</sup>–Na1–O2 112.65(8), N1<sup>i</sup>–Na1–Se1<sup>i</sup> 68.15(5), Na1–Se1–Na1<sup>i</sup> 80.86(3), O1–Na1–Se1<sup>i</sup> 83.95(6), O2–Na1–Se1<sup>i</sup> 171.24(6).



**Fig. 3** Solid state structure of compound **6**; ellipsoids are drawn to encompass 30% probability, omitting hydrogen atoms. Selected bond lengths [Å] and bond angles [°]: K–N 2.725(3), K–Se2a 3.3090(10), K–Se2a<sup>i</sup> 3.5150(9), K–O1 2.659(3), K–O7 2.695(3), K–C1c<sup>i</sup> 3.194(3), K–P 3.5579(12), N–P 1.589(3), P–Se2a 2.1476(9), Se2a–K–Se2a<sup>i</sup> 91.12(2), Se2a–K–N 61.31(6), Se2a–K–P 36.22(17), Se2a–K–O1 171.26(8), Se2a–K–O7 94.77(10), N–K–P 25.09(6), N–K–O1 109.95(10), N–K–O7 102.29(10), N–K–Se2a<sup>i</sup> 90.75(6), K–Se2a–K<sup>i</sup> 88.88(2), O1–K–Se2a<sup>i</sup> 88.87(8), O7–K–Se2a<sup>i</sup> 166.95(9).

parameters are given in Table 1. In the centrosymmetric molecule 5, two phosphinoselenoic amide ligands are coordinated to each of two sodium atoms by one selenium, one phosphorus and one amido nitrogen atom exhibiting a diamond shaped Na<sub>2</sub>Se<sub>2</sub> core with mean angles Se1-Na-Se1<sup>i</sup> of 99.14(3)° and Na1-Se1-Na1<sup>i</sup> of 80.86(3)°. The Na1-Se1 and Na1-Se1<sup>i</sup> bond distances are also almost the same at 2.9956(12) Å and 3.0694(11) Å, respectively. Each of the selenium atoms is μ-coordinated between the two sodium atoms. Additionally, each phosphorus atom is weakly coordinated to each sodium atom to form highly strained three membered metallacycles having P1-Na1-distance 3.2214(14) Å. In complex 5, two additional THF molecules are also coordinated to each sodium atom and the geometry of each sodium atom can be best described as distorted octahedral. The bond distances Na1-N1 2.380(2), Na1-O1 2.426(2), and Na1-O2 2.399(2) Å are in the range of the previously observed sodium phosphinthioic amide complexes reported by us.<sup>16</sup> The whole structure consists of four three-member rings fused together forming a penta-metallacyclo[4.2.0.0<sup>1,7</sup>.0<sup>2,5</sup>.0<sup>2,4</sup>]octane structure. Such a structural motif in sodium complexes due to the presence of three adjacent hetero donor atoms selenium, phosphorus and nitrogen was recently reported by us.<sup>25</sup>

The potassium phosphinoselenoic amido complex **6** crystallizes in the triclinic space group  $P\bar{1}$  having one molecule in the unit cell and is isostructural with the sodium complex **5** due to the similar ionic radii of sodium and potassium. The details of the structural parameters are given in Table **1**. The solid state structure of complex **6** is given in Fig. 3. Each potassium atom in the dimeric complex **6** is coordinated by one {Ph<sub>2</sub>P(Se)-N(CHPh<sub>2</sub>)}<sup>-</sup> ligand and two THF molecules. Similar to complex **5**, a diamond-shaped K<sub>2</sub>Se<sub>2</sub> core with mean angles Se2A-K-Se2A<sup>i</sup> of 91.12(2)° and K-Se2A-K<sup>i</sup> of 88.88(2)° is observed. The K-Se2A and K-Se2A<sup>i</sup> bond distances are also similar at 3.3090(10) and 3.5150(10) Å, respectively. Each of the selenium atoms is µ-coordinated between each of the two potassium atoms. Additionally, each phosphorus atom is weakly coordinated to each potassium atom to form highly strained three-membered metallacycles having P–K-distance 3.5579(13) Å. Two additional THF molecules are also coordinated to each potassium atom to adopt a distorted octahedral geometry for each potassium metal atom. The bond distances K-N 2.725(3), K-O1 2.659(3), and K-O7 2.695(3) Å are slightly elongated compare to that of sodium complex 5, but are in the range of the previously observed potassium complexes reported in literature. Unlike the analogous sodium complex, a short contact between potassium and one of the phenyl carbons (K…C1C (3.194(3) Å)) is observed, which can be interpreted as a remote or secondary M-C interaction. However, in solution all phenyl carbons appeared equivalent in the <sup>13</sup>C{<sup>1</sup>H} NMR study, presumably due to dynamic behaviour of the complex. Thus in the solid state, two additional five member metallacycles K1-C1C-C20-P1-Se1 and K1<sup>i</sup>-C1C<sup>i</sup>-C20<sup>i</sup>-P1<sup>i</sup>-Se1<sup>i</sup> are formed. An unusual structural motif is formed by fusion of four threemember and two five-member metallacycle rings. To the best of our knowledge, this is the first example of such kind of structural motif in potassium complexes. Even the complexes 5 and 6 are dimeric in the solid state, only one set of signals were recorded in the <sup>1</sup>H, <sup>31</sup>P $^{1}H$  and <sup>13</sup>C $^{1}H$  NMR spectra in each case due to the dynamic nature of the complexes in solution.

#### Alkaline earth metal complexes

Reaction of 3 with alkaline earth metal bis(trimethylsilyl)amides  $[M{N(SiMe_3)_2}_2(THF)_n]$  (M = Ca, Sr, Ba) in a 2:1 molar ratio in THF followed by crystallization from THF-n-pentane, homoleptic phosphinoselenoic amido alkaline earth metal complexes of composition  $[M(THF)_2 \{Ph_2P(Se)N(CHPh_2)\}_2]$ (M = Ca (7), Sr (8), Ba (9)) were obtained in good yield via the elimination of hexamethyldisilazane (Scheme 2).27 The same alkaline earth metal complexes 7-9 can also be prepared by another route, salt metathesis reaction involving the alkali metal phosphinoselenoic amides with alkaline earth metal diiodides in THF. The silylamide route was followed for all the three complexes 7-9, whereas both the routes were used for calcium complex 7 only. The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures were established by single-crystal X-ray diffraction analysis. A strong absorption at 570  $\text{cm}^{-1}$  (for 7), 569 cm<sup>-1</sup> (for 8) and 569 cm<sup>-1</sup> (for 9) in FT IR spectra indicates the evidence of P=Se bond into the each complex. The signals of the methine proton ( $\delta$  5.93–5.87 ppm for 7, 5.40–5.33 ppm for 8 and 5.46–5.39 ppm for 9) in the <sup>1</sup>H NMR spectrum of the diamagnetic complexes 7-9 are unaffected due to complex formation. In  ${}^{31}P{}^{1}H$  NMR spectra, complexes 7-9 show only one signal at 71.9 ppm, 71.8 ppm and 71.9 ppm, respectively, and these values are significantly downfield shifted compared to that of compound 3 (58.0 ppm)



Fig. 4 Solid-state structure of compound 7; ellipsoids are drawn to encompass 30% probability, omitting hydrogen atoms for clarity. Selected bond lengths [Å] and bond angles [°]: Ca1–N1 2.479(5), Ca1–P1 3.2737(16), Ca1–Se1 2.9889(8), Ca1–O1 2.427(5), N1–Ca1–O1 89.23(17), N1–Ca1–P1 28.95(13), P1–Se1–Ca1 77.31(5), P1–Ca1–Se1 39.73(3), Se1–Ca1 N1 68.20(13), O1–Ca1–O<sup>i</sup> 180.000(1), Se1–Ca–Se1<sup>i</sup> 180.0.



**Fig. 5** Solid state structure of compound **8**; ellipsoids are drawn to encompass 30% probability, omitting hydrogen atoms for clarity. Selected bond lengths [Å] and bond angles [°]: Sr1–N1 2.609(3), Sr1–P1 3.4255(15), Sr1–Se1 3.1356(9), Sr1–O1 2.567(3), N1–Sr1–O1 91.72(9), N1–Sr1–P1 26.86(6), P1–Sr1–Se1 37.89(2), Se1–Sr1–N1 64.23(7), O1–Sr1–O<sup>i</sup> 180.00(10), Se1–Sr–Se1<sup>i</sup> 180.0.

upon coordination of calcium, strontium or barium atom onto the selenium atom of the phosphinoselenoic amido ligand. The two phosphorus atoms present in the two  $\{Ph_2P(Se)N-(CHPh_2)\}^-$  moieties are chemically equivalent.

The calcium and strontium complexes 7 and 8 crystallize in the triclinic space group  $P\overline{1}$ , having one molecule of either 7 or 8 and two THF molecules as solvate in the unit cell. The details of the structural parameters are given in Table 1. The solid-state structures of the complexes 7 and 8 are shown in Fig. 4 and 5, respectively. Both the complexes 7 and 8 are isostructural to each other due to similar ionic radii (1.00 and 1.18 Å for coordination number 6).<sup>28</sup>

In the centrosymmetric molecule 7, the coordination polyhedron is formed by two monoanionic  $\{Ph_2P(Se)N(CHPh_2)\}^-$ 

ligands, and two THF molecules which are trans to each other. Each  $\{Ph_2P(Se)N(CHPh_2)\}^-$  ligand coordinates to the calcium atom via chelation of one amido nitrogen atom and one selenium atom and a very weak P-Ca interaction (3.274 Å) of the  $\{Ph_2P(Se)N(CHPh_2)\}^-$  moiety is observed. Thus the  $\{Ph_2P(Se)N (CHPh_2)^{-}$  group can be considered as a pseudo-bidentate ligand. The central atom calcium adopts a distorted octahedral geometry due to coordination from two  $\{Ph_2P(Se)N(CHPh_2)\}^{-1}$ moieties and two THF molecules. The Ca-N distance (2.479(5) Å) is slightly elongated compare with the calcium-nitrogen covalent bond (2.361 (2) and 2.335(2)) reported for  $[Ca(Dipp_2DAD)(THF)_4]$  (Dipp\_2DAD = N,N'-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene in the literature.29 The most interesting thing is that the Ca-Se bond 2.989(8) Å is within the same range of Ca-Se bond (2.945(1) Å) reported for  $[(THF)_2Ca\{(PyCH)(Se)PPh_2\}_2]^{14}$  and (2.93 to 3.00 Å) reported for [(THF)<sub>4</sub>Ca(SeMes')<sub>2</sub>] and (2.958(2) to 3.001(2) Å) reported for [(THF)<sub>2</sub>Ca(Se<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] in the literature.<sup>13,15</sup> Thus the compound 7 is one example of the few complexes known having a direct calcium-selenium bond.11-13 The P-Se distance (2.1449(2) Å) in complex 5 is slightly elongated (2.111(2) Å) but within the same range as that of free ligand 3 indicating no impact on P-Se bond upon coordination of the calcium atom to the selenium atom. In compound 8, the strontium atom is hexacoordinated by two selenium atoms, two amido nitrogen atoms of two {Ph2P(Se)N(CHPh2)} ligands and two THF molecules. The solvate THF molecules are trans to each other and the strontium atom adopts a distorted octahedral geometry.

Like compound 5, a weak interaction (P-Sr 3.426(2) Å) between phosphorus and metal atom is noticed. The strontium-nitrogen bond distance (2.609(3) Å) fits well (2.6512(2) and 2.669(2) Å) with our previously observed strontium complex  $[(Imp^{Dipp})_2Sr(THF)_3]$   $(Imp^{Dipp} = 2,6^{-i}Pr_2C_6H_3N=CH)$ - $C_4H_3N$ ).<sup>30</sup> The Sr-Se bond distance (3.136(9) Å) is slightly elongated compare to that of Ca–Se bond distance (2.989(8) Å) observed in complex 7 due to the larger ionic radius of strontium than calcium ion. The observed Sr-Se distance in our compound 8 is within the range of Sr-Se distances (3.138(7) to 3.196(9) Å) of structurally characterized complex [(THF)<sub>3</sub>Sr- $(Se_2PPh_2)_2$  published very recently by Westerhausen and coworkers<sup>16b</sup> and that (3.066(1) Å) for the complex [Sr{Se(2,4,6 $tBu_3C_6H_2)_2(THF)_4]$ .<sup>16a</sup> Thus our phosphinoselenoic amido strontium complex 8 is another example of a fully structurally characterized strontium complex having direct Sr-Se bond.

Unlike compounds 7–8, the barium complex 9 crystallizes in the monoclinic space group  $P_{2_1}$ , having two molecules in the unit cell. The details of the structural parameters are given in Table 1. The solid-state structure of complex 9 is given in Fig. 6. Similar to the calcium and strontium complexes, in the barium complex 9 the coordination polyhedron is formed by two {Ph<sub>2</sub>P(Se)N(CHPh<sub>2</sub>)}<sup>-</sup> ligands and two *trans* THF molecules. The amido nitrogen atom along with the selenium atom of each of the phosphinoselenoic amido ligands coordinates to the barium atoms to adopt a distorted octahedral geometry for the barium atom, considering the {Ph<sub>2</sub>P(Se)N-(CHPh<sub>2</sub>)}<sup>-</sup> ligand as bidentate. The Ba–P distance is even



Fig. 6 Solid state structure of compound 9; ellipsoids are drawn to encompass 30% probability, omitting hydrogen atoms. Selected bond lengths [Å] and bond angles [°]: Ba1–N1 2.777(6), Ba1–P1 3.662(2), Ba1–Se1 3.3553(10), Ba1–O1 2.716(6), Ba1–N2 2.778(6), Ba1–P2 3.665(2), Ba1–Se2 3.3314(10), B1–O2 2.734(6), N1–Ba1–O1 91.2(2), N1–Ba1–P1 24.34(15), P1–Ba1–Se1 35.37(4), Se1–Ba1–N1 59.62(15), O1–Ba1–O2 177.3(2), Se1–Ba–Se2 175.66(3), N1–Ba1–N2 175.8(2), N2–Ba1–O2 94.8(2), N2–Ba1–Se2 59.46(15).

larger (3.662(2) Å) compare to that of complexes 7 (3.2737(16) Å)and 8 (3.4255(15) Å), indicating a very weak interaction between the barium atom and phosphorus atom. The Ba-N distances (2.777(6) and 2.778(6) Å) are similar to the values (2.720(4) 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>30</sup> The Ba–Se distance (3.3553(1) Å) is the largest among the above mentioned M-Se distances for calcium and strontium complexes (2.9889(8) and 3.1355(9) Å, respectively; vide supra) and can be attributed to the larger ionic radii of the barium atoms compared to calcium and strontium atoms. The Ba-Se distance (3.3553(1) Å) of compound 9 is similar to the reported values of 3.2787(11) Å for the complex  $[Ba(THF)_4(SeMes^*)_2]$  (Mes<sup>\*</sup> = 2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and 3.2973(3) Å for  $[{Ba(Py)_3(THF)(SeTrip)_2}_2]$  (Trip = 2,4,6 iPr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) reported by Ruhlandt-Senge and coworkers.<sup>23</sup> Nevertheless complex 9 is a unique example of a barium-seleno complex where two other heteroatoms, nitrogen and phosphorus, coordinate to the barium atom. The P-Se bond (2.152(2) Å) is slightly elongated upon coordination of selenium to the barium atom. A weak interaction between barium and phosphorus (Ba1-P1 3.662(2) and 3.665(2) Å) is also observed. Upon coordination to the barium atom each of the ligand fragments form two three-member metallacycles which are fused together to give a four-member metallacycle Se1-P1-N1-Ba1. The bite angles (Se1-Ba1-N1 59.62(15)° and Se2-Ba1-N2 59.46(15)°, P1-Se1-Ba1 80.11(6)° and 80.77(6)°) indicate a highly strained structure of the molecule.

## **Experimental**

#### General considerations

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamedried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum  $(10^{-4} \text{ Torr})$  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  $LiAlH_4$  and stored in the glove box. <sup>1</sup>H NMR (400 MHz), <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>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. Sodium and potassium bis(trimethylsilyl)amide were purchased from Sigma Aldrich and used as such. The phosphinamines 1, 2,<sup>24</sup> and  $[M{N(SiMe_3)_2}_2(THF)_2]$  (M = Ca, Sr, Ba)<sup>31</sup> were prepared according to literature procedures by using respective metal diiodides and [KN(SiMe<sub>3</sub>)<sub>2</sub>]. The NMR solvent C<sub>6</sub>D<sub>6</sub> was purchased from Sigma Aldrich and dried under Na/K alloy prior to use.

Preparation of [Ph<sub>2</sub>P(Se)NH(CHPh<sub>2</sub>)] (3). N-Benzhydryl-1,1diphenylphosphinamine 1 (1.0 gm, 2.72 mol) and elemental selenium (250 mg, 3.16 mol) were heated to 60 °C in THF (10 ml) for 12 h. Unreacted excess selenium was filtered off through a G4 frit and the filtrate was collected. After evaporation of solvent from filtrate in vacuo, a light yellow solid residue was obtained (yield: 1.20 gm, 99%). The title compound was recrystallized from THF at room temperature. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.72–7.77 (m, 4H, ArH), 7.12–7.33 (m, 16H, ArH), 5.62–5.68 (dd, 1H, J = 14.8 Hz, 6.4 Hz, CH), 3.17–3.14 (br t, 1H, J = 5.2 Hz, NH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz,  $CDCl_3$ ):  $\delta$  142.9 (ArC), 142.8 (ArC), 134.2 (P-ArC), 133.3 (P-ArC), 131.9 (P attached o-ArC), 131.8 (P attached o-ArC), 131.6 (P attached p-ArC), 128.4 (m-ArC), 128.3 (P attached m-ArC), 128.1 (P attached m-ArC), 127.8 (o-ArC), 127.2 (p-ArC), 59.8 (CH) ppm.  ${}^{31}P{}^{1}H{}NMR$ (161.9 MHz, CDCl<sub>3</sub>):  $\delta$  58.0 ppm. FT-IR (selected frequencies):  $\nu = 3242$  (N–H), 1435 (P–C), 898 (P–N), 568 (P=Se) cm<sup>-1</sup>. (C25H22NPSe) Calc. C 67.27, H 4.97, N 3.14; found C 66.99 H 4.43, N 2.93.

**Preparation of [Ph<sub>2</sub>P(Se)NH(CPh<sub>3</sub>)] (4).** Similar to compound 3. Yield 1.20 g, 100%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.74–7.79 (m, 4H, ArH), 7.19–7.22 (m, 6H, ArH), 6.59–6.99 (m, 15H, ArH), 3.71 (d, 1H, *J* = 3.16 Hz, CH), ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  143.9 (ArC), 143.8 (ArC), 136.1 (P-ArC), 135.1 (P-ArC), 130.8 (P attached *o*-ArC), 130.6 (P attached *m*-ArC), 129.5 (P attached *p*-ArC), 129.4 (P attached *p*-ArC), 129.1 (*o*-ArC), 126.7 (*m*-ArC), 126.1 (*p*-ArC), 71.3 (CH) ppm. <sup>31</sup>P{<sup>1</sup>H}NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  62.6 ppm. FT-IR (selected frequencies):  $\nu$  = 3300 (N–H, very week), 1435 (P–C), 910 (P–N), 599 (P—Se) cm<sup>-1</sup>. (C<sub>35</sub>H<sub>34</sub>NOPSe) (4·THF) Calc. C 70.70, H 5.76, N 2.36; found C 70.13 H 5.39, N 2.18.

**Preparation of**  $[{(THF)_2NaPh_2P(Se)N(CHPh_2)}_2]$  (5). In a 10 ml sample vial one equivalent (50 mg, 0.112 mmol) of ligand 3 and one equivalent of sodium bis(trimethylsilyl)-amide (20.5 mg, 0.112 mmol) were mixed together with a small amount (2 ml) of toluene. After 6 h, a small amount of

THF (2 ml) and *n*-pentane (2 ml) were added to it and kept at -40 °C. After 24 h, colorless crystals of 5 were obtained.

Yield 95%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.73–7.67 (m, 4H, ArH), 6.96–6.94 (m, 4H, ArH), 6.84–6.66 (m, 12H, ArH), 5.82–5.76 (dd, 1H, *J* = 16.0 Hz, 6.0, 8.0 Hz CH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  143.6 (ArC), 143.5 (ArC), 135.4 (P-ArC), 134.5 (P-ArC), 132.3 (P attached *o*-ArC), 132.2 (P attached *o*-ArC), 131.3 (P attached *p*-ArC), 131.2 (P attached *p*-ArC), 128.4 (P attached *m*-ArC), 128.2 (*m*-ArC), 128.0 (*o*-ArC), 127.1 (*p*-ArC), 59.6 (CH) ppm. <sup>31</sup>P–{<sup>1</sup>H}NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  71.9 ppm. FT-IR (selected frequencies):  $\nu$  = 3365 (N–H), 1435 (P–C), 894 (P–N), 570 (P=Se) cm<sup>-1</sup>. (C<sub>66</sub>H<sub>74</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Se<sub>2</sub>) Calc. C 64.70, H 6.09, N 2.29; found C 64.15 H 5.82, N 1.76.

**Preparation of** [{(THF)<sub>2</sub>KPh<sub>2</sub>P(Se)N(CHPh<sub>2</sub>)}<sub>2</sub>] (6). In a 10 ml sample vial, one equivalent (50 mg, 0.112 mmol) of ligand 3 and one equivalent of potassium bis(trimethylsilyl)amide (22.4 mg, 0.112 mmol) were mixed together with 2 ml of toluene. After 6 h, a small amount of THF (2 ml) and *n*-pentane (2 ml) were added to it and kept at -40 °C. After 24 h, colorless crystals of **6** were obtained.

Yield 90%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.88–7.82 (m, 4H, ArH), 7.07–7.06 (m, 4H, ArH), 6.96–6.82 (m, 13H, ArH), 5.84–5.78 (dd, 1H, J = 8.8 Hz, 6.0 Hz CH) ppm, 3.46 (m, THF), 1.31 (m, THF) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 143.8 (ArC), 143.7 (ArC), 135.9 (P-ArC), 134.9 (P-ArC), 132.2 (P attached *o*-ArC), 132.1 (P attached *o*-ArC), 131.2 (P attached *p*-ArC), 131.1 (P attached *p*-ArC), 128.4 (P attached *m*-ArC), 128.2 (*m*-ArC), 127.9 (*o*-ArC), 127.1 (*p*-ArC), 58.9 (CH) ppm. <sup>31</sup>P{<sup>1</sup>H}NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ 71.9 ppm. FT-IR (selected frequencies):  $\nu$  = 3373 (N-H), 1436 (P-C), 931 (P-N), 569 (P=Se) cm<sup>-1</sup>. (C<sub>66</sub>H<sub>74</sub>K<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Se<sub>2</sub>) Calc. C 63.04, H 5.93, N 2.23; found C 62.68 H 5.62, N 1.78.

Preparation of  $[M(THF)_2{Ph_2P(Se)N(CHPh_2)}_2]$  (M = Ca (7), Sr (8), Ba (9)). *Route 1:* In a 10 ml sample vial, two equivalents (100 mg, 0.224 mmol) of ligand 3 and one equivalent of  $[M{N-(SiMe_3)_2}_2(THF)_n]$  (M = Ca, Sr, Ba) were mixed together with 2 ml of toluene. After 6 h of stirring another 2 ml of THF and *n*-pentane (2 ml) were added to it and kept at -40 °C. After 24 h, colorless crystals were obtained.

*Route 2:* In a 25 ml pre-dried Schlenk flask, potassium salt of ligand 3 (200 mg, 0.32 mmol) was mixed with CaI<sub>2</sub> (46.8 mg, 0.16 mmol) in 10 ml THF solvent at ambient temperature and stirring continued for 12 h. The white precipitate of KI was filtered off 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 °C.

7: Yield: *Route 1* 85% and *Route 2* 80%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.84–7.78 (m, 4H, ArH), 7.07–7.05 (m, 4H, ArH), 6.95–6.78 (m, 12H, ArH), 5.93–5.87 (dd, 1H, *J* = 15.3 Hz, 6.5 Hz, CH) ppm, 3.46 (m, THF), 1.31 (m, THF) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  143.6 (ArC), 143.5 (ArC), 135.4 (P-ArC), 134.5 (P-ArC), 132.3 (P attached *o*-ArC), 132.2 (P attached *o*-ArC), 131.3 (P attached *p*-ArC), 131.2 (P attached *p*-ArC), 128.4 (P attached *m*-ArC), 128.3 (*m*-ArC), 128.0 (*o*-ArC),

127.1 (*p*-ArC), 67.7 (THF) 59.6 (CH), 25.6 (THF) ppm.  ${}^{31}P{}^{1}H{}$ NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  71.9 ppm. FT-IR (selected frequencies):  $\nu$  = 3381 (N-H), 1436 (P-C), 930 (P-N), 570 (P=Se) cm<sup>-1</sup>. (C<sub>66</sub>H<sub>70</sub>CaN<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Se<sub>2</sub>) (7·2THF) Calc. C 65.23, H 5.81, N 2.31; found C 64.88 H 5.32, N 2.11.

8: Yield 78%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.84–7.78 (m, 4H, ArH), 7.33–7.31 (m, 4H, ArH), 6.95–6.79 (m, 12H, ArH), 5.40–5.33 (d, 1H, J = 27.6 Hz, CH) ppm, 3.48 (m, THF), 1.27 (m, THF) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 143.6 (ArC), 143.5 (ArC), 135.4 (P-ArC), 134.5 (P-ArC), 132.3 (P attached *o*-ArC), 132.2 (P attached *o*-ArC), 131.3 (P attached *p*-ArC), 131.2 (P attached *p*-ArC), 128.8 (P attached *m*-ArC), 128.4 (*m*-ArC), 127.3 (*o*-ArC), 127.1 (*p*-ArC), 68.1 (THF), 59.6 (CH), 25.5 (THF) ppm. <sup>31</sup>P–{<sup>1</sup>H}NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>): δ 71.9 ppm. FT-IR (selected frequencies):  $\nu = 1436$  (P–C), 931 (P–N), 569 (P=Se) cm<sup>-1</sup>. (C<sub>66</sub>H<sub>74</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Se<sub>2</sub>Sr) (8-2THF) Calc. C 62.58, H 5.89, N 2.21; found C 62.03 H 5.43, N 2.05.

9: Yield 83%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.88–7.83 (m, 4H, ArH), 7.26–7.24 (m, 4H, ArH), 7.06–6.85 (m, 12H, ArH), 5.46–5.39 (d, 1H, *J* = 26.1 Hz, CH) ppm, 3.47 (m, THF), 1.30 (m, THF) ppm. <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  143.6 (ArC), 143.5 (ArC), 135.4 (P-ArC), 134.5 (P-ArC), 132.3 (P attached *o*-ArC), 132.2 (P attached *m*-ArC), 131.3 (P attached *p*-ArC), 131.2 (P attached *p*-ArC), 128.4 (*o*-ArC), 128.2 (*m*-ArC), 127.1 (*p*-ArC), 67.7 (THF), 59.6 (CH), 25.6 (THF) ppm. <sup>31</sup>P–{<sup>1</sup>H}NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  71.9 ppm. FT-IR (selected frequencies):  $\nu$  = 1437 (P-C), 911 (P-N), 569 (P=Se) cm<sup>-1</sup>. (C<sub>58</sub>H<sub>58</sub>Ba-N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Se<sub>2</sub>) Calc. C 59.42, H 4.99, N 2.39; found C 58.93, H 5.01, N 2.08.

#### X-ray crystallographic studies of 3-9

Single crystals of compounds 3 and 4 were grown from a solution of THF at a temperature of -4 °C; compounds 5-9 were grown from a THF and pentane mixture at -40 °C under inert atmosphere. 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 Oxford Supernova X-calibur Eos CCD detector with graphite-monochromatic Cu-Kα (1.54184 Å) or Mo-Kα (0.71069 Å) radiation. Crystal data and structure refinement parameters are summarized in Table 1. The structures were solved by direct methods  $(SIR92)^{32}$  and refined on  $F^2$  by full-matrix least-squares methods using SHELXL-97.33 Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. For compound 5 disordered C30 of a coordinated tetrahydrofuran was refined with split model with site occupation factor 0.49(2) and for compound 6 disordered carbon atoms of two coordinated tetrahydrofuran were refined with split model. C11 in one THF is split with site occupation factor 0.62(4). C13 and C2D are split with site occupation factors 0.42(10) and 0.48(4), respectively. The function minimized was  $\left[\sum w (F_o^2 - F_c^2)^2\right]$  $(w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP])$ , where  $P = (max(F_o^2, 0) + 2F_c^2)/3$ with  $\sigma^2(F_0^2)$  from counting statistics. The function  $R_1$  and  $wR_2$ were  $(\sum ||F_o| - |F_c||) / \sum |F_o|$  and  $[\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$ 

respectively. The ORTEP-3 program was used to draw the molecule. CCDC reference numbers 903850–903856. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32339g.

## Conclusions

In conclusion, we have reported a series of heavier alkalineearth-metal–selenium complexes having direct metal– selenium bonds *via* two synthetic routes using phosphinoselenoic amide ligand. In the first method the silylamide route was used to prepare the target compounds, and in the second method the salt metathesis route was used. Due to similar ionic radii, calcium and strontium complexes are isostructural, and also the M–Se bond distances increase from Ca–Se to Sr–Se and a further increase is observed for the Ba–Se bond. Further reactivity studies on these complexes are underway in our laboratory.

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