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Unprecedented Calcium Metalla-macrocycle Having Phosphinoselenoic Amide and Diphenylphosphinate in the Coordination Sphere

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Abstract. An eight-membered calcium metalla-macrocycle of the composition $[Ca\{Ph_2P(Se)N(Ar)\}\{Ph_2P(O)O\}(THF)_2]_2$ (**2**) (Ar = 2,6-dimethylphenyl) can be isolated with a good yield by the reaction of neutral phosphinoselenoic amide $[Ph_2P(Se)NH(Ar)]$ (**1**) and calcium bis(trimethylsilyl)amides $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ in toluene followed by crystallization in air. The homoleptic calcium phosphinoselenoic amido complex of the composition $[Ca\{Ph_2P(Se)N(Ar)\}_2(THF)_2]$ (**3**) can also be obtained through two synthetic routes. In the first route, $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ is treated with phosphinoselenoic amide $[Ph_2P(Se)NH(Ar)]$ (**1**) at an ambient temperature followed by recrystallization in an inert atmosphere to give complex **3** of high purity. In the second route, a one-pot reaction is carried out involving **1**, calcium diiodide,CaI_2, and potassium bis(trimethylsilyl)amide $[K\{N(SiMe_3)_2\}]$ in toluene in an inert atmosphere. When complex **3** is treated with diphenylphosphinic acid in THF, compound **2** is also obtained with a good yield. Both complexes are confirmed using single-crystal X-ray diffraction analysis. The solid-state structure of complex **2** reveals an eight-membered macrocycle formed by two diphenylphosphinate groups and two calcium ions. In addition, a four-membered calcium metallacycle around each calcium atom is formed by the phosphinoselenoic amido ligand through coordination between the nitrogen and selenium atoms. In complex **3**, the calcium atom is coordinated by two phosphinoselenoic amido groups and a direct metal selenium bond is observed.

Introduction

Determining the structure and reactivity of alkaline earth metal species is an important step towards the design and development of efficient catalysts; however, full realization of the catalytic potential of these elements requires substantial advances in understanding their basic coordination and organometallic chemistry.[1] To stabilize these extremely oxophilic and electropositive metals, a wide variety of nitrogen-based ancillary ligands, such as tris(pyrazolyl)borates,[2] aminotroponiminates,[3] β-diketiminates,[4] iminopyrroles,[5] and 1,4-diaza-1,3-butadiene[6] 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 through well-defined nitrogen-based ligand architecture. Various phosphine imines and phosphine amines have been used for the design of new alkaline earth metal compounds having well-defined reaction centers.[7,8] More recently, the concept of phosphorus-based ligands with additional donating atoms in the periphery have achieved greater importance in catalysis and in the design of self-assembling ligands.[9] Recently, *Stalke* et al. demonstrated various phosphorus-based ligands with the incorporation of heteroaromatic substituents at the phosphorus atom to lead the design of multidentate Janus-head ligands.[10,11] These ligand systems with sidearm donation have already proved to be useful in various catalytic reactions involving chelating phosphanes with selectivity for hard/soft coordination sites.[12]

Our work focuses on the exploration of synthetic methodologies allowing for a facile, clean, high-yield production of the required molecules and determination of the molecular structure and function. In our ongoing project we have synthesized *N*-(diphenylphosphanyl)-2,6-dimethylaniline $[Ph_2PNH(2,6\text{-}Me_2C_6H_3)]$ and its chalcogenides $[Ph_2P(O)NH(2,6\text{-}Me_2C_6H_3)]$ and $[Ph_2P(S)NH(2,6\text{-}Me_2C_6H_3)]$[13] and their complexes with alkali metals. Recently we reported a number of alkali metal polycyclic compounds using various phosphinamine chalcogenide ligands.[14] Further, we have introduced the new bulky seleno-phosphinamines $[Ph_2P(Se)NH(CHPh_2)]$ and $[Ph_2P(Se)NH(CPh_3)]$ derived from the bulky phosphinamines $[Ph_2PNH(CHPh_2)]$ and $[Ph_2PNH(CPh_3)]$ with elemental selenium, having (Se, P, N)-chelating coordination sites, into alkaline earth metal chemistry. These unique ligands are potentially capable of coordinating through the hard nitrogen and phosphorus donor atoms along with the soft selenium donor atom. The heavier alkaline earth metal complexes $[M(THF)_2\text{-}\{Ph_2P(Se)\text{-}N(CHPh_2)\}_2]$ (M = Ca, Sr, Ba) that we reported show four-membered metallacycles with calcium and its higher congeners.[15]

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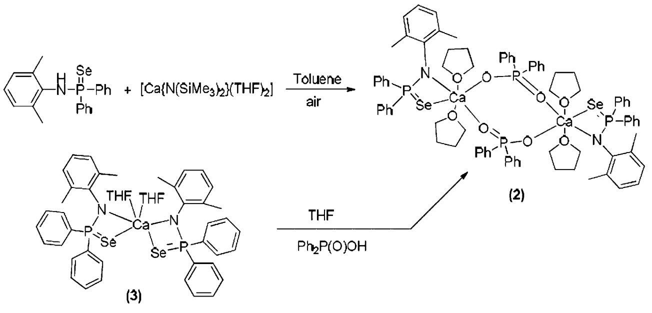
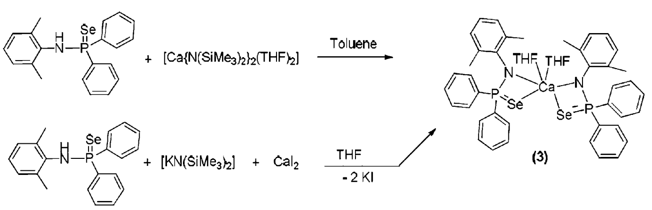
Herein we report the syntheses and-solid-state structures of eight-membered calcium metalla-macrocycle of the composition [Ca{$Ph_2P(Se)N(Ar)$}{$Ph_2P(O)O$}$(THF)_2]_2$ (**2**) along with the homoleptic calcium phosphinoselenoic amido complex of the composition [M{$Ph_2P(Se)N(Ar)$}$_2(THF)_2$] (**3**).

Results and Discussion

The complex [Ca{$Ph_2P(Se)N(Ar)$}{$Ph_2P(O)O$}$(THF)_2]_2$ (**2**) (Ar = 2,6-dimethylphenyl) was isolated, with a good yield, when phosphinoselenoic amide [$Ph_2P(Se)NH(Ar)$] (**1**) was made to react with calcium bis(trimethylsilyl)amides [Ca{N-$(SiMe_3)_2$}$_2(THF)_2$] in toluene followed by crystallization in hydrous condition in air (see Scheme 1). However, when the reaction mixture was subjected to crystallization in an inert atmosphere, calcium complex **3** was isolated, with a good yield. Complex **3** can also be prepared by a one-pot reaction involving ligand **1**, calcium diiodide, and potassium bis(trimethylsilyl)amide in THF at an ambient temperature in an inert atmosphere (see Scheme 2). Complex **2** can also be obtained by the treatment of complex **3** and diphenyl phosphinic acid in an inert atmosphere (see Scheme 1). Both compounds **2** and **3** were characterized by standard combustion analysis as well as spectroscopic techniques. The solid-state structures of complexes **2** and **3** were established by single-crystal X-ray diffraction analysis.



Scheme 1. Synthesis of complex **2**.



Scheme 2. Synthesis of complex **3**.

The FT-IR spectra of compounds **2** and **3** showed strong absorption bands for P=Se bond stretching at 568 cm^{-1} and 569 cm^{-1} respectively. These values are well in agreement with previously observed P=Se stretching frequencies.[13] When the ^1H NMR spectra of compounds **2** and **3** were recorded in C_6D_6, one set of signals was observed in each case. A sharp singlet at δ = 1.99 and 2.05 ppm can be assigned to the 12 methyl protons attached in the 2,6-dimethylphenyl moieties of complexes **2** and **3**, respectively. Eight *ortho*-protons of the four phenyl rings attached to diphenylphosphinates were highly deshielded and appeared at δ = 8.30 ppm as a broad singlet signal for compound **2**, whereas a multiplet signal at δ = 7.98–7.92 ppm and a broad singlet at δ = 6.90 ppm were observed in other phenyl protons for complex **2**. In both complexes, the broad peaks at δ = 3.42 and 1.14 ppm corresponded to the coordinated four THF molecules attached to two calcium atoms for complex **2** and two THF molecules for complex **3**, which were confirmed by the solid-state structures (vide infra). In proton decoupled ^{31}P spectra, complex **2** showed two equally intense peaks at δ = 64.7 ppm and 42.6 ppm whereas compound **3** showed only a singlet at δ = 65.7 ppm. The singlet at δ = 64.7 ppm (for **2**) and 65.6 ppm (for **3**) can be assigned to the diphenylphosphinoselenoic amido group present in both complexes. The signal at δ = 42.6 ppm for complex **2** therefore can be assigned to the phosphorus atom, which is highly shielded due to the greater number of electronegative oxygen atoms present adjacent to it in bridging diphenylphosphinate groups. In addition, for compound **3**, two satellite peaks on either side of the signal at δ = 65.7 ppm were also observed due to the coupling of ^{31}P and the less abundant (7.6 per cent) ^{77}Se, for both nuclei having a nuclear spin I = ½.

The solid-state structures of compounds **2** and **3** were confirmed by single-crystal X-ray diffraction analysis. The data collection parameters are set out in Table 1. The centrosymmetric compound **2** was crystallized in a monoclinic space group $P2_1/c$ having two molecules in the unit cell along with one toluene molecule as the solvent, whereas compound **3** was

Table 1. Crystallographic details of [Ca{$Ph_2P(Se)N(Ar)$}{$Ph_2P(O)O$}$(THF)_2]_2$ (**2**) and [Ca$(THF)_2${$Ph_2P(Se)N(Ar)$}$_2$] (**3**).

	2·2toluene	**3**
Formula	$C_{94}H_{106}Ca_2N_2O_8P_4Se_2$	$C_{48}H_{54}CaN_2O_2P_2Se_2$
Formula weight	1753.77	950.87
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$/c	*Pbca*
a /Å	18.2918(4)	17.7165(4)
b /Å	17.1014(3)	17.2738(4)
c /Å	5.1820(3)	29.6492(12)
α /°	90	90
β /°	94.399(2)	90
γ /°	90	90
V /Å^3	4735.17(16)	9073.6(5)
Z	2	8
Density /mg·m^{-3}	1.230	1.392
T /K	150(2)	150(2)
Radiation	Cu-K_α (λ = 1.54184 Å)	Cu-K_α (λ = 1.54184 Å)
μ /mm^{-1}	2.974	4.000
F(000)	1832	3920
Absorption correction	multi-scan	multi-scan
Reflections collected	19659	25968
Unique reflections	8798 [R_{int} = 0.0363]	8600 [R_{int} = 0.0379]
Completeness to θ	97.0 %	98.4 %
GOF	1.042	1.032
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
R_1; wR_2	0.0893; 0.2188	0.0456; 0.0943

crystallized in an orthorhombic space group *Pbca* with eight molecules in the unit cell.

Figure 1 shows the solid-state structure of compound **2** along with the macrocyclic ring of molecule **2**; the molecular structure of compound **3** is given in Figure 2. Compound **2** is a dimer of the asymmetric unit [Ca{Ph$_2$P(Se)N(Ar)}{Ph$_2$P(O)O}(THF)$_2$], where each calcium polyhedron is formed by the chelation of bidentate mono-anionic diphenylphosphinoselenoic amido moiety and diphenylphosphinate [PhP$_2$P(O)O] along with two THF molecules. In {Ph$_2$P(Se)N(Ar)}$^-$ moiety, nitrogen and selenium atoms coordinate with the calcium atom and two oxygen atoms in the [PhP$_2$P(O)O] group act as bridging ligands, coordinating with the two calcium atoms. Thus, each calcium metal is coordinated six fold, and adopts a distorted arrangement around it. Two four-member metallacycles, Ca1–N1–P2–Se1 and Ca1^{i}–N1^{i}–P2^{i}–Se1^{i}, are formed by the coordination of two {Ph$_2$P(Se)N(Ar)}$^-$ moieties and two calcium ions. The bond lengths, Ca1–Se1 [3.0337(9) Å] and Ca1–N1 [2.452(4) Å], are similar in range to the 2.9889(8) Å and 2.479(5) Å observed for [Ca(THF)$_2${Ph$_2$P(Se)N(CHPh$_2$)}$_2$], as we reported.[15] The Ca–P distance 3.287 Å for compound **2** is significantly larger than the sum of the covalent radii (3.07 Å) of phosphorus and calcium, indicating no interaction between these two atoms. The Ca1–O3 [2.470(3) Å] bond [2.372(3) Å] is slightly elongated when compared to the Ca1–O4 bond, presumably due to greater electron release by diphenylphosphinate oxygen *trans* to Ca1–O3 bond. An eight-membered metalla-macrocycle Ca1–O1–P1–O2–Ca1^{i}–O1^{i}–P1^{i}–O2^{i} is formed by the chelation of two diphenylphosphinate groups and two calcium ions. The conformation of the eight-membered ring can be best described as chair shaped (see Figure 1, bottom), with a dihedral angle of 20.30° between the average planes containing Ca1 O1 Ca1^{i} Ca1 O1^{i} and Ca1, O2, P1^{i}, and O1^{i} atoms. The distance between the two opposite calcium atoms is 5.400 Å. To the best of our knowledge this is the first example of an eight-membered calcium metalla-macrocycle. P1–O1 and P1–O2 bond lengths [1.499(3) Å and 1.504(3) Å, respectively] are equal due to the delocalization of the negative charge over two oxygen atoms attached to the phosphorus atom in the diphenylphosphinate group.

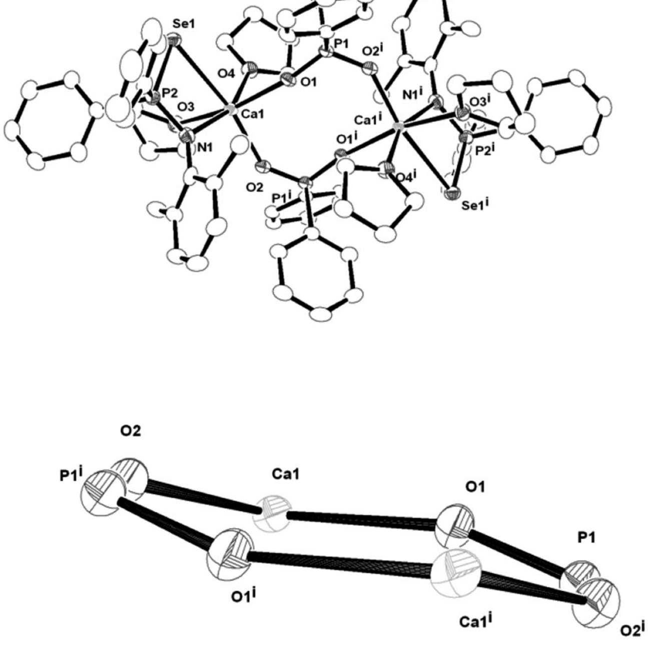


Figure 1. Solid-state structure of compound **2** showing the atom-labelling scheme (top) and macro cyclic ring of compound **2** (bottom). Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and bond angles /° for **2**: Ca1–Se1 3.0337(9), Ca1–N1 2.452(4), Ca1–P2 3.2872(13), Ca1–O1 2.242(3), Ca1–O2 2.257(3), Ca1–O4 2.372(3), Ca1–O3 2.470(3), Ca1–P1^{i} 3.5536(13), N1–P2 1.610(4), O1–P1 1.499(3), O2-P1^{i} 1.504(3), P1-O2^{i} 1.504(3), P1-Ca1^{i} 3.5536(13), P2–Se1 2.1513(11), O1–Ca1–O2 97.64(10), O1–Ca1–N1 103.67(11), O2–Ca1–N1 104.53(12), O4–Ca1–N1 159.12(12), N1–Ca1–O3 91.99(12), O1–Ca1–Se1 90.71(8), O2–Ca1–Se1 169.58(8), N1–Ca1–Se1 67.22(9), O3–Ca1–Se1 87.48(8), O1–Ca1–P2 103.43(8), O2–Ca1–P2 131.43(8), N1–Ca1–P2 28.06(9), Se1–Ca1–P2 39.54(2), O1–Ca1–P1^{i} 82.83(8), N1–Ca1–P1^{i} 112.58(10), O3–Ca1–P1^{i} 99.20(8), Se1–Ca1–P1^{i} 173.32(3), P2–Ca1–P1^{i} 140.64(3), P2–N1–Ca1 106.18(19), P1–O1–Ca1 161.71(18), P1^{i}–O2–Ca1 140.91(16), O1–Ca1–O2 97.64(10), O1–Ca1–O4 85.92(11), O1–Ca1–N1 103.67(11).

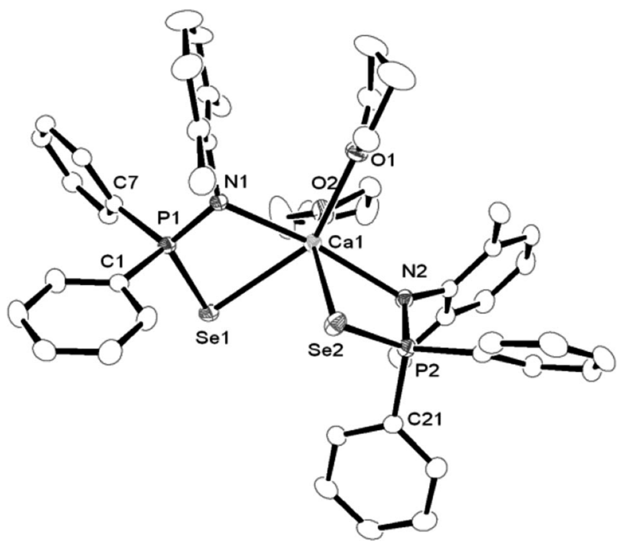


Figure 2. Solid-state structure of compound **3** showing the atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and bond angles /° for **3**: Ca1–N1 2.398(2), Ca1–N2 2.435(2), Ca1–Se1 3.0259(6), Ca1–Se2 3.0418(6), Ca1–P1 3.2819(8), Ca1–P2 3.2984(8), Se1–P1 2.1461(7), Se2–P2 2.1455(7), P1–N1 1.612(2), P2–N2 1.611(2), Ca1–O1 2.3905(19), Ca1–O2 2.424(2), O1–Ca1–N1 85.99(7), O1–Ca1–O2 90.64(7), N1–Ca1–O2 105.62(7), O1–Ca1–N2 95.78(7), N1–Ca1–N2 162.43(7), O2–Ca1–N2 91.86(7), N1–Ca1–Se1 67.28(5), N2–Ca1–Se1 112.93(5), N1–Ca1–Se2 95.95(5), N2–Ca1–Se2 66.49(5), Se1–Ca1–Se2 94.685(16), N1–Ca1–P1 27.79(5).

In molecule **3**, the coordination polyhedron is formed by the chelation of two mono-anionic {Ph$_2$P(Se)N(Ar)}$^-$ ligands, and two THF molecules. Each {Ph$_2$P(Se)N(Ar)}$^-$ ligand coordinates with the calcium atom through chelation of one amido nitrogen and one selenium atom. The P–Ca distances of 3.2819(8) Å and 3.2984(8) Å are significantly greater than the sum of the covalent radii (3.07 Å) of phosphorus and calcium, indicating no interaction between these two atoms. However, P–Ca bond lengths are similar in range (3.287 Å) to those of compound **2** (3.274 Å) and for [Ca(THF)$_2${Ph$_2$P(Se)N-(CHPh$_2$)}$_2$], as we reported.[15] Thus, the {Ph$_2$P(Se)N(Ar)}$^-$ group acts as bidentate ligand and the arrangement around the calcium atom can be best described as a distorted octahedral due to coordination between the two {Ph$_2$P(Se)N(CHPh$_2$)}$^-$ moieties and two THF molecules. Two four-membered calcium metallacycles, Ca1–N1–P1–Se1 and Ca1–N2–P2–Se2, are formed. The Ca–N distances [2.398(2) Å and 2.435(2) Å] are similar in range [2.452(4) Å] to those of complex **2**, but are slightly elongated compared with calcium–nitrogen distances [2.361(2) Å and 2.335(2) Å] reported for [Ca(Dipp$_2$DAD)-(THF)$_4$] [Dipp$_2$DAD = *N*,*N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene] in literature.[6a] The most interesting feature is that the Ca–Se bond lengths [3.0259(6) Å and 3.0418(6) Å] are similar in range with those of complex **2** [3.0337(9) Å] and [Ca(THF)$_2$-{Ph$_2$P(Se)N(CHPh$_2$)}$_2$] [2.989(8) Å] as we reported. Ca–Se bond lengths observed in complexes **2** and **3** also match with the reported Ca–Se values with 2.945(1) Å for [(THF)$_2$Ca{(PyCH)(Se)PPh$_2$}$_2$][16] and 2.9336(4) Å for [(THF)$_4$Ca(SeMes')$_2$][17] in literature. Thus, complexes **2** and **3** are examples of compounds with direct calcium–selenium bond.[15–17] The P–Se distance in complexes **2** and **3** [2.1513(11) Å and 2.1461(7) Å, respectively] is in the same range as that of [Ca(THF)$_2${Ph$_2$P(Se)N(CHPh$_2$)}$_2$] [2.1449(2) Å], indicating similar coordination of diphenylphosphinoselenoic amido group with the calcium atom. It is noteworthy that the two nitrogen atoms and two selenium atoms of the {Ph$_2$P(Se)N(Ar)}$^-$ group are chelated to calcium in *cis* fashion along with two *cis* THF molecules. However, the reverse phenomenon, that is nitrogen, selenium, and oxygen atoms being *trans* in the analogous compound [Ca(THF)$_2$-{Ph$_2$P(Se)N(CHPh$_2$)}$_2$], was observed.

Theoretical Investigation of the Bonding in Compound 2

To confirm the experimentally obtained bonding features of the eight-membered calcium metalla-macrocyclic compound **2**, we performed ab initio calculations (HF/3-21G*) on the isoelectronic model calcium complex **2a**, where bulky phenyl groups are substituted by methyl groups to achieve higher symmetry.[18] The structure of complex **2a** was freely optimized with no geometric constraint and the calculated geometries (see Figure 3) were found to be in good agreement with those established by X-ray diffraction. In complex **2a**, the calculated Ca1–N1 distance of 2.474 Å matched perfectly with the Ca–N1 bond length (2.452 Å), which was experimentally determined for molecules of complex **2**. The calculated Ca1–O1 (2.273 Å) and Ca1–O2 (2.272 Å) lengths also matched the experimental values (2.242 Å and 2.257 Å, respectively). The theoretical bond angles of complex **2a** O1–Ca1–O2 (101.34°), P1–O1–Ca1 (160.58°) were also in good agreement with experimentally determined values (97.64° and 161.71°).

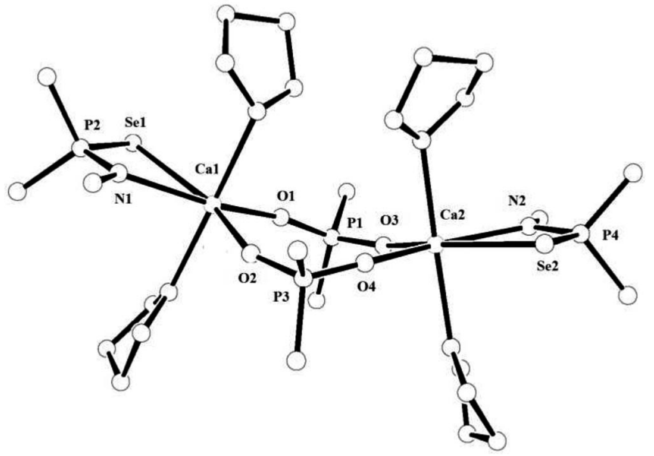


Figure 3. ORTEP drawing of the calculated structure **2a**. Selected bond lengths /Å and bond angles /°, for comparison, experimental values are given in parentheses: Ca1–Se11 3.116 [3.0337], Ca1–N1 2.474 [2.452], Ca1–P2 3.340 [3.2872], Ca1–O1 2.273 [2.242], Ca1–O2 2.272 [2.257], Ca1–P3 3.685 [3.5536], N1–P2 1.597[1.610], O1–P1 1.510[1.499], O2–P3 1.512[1.504], P1–O3 1.510[1.504], P1–Ca2 3.685 [3.5536], P2–Se1 2.148 [2.1513], O1–Ca1–O2 101.34 [97.64], P1–O1–Ca1 160.58 [161.71], P3–O2–Ca1 153.26 [140.91].

Conclusions

We have reported the syntheses and solid-state structures of an eight-membered calcium metalla-macrocycle along with the homoleptic calcium phosphinoselenoic amido complex. The eight-membered ring is formed by the coordination of two diphenylphosphinate groups and two calcium atoms, and each calcium ion is again coordinated with one mono-anionic diphenylphosphinoselenoic amido group and two THF molecules to satisfy the sixfold coordination for each calcium atom. Both complexes also contain the direct calcium–selenium bond.

Experimental Section

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out in an argon atmosphere using the standard Schlenk technique or argon-filled glove box. Hydrocarbon solvents (*n*-pentane, toluene) were distilled in nitrogen from LiAlH$_4$ and stored in the glove box. THF was dried and deoxygenated by distillation over sodium benzophenone ketyl in an argon atmosphere and additionally distilled and dried with CaH$_2$ prior to storing in the glove box. [D$_6$]Benzene was dried with Na/K alloy and stored in the glove box. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{31}P (161.9 MHz) spectra were measured with a Bruker Avance III-400 spectrometer. Elemental analyses were performed with a Bruker Euro EA at the Indian Institute of Technology, Hyderabad. Diphenylphosphinoselenoic amide [Ph$_2$P(Se)NH(Ar)] (**1**)[13] and calcium bis(trimethylsilyl) amides [Ca{N-(SiMe$_3$)$_2$}$_2$(THF)$_2$][19] were prepared according to procedures prescribed in the literature.

[Ca{Ph$_2$P(Se)N(Ar)}{Ph$_2$P(O)O}(THF)$_2$]$_2$ (2): In a dry 25 mL Schlenk tube, the ligand **1** (100 mg, 0.26 mmol) and calcium bis(trimethylsilyl)amide (66 mg, 0.13 mmol) were placed together and toluene (5 mL) was added to it. The reaction mixture was stirred at an ambient temperature for 20 h. The solvent was evaporated to half of its volume and THF (1 mL) was layered on to it. The entire solution was kept outside under controlled air. Colorless crystals were obtained after 3 d. Yield 70 mg (68 %). **^{1}H NMR** (400 MHz, C_6D_6, 25 °C): δ = 8.30 (br., 8 H, ArH), 7.96–7.92 (m, 8 H, ArH), 6.90 (br., 24 H, ArH), 6.88 (br., 6 H, ArH), 3.47 (br., 8 H, THF), 1.99 (s, 12 H, CH_3), 1.14 (br., 8 H, THF). **^{31}P{^{1}H} NMR** (161.9 MHz, C_6D_6): δ = 64.7 (P=Se) and 42.6 (P=O) ppm. **FT-IR** (selected frequencies): ṽ = 1359 (P–C), 1199 (P=O), 924 (P–N), 568 (P=Se) cm^{-1}. $C_{94}H_{106}Ca_2$ $N_2O_8P_4Se_2$ (**2**·2toluene, 1753.83): calcd. C 61.22, H 5.78, N 1.78 %; found, C 60.91, H 5.63, N 1.52 %.

[Ca(THF)$_2${Ph$_2$P(Se)N(Ar)}$_2$] (3): Route 1: Same as above. The recrystallization was accomplished in an inert atmosphere at –35 °C. Colorless crystals were obtained. Yield 65 %.

Route 2: A mixture of the ligand **1** (100 mg, 0.26 mmol), potassium bis(trimethylsilyl)amide (52 mg, 0.26 mmol) and calcium iodide (38 mg, 0.13 mmol) was charged with dry THF (5 mL) and the reaction mixture was stirred for 12 h. The white precipitate of KI was filtered to leave behind a colorless filtrate. The filtrate was evaporated to half of its volume and pentane (3 mL) was layered on to it. Colorless crystals of **3** were obtained at –35 °C. Yield 81 mg, 65 %. **^{1}H NMR** (400 MHz, C_6D_6, 25 °C): δ = 7.98–7.92 (m, 8 H, ArH), 7.01–6.98 (m, 12 H, ArH), 6.89 (br., 6 H ArH), 3.47 (br., 8 H, THF), 2.05 (s, 12 H, CH_3), 1.14 (br., 8 H, THF). **^{31}P{^{1}H} NMR** (161.9 MHz, C_6D_6): δ = 65.7 (P=Se) ppm. **FT-IR** (selected frequencies): ṽ = 1357 (P–C), 920 (P–N), 569 (P=Se) cm^{-1}. $C_{48}H_{54}CaN_2O_2P_2Se_2$ (950.90): calcd. C 60.63, H 5.72, N 2.95 %; found, C 60.24, H 5.43, N 2.69 %.

X-ray Crystallographic Analyses: Single crystals of complex **2** were obtained from a solution of THF/pentane (1:2) under hydrous condition, whereas single crystals of complex **3** were obtained in an argon atmosphere at a temperature of –35 °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 with an Oxford Supernova X-calibur Eos CCD detector with graphite-monochromatic Cu-K_α (1.54184 Å) radiation. Crystal data and structure refinement parameters are summarized in Table 1. The structures were solved by direct methods (SIR2004)[20] and refined on F^2 using the full-matrix least-squares method using SHELXL-97.[21] Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\Sigma w(F_o^2 - F_c^2)^2]$ ($w = 1 / [\sigma^2 (F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2F_c^2) / 3$ with $\sigma^2(F_o^2)$ from counting statistics. The function R_1 and wR_2 were $(\Sigma||F_o| - |F_c||) / \Sigma|F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma(wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program[22] was used to draw the molecule.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-960672 (**2**) and CCDC-960673 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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