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Oxidation Products of Calcium and Strontium Bis(diphenylphosphanide)

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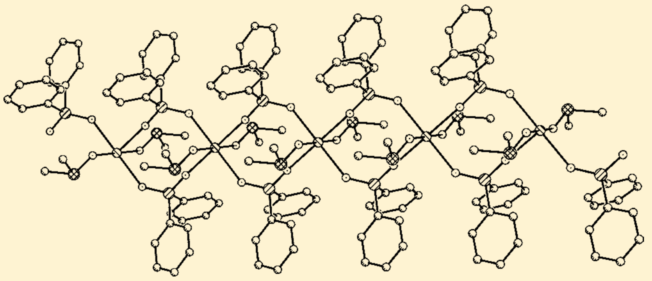
Supporting Information



ABSTRACT: The tetrahydrofuran adducts $[(thf)_4M(PPh_2)_2]$ (M = Ca, Sr) are air sensitive and can easily be oxidized by chalcogens. Metalation of diphenylphosphane oxide, diphenylphosphinic acid, and diphenyldithiophosphinic acid as well as salt metathetical approaches of the potassium salts with MI_2 allow the synthesis of $[(thf)_4Ca(OPPh_2)_2]$ (**1**), $[(dmso)_2Ca(O_2PPh_2)_2]$ (**2**), $[(thf)_3Ca(O_2PPh_2)I]_2$ (**3**), $[(thf)_3Ca(S_2PPh_2)_2]$ (**4**), $[(thf)_2Ca(Se_2PPh_2)_2]$ (**5**), $[(thf)_3Sr(S_2PPh_2)_2]$ (**6**), $[(thf)_3Sr(Se_2PPh_2)_2]$ (**7**), and $[(thf)_2Ca(O_2PPh_2)(S_2PPh_2)]_2$ (**8**), respectively. The diphenylphosphinite anion in **1** contains a phosphorus atom in a trigonal pyramidal environment and binds terminally via the oxygen atom to calcium. The diphenylphosphinate anions act as bridging ligands leading to polymeric structures of calcium bis(diphenylphosphinates). Therefore strong Lewis bases such as dimethylsulfoxide (dmso) are required to recrystallize this complex yielding chain-like **2**. The chain structure can also be cut into smaller units by ligands which avoid bridging positions such as iodide and diphenyldithiophosphinate (**3** and **8**, respectively). In general, diphenyldithio- and -diselenophosphinate anions act as terminal ligands and allow the isolation of mononuclear complexes **4** to **7**. In these molecules the alkaline earth metals show coordination numbers of six (**5**) and seven (**4**, **6**, and **7**).

■ INTRODUCTION

Phosphorus-containing anions can be derived from the neutral acids. Contrary to homologous nitrogen-based oxoacids, phosphorus often favors tetra-coordination and, hence, (distorted) tetrahedral environments. Step-wise oxidation of phosphane PH_3 leads to phosphinous acid ($H_2P{-}OH$) or phosphane oxide (H_3PO), phosphonous acid $[HP(OH)_2]$ or phosphinic acid $[H_2P(O)OH]$, and finally to phosphorous acid $[P(OH)_3]$ or phosphonic acid $[HP(O)(OH)_2]$. The tautomeric couples differ by the coordination number of the phosphorus center. Substitution of H atoms by phenyl groups hinders this migration, and the phenyl groups remain bound at phosphorus, leading to the oxidation products diphenylphosphinous acid (Ph_2POH) or diphenylphosphane oxide (Ph_2HPO) and also to higher oxidized diphenylphosphinic acid $[Ph_2P(O)OH]$. Deprotonation yields diphenylphosphinite (Ph_2PO^-) and diphenylphosphinate ($Ph_2PO_2^-$) anions.

The bis(diphenylphosphanides) (the deprotonation product of diphenylphosphane Ph_2PH) of the heavy alkaline earth metals M represent a well investigated substance class which has attracted interest for many years for several reasons. The tetrahydrofuran (thf) adducts $[(thf)_4M(PPh_2)_2]$ (M = Ca, Sr) are soluble in common organic donor solvents (Lewis bases), are easily prepared,[1,2] and are effective catalysts in hydrophosphanylation reactions. For the calcium complex, cis and trans isomers were observed in the solid state with the option to stabilize cis-isomeric calcium bis(diphenylphosphanide) with tetradentate hexamethyltriethylenetetraamine.[3] Heteroleptic diphenylphosphanides were prepared via calciation of Ph_2PH[4,5] and metathetically from $[(thf)_4Ca(Ph)I]$ and $KPPh_2$ yielding $[(thf)_4Ca(Ph)PPh_2]$.[6] Calcium-catalyzed intermolecular hydrophosphanylation of carbodiimides,[7,8] alkenes,[5] and alkynes[5,9,10] led to the formation of tertiary phosphanes. The high reactivity of calcium phosphanides was employed to intramolecularly cleave an aryl alkyl ether yielding derivatives of calcium 2-(alkylphosphanido)phenolate.[11,12]

The diphenylphosphinites of the alkaline earth metals represent a poorly investigated substance class. Metalation of diphenylphosphane oxide with phenylmagnesium bromide yielded $Ph_2PO{-}MgBr$ with a chemical shift of $\delta(^{31}P) = 90.0$.[13] Whereas attempts to prepare homoleptic calcium bis(diphenylphosphinites) failed, Hill and co-workers[14] obtained heteroleptic dimeric diketiminatocalcium diphenylphosphinite with bridging phosphinite anions binding via the oxygen atom. The isolation of another heteroleptic complex $[(thf)_4Ca(PPh_2)(OPPh_2)]$ with a terminal O-bound phosphinite anion succeeded after inadvertent aerial oxidation of $[(thf)_4Ca(PPh_2)_2]$.[3]

Contrary to the shadowy existence of the alkaline earth metal phosphinites, the higher oxidized diphenylphosphinates have attracted much more interest. Beryllium phosphinates form coordination polymers which were studied approximately half a century ago;[15−18] thereafter the interest in these compounds

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diminished most probably because of the toxicity of beryllium dusts. The phosphinates of the heavier alkaline earth metals were studied by IR spectroscopy to investigate the symmetry of the O−P−O moiety.[19] Calcium methylphenylphosphinates were soluble in water and methanol and precipitated as dihydrates; the anhydrous complexes could be isolated at 100 °C in vacuo.[20] Singly and doubly deprotonated *P,P′*-diphenylmethylenediphosphinic acid $H_2C[P(Ph)(O)OH]_2$ forms polymeric structures with magnesium and calcium ions.[21]

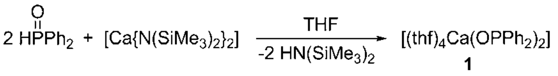
The oxidation of diphenylphosphanide with the homologous chalcogens leads to thio- and selenophosphinites and -phosphinates. Especially the phosphinates have been reported extensively mainly as ligands in transition metal chemistry because they show diverse coordination patterns as monodentate (monometallic monoconnective), iso- and anisobidentate (monometallic biconnective, symmetric or asymmetric binding mode), or bridging (bimetallic biconnective and triconnective) ligands.[22−25] Special interest is given to these anions because their complexes offer applications in catalysis, MOCVD processes, separation procedures, and as lubricants.

Bildstein and Sladky investigated the oxidation of $LiPPh_2$ with chalcogens in THF and found a linear correlation between the chemical ^{31}P NMR shift and the Pauling electronegativity of the chalcogen for $Ph_2PE\text{-}Li$ (diphenylchalcogenophosphinites) and Ph_2PE_2Li (diphenyldichalcogenophosphinates).[26] Reduction of diphenylphosphinic and -thiophosphinic chloride with sodium or magnesium as well as metalation of diphenylphosphane oxide and sulfide also yielded the corresponding diphenylchalcogenophosphinites.[27] These Ph_2PE^- anions show a diverse coordination behavior as terminal or bridging ligands via the chalcogen atom or as bridging ligands via the phosphorus and chalcogen bases. The last mentioned binding mode was found in $[(tmeda)LiSePPh_2]_2$.[28] Addition of borane BH_3 to the diphenylchalcogenophosphinites led to blocking of the Lewis basic behavior at the phosphorus atom, and thus protected phosphinites acted as terminal ligands at potassium.[29] Also sterically protected d^0 metals only allowed that the diphenylthiophosphinites acted as terminal ligands in $[Cp_2Ti(SPPh_2)_2]$.[30] The diphenyldichalcogenophosphinate anions $Ph_2PE_2^-$ generally act as bidentate ligands which can be bound terminally at one metal center[28,30] or occupy bridging positions.[31] In hydrate complexes the water molecules are able to replace the soft chalcogeno bases in the inner coordination sphere of the s-block metals as shown for $[(H_2O)_5(thf)Na_2(Se_2PPh_2)_2]$.[32]

The lack of information on heavier alkaline earth metal complexes initiated investigations regarding synthesis and coordination behavior of diphenylphosphinites and -phosphinates toward calcium and strontium.

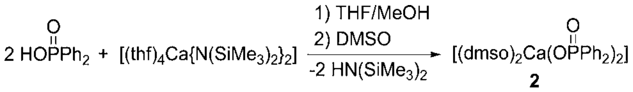
■ RESULTS AND DISCUSSION

Synthesis. Inadvertent oxidation of $[(thf)_4Ca(PPh_2)_2]$ with air led to the formation of heteroleptic $[(thf)_4Ca(PPh_2)(OPPh_2)]$.[3] However, aerial oxidation does not provide an effective access to these phosphinites because they were also air sensitive. The acidity of diphenylphosphane oxide is rather low but metalation with $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$ yielded calcium bis(diphenylphosphinite) **1** as tetrakis(thf) adduct $[(thf)_4Ca(OPPh_2)_2]$ according to eq 1. This complex was isolated as an air-sensitive colorless crystalline solid. The $\delta(^{31}P)$ value of **1** $[\delta(^{31}P) = 83.0]$ is in accordance with the chemical shifts of $LiOPPh_2$ $[\delta(^{31}P) = 93.8,$[27] 88.9[33]$]$ and of $ClMgOPPh_2$ $[\delta(^{31}P) = 90.0$[27,34]$]$.



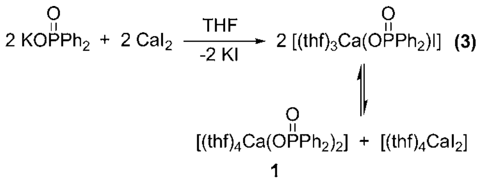
$$2\,\mathrm{H\overset{O}{\overset{\|}{P}}Ph_2} + [\mathrm{Ca\{N(SiMe_3)_2\}_2}] \xrightarrow[-2\,\mathrm{HN(SiMe_3)_2}]{\mathrm{THF}} \underset{\mathbf{1}}{[(\mathrm{thf})_4\mathrm{Ca(OPPh_2)_2}]} \qquad (1)$$

Calciation of diphenylphosphinic acid with $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$ yielded insoluble, colorless, and air-stable calcium bis(diphenylphosphinate) according to eq 2. Addition of



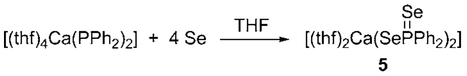
$$2\,\mathrm{HO\overset{O}{\overset{\|}{P}}Ph_2} + [(\mathrm{thf})_4\mathrm{Ca\{N(SiMe_3)_2\}_2}] \xrightarrow[-2\,\mathrm{HN(SiMe_3)_2}]{\text{1) THF/MeOH} \atop \text{2) DMSO}} \underset{\mathbf{2}}{[(\mathrm{dmso})_2\mathrm{Ca(O\overset{O}{\overset{\|}{P}}Ph_2)_2}]} \qquad (2)$$

dimethylsulfoxide (DMSO) allowed growing single crystals of $[(dmso)_2Ca(O_2PPh_2)_2]$ (**2**) suitable for X-ray diffraction studies, but the insolubility still hampered recording of NMR data. Oxidation of $[(thf)_4Ca(PPh_2)_2]$ with N_2O or air also allowed the preparation of $Ca(O_2PPh_2)_2$. To isolate more soluble diphenylphosphinate complexes of calcium, a metathetical approach was chosen. The reaction of $K(O_2PPh_2)$ with calcium diiodide in tetrahydrofuran initially yielded $[(thf)_3Ca(O_2PPh_2)I]_2$ (**3**) and insoluble KI allowing NMR spectroscopic characterization, and a chemical shift of $\delta(^{31}P) = 17.1$ was recorded. However, this calcium phosphinate complex showed a Schlenk-type equilibrium with the homoleptic congeners, $Ca(O_2PPh_2)_2$ and CaI_2 being favored (eq 3). The insolubility of $Ca(O_2PPh_2)_2$ in common organic solvents eased isolation of a pure complex but also pulled the equilibrium toward these homoleptic derivatives. This solubility behavior and a melting point above 300 °C hint toward a polymeric structure of calcium diphenylphosphinate.



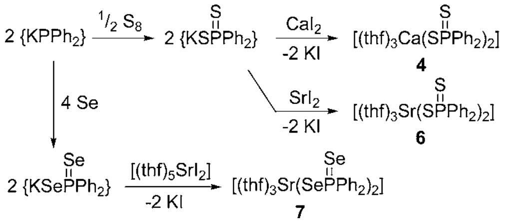
$$2\,\mathrm{KO\overset{O}{\overset{\|}{P}}Ph_2} + 2\,\mathrm{CaI_2} \xrightarrow[-2\,\mathrm{KI}]{\mathrm{THF}} 2\,[(\mathrm{thf})_3\mathrm{Ca(O\overset{O}{\overset{\|}{P}}Ph_2)I}]\ \mathbf{(3)} \rightleftharpoons \underset{\mathbf{1}}{[(\mathrm{thf})_4\mathrm{Ca(O\overset{O}{\overset{\|}{P}}Ph_2)_2}]} + [(\mathrm{thf})_4\mathrm{CaI_2}] \qquad (3)$$

The diphenyldichalcogenophosphinates were prepared by oxidation of $[(thf)_4Ca(PPh_2)_2]$ with selenium (eq 4) or by

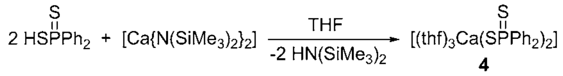


$$[(\mathrm{thf})_4\mathrm{Ca(PPh_2)_2}] + 4\,\mathrm{Se} \xrightarrow{\mathrm{THF}} \underset{\mathbf{5}}{[(\mathrm{thf})_2\mathrm{Ca(Se\overset{Se}{\overset{\|}{P}}Ph_2)_2}]} \qquad (4)$$

oxidation of $\{KPPh_2\}$ with the corresponding chalcogen and subsequent metathesis reaction with MI_2 (M = Ca, Sr) according to eq 5 yielding $[(thf)_3Ca(S_2PPh_2)_2]$ (**4**), $[(thf)_2Ca(Se_2PPh_2)_2]$ (**5**), $[(thf)_3Sr(S_2PPh_2)_2]$ (**6**), and $[(thf)_3Sr(Se_2PPh_2)_2]$ (**7**), respectively. Analogously to the synthesis of $[(dmso)_2Ca(O_2PPh_2)_2]$ **2**, metalation of diphenyldithiophosphinic acid with $[Ca\{N(SiMe_3)_2\}_2]$ yielded $[(thf)_3Ca(S_2PPh_2)_2]$ (**4**), according to eq 6. The isolation of



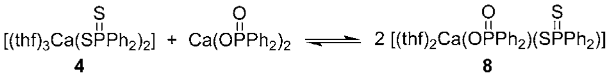
(5)



$$2\,\mathrm{HS\overset{S}{\overset{\|}{P}}Ph_2} + [\mathrm{Ca\{N(SiMe_3)_2\}_2}] \xrightarrow[-2\,\mathrm{HN(SiMe_3)_2}]{\mathrm{THF}} \underset{\mathbf{4}}{[\mathrm{(thf)_3Ca(S\overset{S}{\overset{\|}{P}}Ph_2)_2}]} \qquad (6)$$

$M(Te_2PPh_2)_2$ (M = Ca, Sr) from the reaction of the diphenylphosphanides of calcium and strontium with tellurium did not succeed. In dependency of the chalcogen atom, strikingly different solubility behavior was observed. Whereas the diphenylphosphinates are insoluble in common organic solvents, the dithio- and diselenophosphinates exhibited significant solubility in donor solvents such as tetrahydrofuran. The ^{31}P NMR shifts of these compounds are nearly independent from the alkaline earth metal and show $\delta(^{31}P)$ values of 61 and 22 for $Ph_2PS_2^-$ and $Ph_2PSe_2^-$, respectively. The independency of the shift from the metal clearly speaks for highly ionic complexes with electrostatic forces dominating the bonding situation.

For the preparation of mixed diphenylphosphinates two pathways are feasible. On the one hand, a mixture of $Ca(O_2PPh_2)_2$ and $[(thf)_3Ca(S_2PPh_2)_2]$ (**4**) allowed the isolation of crystalline $[(thf)_2Ca(O_2PPh_2)(S_2PPh_2)]_2$ (**8**); however, the insolubility of $Ca(O_2PPh_2)_2$ leads to an unfavorable shift of the equilibrium (eq 7). Nevertheless, a few single crystals of **8** were obtained enabling a crystal structure determination. On the other hand, another procedure involved the oxidation of $[(thf)_4Ca(PPh_2)_2]$ with an equimolar mixture of sulfur and selenium.



$$\underset{\mathbf{4}}{[\mathrm{(thf)_3Ca(S\overset{S}{\overset{\|}{P}}Ph_2)_2}]} + \mathrm{Ca(O\overset{O}{\overset{\|}{P}}Ph_2)_2} \rightleftharpoons 2\,\underset{\mathbf{8}}{[\mathrm{(thf)_2Ca(O\overset{O}{\overset{\|}{P}}Ph_2)(S\overset{S}{\overset{\|}{P}}Ph_2)}]} \qquad (7)$$

The ^{31}P NMR spectrum clearly showed the formation of $Ph_2PS_2^-$ (δ = 61.6), Ph_2PSSe^- (δ = 44.1), and $Ph_2PSe_2^-$ anions (δ = 22.8) with the mixed chalcogen species being the minor component. Crystals from this reaction mixture were investigated by desorption electron impact (DEI) mass spectrometry (Figure 1). The mass distribution of the mother peaks clearly verifies that all possible isomers are formed; the signal intensity decreases with increasing mass and, hence, selenium content. In addition, the isotopic pattern agrees with the expected isotope distribution.

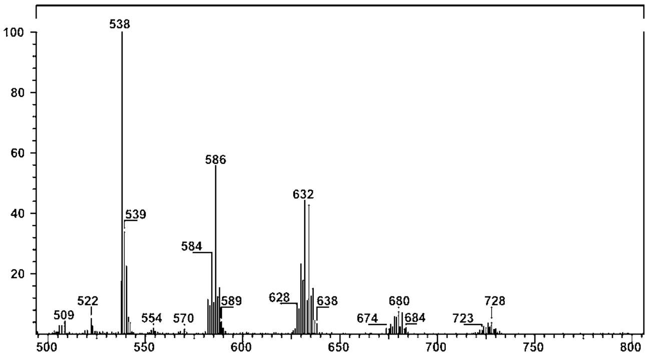


Figure 1. DEI mass spectrum of a mixture obtained via oxidation of $[(thf)_4Ca(PPh_2)_2]$ with sulfur and selenium. Masses for $[Ca(S_2PPh_2)_2]$ (538), $[Ca(S_2PPh_2)(SSePPh_2)]_2$ (586), indistinguishable $[Ca(S_2PPh_2)(Se_2PPh_2)]_2$ and $[Ca(SSePPh_2)_2]_2$ (634), $[Ca(SSePPh_2)(Se_2PPh_2)]_2$ (682), and $[Ca(Se_2PPh_2)_2]_2$ (730 *m*/*e*) are detected with decreasing intensity for increasing amount of selenium. The isotopic pattern supports the assignment to the corresponding formula.

NMR Characterization. Selected NMR parameters are summarized in Table 1 clarifying dependencies between oxidation state of P, chalcogen and NMR values. The chemical shift of the phosphorus atom of the diphenylphosphanide anion in $[(thf)_4Ca(PPh_2)_2]$ was observed at rather high field.[1,2] Oxidation to diphenylphosphanide leads to a significant low field shift as one could expect for deshielded atoms and in agreement with the lithium derivatives. For $LiEPPh_2$ substitution of oxygen by its heavier homologues leads to high field shifted ^{31}P resonances [$\delta(^{31}P)$ = 88.9 (E = O), 20.7 (S), 6.5 (Se), and −35.7 (Te)].[26] In both complexes, $[(thf)_4Ca(PPh_2)_2]$ as well as **1**, the tricoordinate P atoms are in distorted trigonal pyramidal environments. Further oxidation and enhancement of the coordination number (formation of distorted tetrahedral coordination spheres at P) leads to slightly high field shifted $\delta(^{31}P)$ values compared to the phosphinite derivative **1**. Surprisingly, the ^{31}P NMR resonance of oxygen-containing diphenylphosphinate deviates significantly from those of homologous thio- and selenophosphinates. This finding could be a consequence of different structural characteristics such as the widened O−P−O bond angle and the significantly different coordination pattern; whereas $Ph_2PO_2^-$ acts as a bridging ligand the heavier homologous anions $Ph_2PS_2^-$ and $Ph_2PSe_2^-$ anions coordinate terminally as chelate bases. The chemical shifts of the ipso-carbon atoms are rather similar for the oxidized phosphinite and phosphinate anions but a low field shifted resonance was detected for $[(thf)_4Ca(PPh_2)_2]$.[1] In accordance with a larger P−C bond length for $[(thf)_4Ca(PPh_2)_2]$ a smaller $^1J(PC)$ coupling constant was observed.

Table 1. Selected NMR Data of 1 and 3 to 7[a]

compound	M[b]	E[c]	$\delta(^{31}P)$	$\delta(i\text{-}^{13}C)$	$^1J(PC)$	$^1J(PSe)$
$[(thf)_4Ca(PPh_2)_2]$	Ca		−13.1	153.2	33.8	
1	Ca	O	83.0	157.0	35.5	
3	Ca	O	17.1	139.8	136.9	
4	Ca	S	61.5	143.9	78.0	
5	Ca	Se	21.8	142	(broad)[d]	574.1
6	Sr	S	61.5	144.2	79.2	
7	Sr	Se	22.4	142.0	61.4	633.6

[a] M, alkaline earth metal; E, chalcogen. Complex **2** was insoluble and therefore, no reliable NMR data were obtained. For comparison reasons, selected parameters of $[(thf)_4Ca(PPh_2)_2]$ are included.[1]. [b] M, alkaline earth metal. [c] E, chalcogen. [d] Resonance is very broad and doublet pattern is not resolved.

To evaluate the coordination behavior of these phosphorus-based anions, the crystal structures were determined.

Molecular Structures. Molecular structure and numbering scheme of $[(thf)_4Ca(OPPh_2)_2]$ (**1**) are shown in Figure 2. The calcium atom Ca1 lies on a crystallographic inversion center and is embedded in a distorted octahedral environment with *trans* arranged anionic phosphinite ligands. The phosphinite anion contains a trigonal pyramidal phosphorus atom (av. angle sum at P1 306.34°) with a C1−P1−C7 bond angle of 98.30(6)°. The O1−P1−C1/7 angles are slightly larger (104.41(6)° and 103.63(6)°) because of repulsion between the P−O and P−C bonds. These angles suggest mainly p(P)-orbital character of the bonds and a lone pair of mainly s-character. This finding explains the low basicity of the phosphorus atom and the reduced tendency to act as a Lewis base. Nevertheless, borane adducts of phosphinites with P−B bonds were studied by Wagner and co-workers.[29] The P1−O1 distance of 155.7(1)

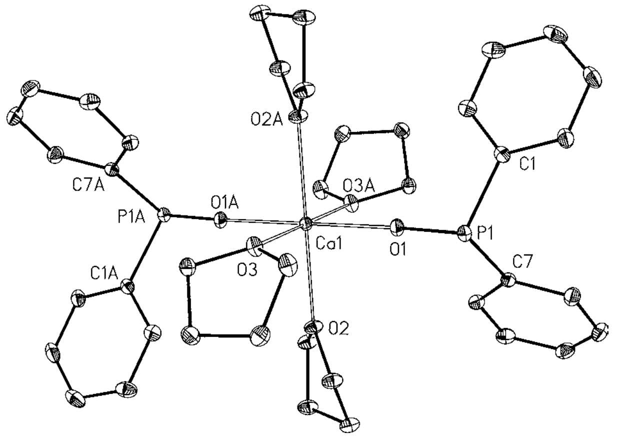


Figure 2. Molecular structure and numbering scheme of $[(\text{thf})_4\text{Ca}(\text{OPPh}_2)_2]$ (**1**). Symmetry related atoms ($-x+1$, $-y-1$, $-z+1$) are marked with the letter "A". The ellipsoids represent a probability of 40%. H atoms are neglected for clarity reasons. Selected bond lengths (pm): Ca1–O1 220.65(9), Ca1–O2 239.20(9), Ca1–O3 238.53(10), O1–P1 155.73(10), P1–C1 185.3(1), P1–C7 185.6(1); angles (deg.): O1–Ca1–O1A 180, O1–Ca1–O2 91.18(3), O1–Ca1–O3 87.71(4), O2–Ca1–O3 93.35(3), O1–P1–C1 104.41(6), O1–P1–C7 103.63(6), C1–P1–C7 98.30(6).

pm represents a characteristic single bond as do the P1–C1 and P1–C7 values (av. 185.5 pm). The rather small Ca1–O distances are a consequence of small intramolecular steric strain. The Ca1–O1 distance to the phosphinite anion is significantly smaller than the values of the $\text{Ca1–O}_{\text{thf}}$ bonds because of enhanced electrostatic attraction.

For the higher oxidized phosphorus-based anions, the root compound diphenylphosphinic acid $[\text{Ph}_2\text{P(O)OH}]$ may serve as a reference.[35] The P–O [152.6(6) pm] and P=O [148.6(6) pm] bond lengths differ only slightly because this acid shows intermolecular asymmetric O–H···O hydrogen bridges leading to O–H distances of 117 and 130 pm. The P–C bond lengths exhibit an average value of 178.6 pm. The P–O as well as P–C bonds are shorter than observed in the phosphinite anion because the higher oxidation state reduces the radius of the phosphorus atom and strengthens the electrostatic attraction to negatively polarized substituents.

Molecular structure and numbering scheme of polymeric $[(\text{dmso})_2\text{Ca}(\text{O}_2\text{PPh}_2)_2]$ (**2**) is displayed in Figure 3. Again, the calcium ions have distorted octahedral coordination spheres with the dmso ligands in a trans arrangement. The diphenylphosphinate anions occupy a bridging position leading to eight-membered $(\text{CaOPO})_2$ rings. These structural units are aligned to a one-dimensional chain-like coordination polymer.

The phosphinate anions exhibit equal P–O bond lengths with an average value of 149.6 pm. These parameters verify a charge delocalization within the OPO fragment leading to a strengthening of the PO bonds. The P–C distances with an average value of 181.7 pm are elongated by 3 pm compared to the diphenylphosphinic acid. Charge delocalization reduces the electrostatic attraction between the phosphinate anion and the metal cation leading to an average Ca–O distance of 231.4 pm which is only slightly smaller than the value of the $\text{Ca–O}_{\text{dmso}}$ bond (av. 235.9 pm).

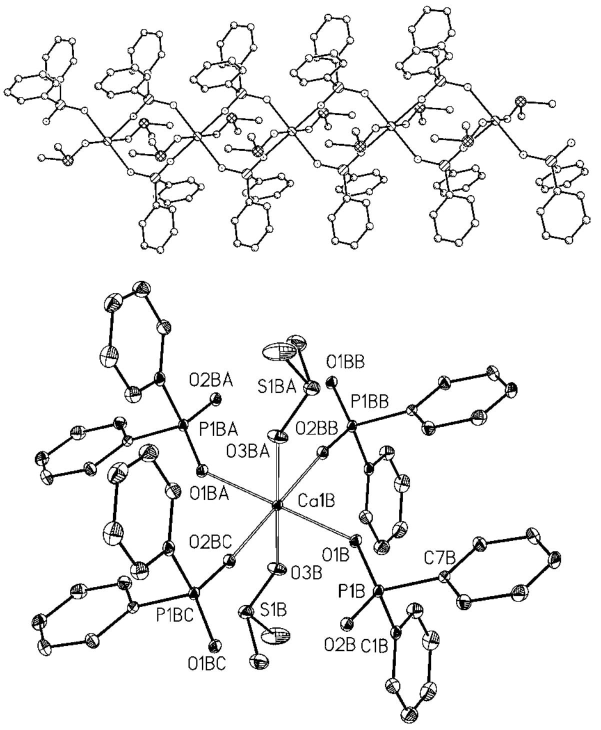


Figure 3. Cut-out of the strand of polymeric $[(\text{dmso})_2\text{Ca}(\text{O}_2\text{PPh}_2)_2]_\infty$ (**2**) (top). The asymmetric unit contains two half molecules A and B. In the cut-out the atoms are shown with arbitrary radii and the hydrogen atoms are neglected for clarity reasons. At the bottom, the distorted octahedral coordination sphere of calcium Ca1B (molecule B) and the numbering scheme is displayed. Selected bond lengths for molecule A [molecule B] (pm): Ca1A–O1A 231.1(2) [235.8(2)], Ca1A–O2A 229.9(2) [228.7(2)], Ca1A–O3A 236.0(2) [235.8(2)], S1A–O3A 153.6(3) [149.7(3)], P1A–O1A 149.6(2) [149.9(2)], P1A–O2A 149.2(2) [149.9(2)], P1A–C1A 181.7(3) [181.7(3)], P1A–C7A 181.6(3) [181.6(3)]; angles (deg.): O1A–P1A–O2A 119.8(1) [119.9(1)], O1A–P1A–C1A 107.5(1) [109.4(1)], O1A–P1A–C7A 108.6(1) [108.6(1)], O2A–P1A–C1A 109.1(2) [108.2(1)], O2A–P1A–C7A 107.6(1) [107.8(1)], C1A–P1A–C7A 103.0(2) [101.4(1)].

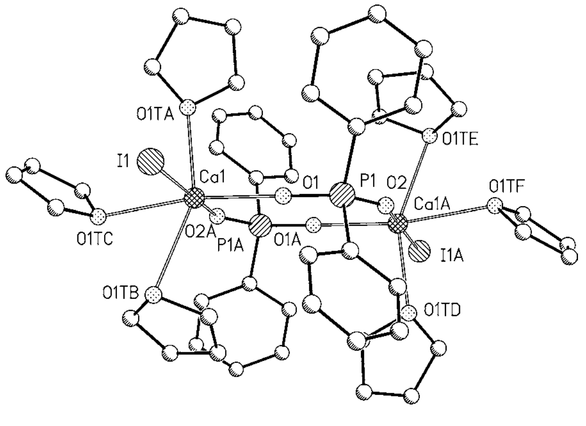


Figure 4. Structural motif of $[(\text{thf})_3\text{Ca}(\text{O}_2\text{PPh}_2)\text{I}]_2$ (**3**) showing the connectivity of the dimer and the formation of an eight-membered $(\text{Ca–O–P–O})_2$ ring with bridging phosphinate anions. The atoms are drawn with arbitrary radii.

The structural motif of $[(\text{thf})_3\text{Ca}(\text{O}_2\text{PPh}_2)\text{I}]_2$ (**3**) is represented in Figure 4. The quality of the structure is rather poor because of poor crystal quality. Recrystallization efforts led to formation of homoleptic insoluble $\text{Ca}(\text{O}_2\text{PPh}_2)_2$ and CaI_2 hampering the collection of high quality single crystals. The central structural motif is again the eight-membered $(\text{CaOPO})_2$ ring with the alkaline earth metal atoms in distorted octahedral environments. The iodide anion is trans positioned to one of the diphenylphosphinate oxygen atoms. Vacant coordination sites are filled with thf ligands in a meridional fashion. A detailed discussion of bond parameters is not recommended but the structure of the diphenylphosphinate anion is very similar to that described for **2**.

Molecular structures and numbering schemes of the calcium derivatives $[(thf)_3Ca(S_2PPh_2)_2]$ (**4**) and $[(thf)_2Ca(Se_2PPh_2)_2]$ (**5**) are displayed in Figures 5 and 6, respectively. Surprisingly, the thf content of **5** is lower than that of **4**; this fact leads to significantly smaller Ca–O$_{thf}$ distances for **5** whereas the intramolecular repulsion of the ligands in **4** lengthens the Ca–O$_{thf}$ bonds. The coordination sphere of the heptacoordinate calcium atom of **4** is a pentagonal bipyramid with the sulfur atoms in the pentagonal plane and two thf ligands in axial positions. Because of different coordination numbers, the calcium–sulfur and calcium–selenium bonds differ only by a rather small value of 6 pm or 2.0%. In complex **5** with a hexacoordinate calcium center in a distorted octahedral coordination sphere the thf ligands show a cis arrangement. This fact leads to the formation of enantiomeric Λ- and Δ-isomers, which crystallize in a non-centrosymmetric space group, however, the Flack parameter of 0.786(7) suggests twinning and crystallization of both isomers.

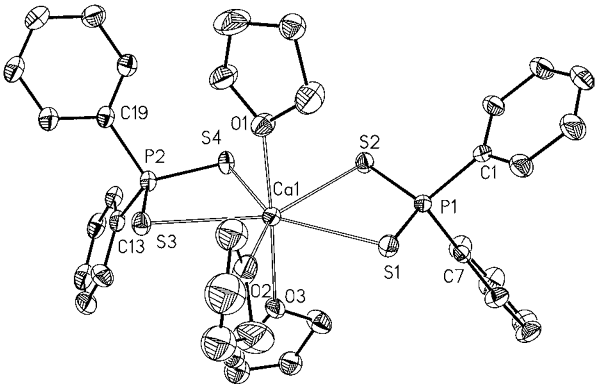


Figure 5. Molecular structure and numbering scheme of $[(thf)_3Ca(S_2PPh_2)_2]$ (**4**). The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons. Selected bond lengths (pm): Ca1–O1 240.7(2), Ca1–O2 243.5(2), Ca1–O3 237.3(2), Ca1–S1 291.18(10), Ca1–S2 292.17(9), Ca1–S3 294.34(10), Ca1–S4 291.03(10), P1–S1 199.6(1), P1–S2 198.8(1), P2–S3 199.4(1), P2–S4 199.3(1), P1–C1 181.6(3), P1–C7 182.2(3), P2–C13 182.8(3), P2–C19 181.4(3); angles (deg.): S1–Ca1–S2 69.80(2), S1–Ca1–S3 149.17(3), S1–Ca1–S4 140.98(3), S2–Ca1–S3 140.87(3), S2–Ca1–S4 71.47(2), S3–Ca1–S4 69.83(2), O1–Ca1–O2 84.48(10), O1–Ca1–O3 172.15(9), O2–Ca1–O3 87.70(10), O2–Ca1–S1 74.62(7), O2–Ca1–S3 74.59(7).

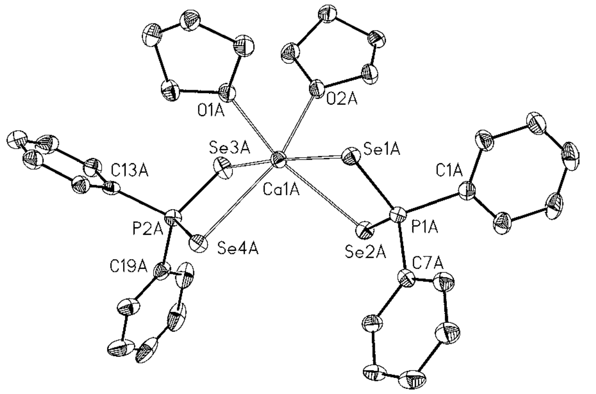


Figure 6. Molecular structure and numbering scheme of $[(thf)_2Ca(Se_2PPh_2)_2]$ (**5**). The asymmetric unit contains two molecules A and B, only molecule A is shown. The ellipsoids represent a probability of 40%, H atoms are not drawn. Selected bond lengths of molecule A [molecule B] (pm): Ca1A–O1A 235.3(4) [232.8(4)], Ca1A–O2A 234.3(4) [233.8(4)], Ca1A–Se1A 298.0(2) [298.8(1)], Ca1A–Se2A 297.6(2) [295.8(2)], Ca1A–Se3A 295.8(2) [298.1(1)], Ca1A–Se4A 299.9(2) [300.1(2)], P1A–Se1A 216.2(2) [215.9(2)], P1A–Se2A 215.3(2) [215.7(2)], P2A–Se3A 215.5(2) [215.5(2)], P2A–Se4A 215.8(2) [216.2(2)], P1A–C1A 182.8(7) [182.7(6)], P1A–C7A 182.0(6) [182.4(5)], P2A–C13A 182.3(7) [181.7(6)], P2A–C19A 181.7(6) [182.4(6)].

The strontium derivatives $[(thf)_3Sr(S_2PPh_2)_2]$ (**6**) and $[(thf)_3Sr(Se_2PPh_2)_2]$ (**7**) both contain hepta-coordinate alkaline earth metal centers, and the Sr–S and Sr–Se bonds differ by 15 pm or 4.7%. The structure of one molecule of **6** is represented in Figure 7. Contrary to the diphenylphosphinate anions which coordinate as bridging ligands to two calcium atoms, the diphenyldithio- and -diselenophosphinate anions always bind as bidentate chelate ligands to one alkaline earth metal atom.

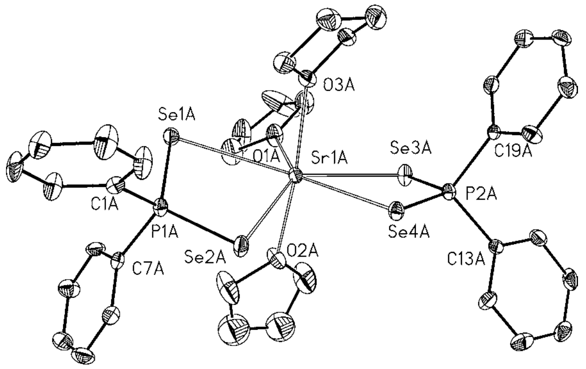


Figure 7. Molecular structure and numbering scheme of $[(thf)_3Sr(Se_2PPh_2)_2]$ (**7**). Only molecule A of three crystallographically independent molecules A, B, and C is displayed. The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons. Selected bond lengths of molecule A [molecule B] {molecule C}: Sr1A–O1A 258.1(4) [255.3(4)] {256.6(4)}, Sr1A–O2A 254.3(4) [253.2(4)] {253.5(4)}, Sr1A–O3A 251.6(4) [257.2(4)] {251.6(4)}, Sr1A–Se1A 318.12(9) [319.34(9)] {319.61(9)}, Sr1A–Se2A 315.95(8) [317.83(8)] {316.83(8)}, Sr1A–Se3A 316.17(9) [325.63(9)] {322.01(9)}, Sr1A–Se4A 318.04(7) [313.81(7)] {316.26(8)}.

To verify this coordination behavior mixed $[(thf)_2Ca(O_2PPh_2)(S_2PPh_2)]_2$ (**8**) was isolated. Molecular structure and numbering scheme of centrosymmetric **8** is displayed in Figure 8. All structural features discussed above are realized in this dimeric molecule. The diphenylphosphinate anions act as bridging ligands leading to a dinuclear complex. The homologous diphenyldithiophosphinate anions appear as terminal chelate ligands. Nevertheless, the environment of the hexa-coordinate calcium atom resembles the coordination sphere of $[(dmso)_2Ca(O_2PPh_2)_2]$ (**2**) with the thf ligands in a trans arrangement. The anionic ligands show similar parameters as in the complexes discussed above.

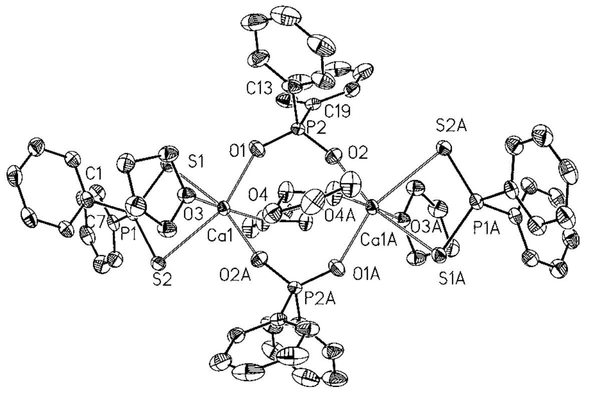


Figure 8. Molecular structure and numbering scheme of $[(thf)_2Ca(O_2PPh_2)(S_2PPh_2)]_2$ (**8**). The ellipsoids represent a probability of 40%, H atoms are not shown for clarity reasons. Symmetry related atoms ($-x+1$, $-y$, $-z$) are marked with the letter "A". Selected bond lengths (pm): Ca1−O1 223.6(3), Ca1−O2A 221.2(3), Ca1−O3 237.4(3), Ca1−O4 236.4(3), Ca1−S1 284.4(1), Ca1−S2 290.9(1), P1−S1 200.5(1), P1−S2 199.4(1), P1−C1 182.8(4), P1−C7 182.1(4), P2−O1 148.8(3), P2−O2 149.7(3), P2−C13 181.4(4), P2−C19 180.4(4); environment of Ca1 (deg.): O1−Ca1−O2A 107.0(1), O1−Ca1−O3 85.6(1), O1−Ca1−O4 91.8(1), O1−Ca1−S1 89.24(8), O1−Ca1−S2 159.72(9), O3−Ca1−O2A 89.4(1), O3−Ca1−O4 174.7(1), O3−Ca1−S1 93.45(8), O3−Ca1−S287.35(7), O4−Ca1−O2A 86.8(1), O4−Ca1−S1 91.20(8), O4−Ca1−S2 96.58(8), S1−Ca1−O2A 163.65(8), S1−Ca1−S2 72.22(3), S2−Ca1−O2A 91.86(8).

■ SUMMARY AND CONCLUSION

The oxidation of $[(thf)_4Ca(PPh_2)_2]$ leads to $[(thf)_4Ca(OPPh_2)_2]$ (**1**) which was prepared via calciation of diphenylphosphane oxide. The phosphinates are insoluble in common organic solvents but in the presence of dmso polymeric $[(dmso)_2Ca(O_2PPh_2)_2]_\infty$ (**2**) was isolated. Homologous derivatives are accessible either via deprotonation of diphenyldithiophosphinic acid or metathetically via reaction of the potassium salts $K(E_2PPh_2)$ (E = O, S, Se) with $[(thf)_4CaI_2]$ or $[(thf)_5SrI_2]$. All complexes with the exception of calcium bis(diphenylphosphinate) are soluble in THF. This anion acts as a bridging ligand leading to polymeric chain-like structures whereas diphenylphosphinite, diphenyldithio-, and -diselenophosphinate anions appear as terminally bound chelate ligands at calcium and strontium. This coordination behavior is maintained in heteroleptic complexes $[(thf)_3Ca(O_2PPh_2)I]_2$ (**3**) and $[(thf)_2Ca(O_2PPh_2)(S_2PPh_2)]_2$ (**8**).

All these alkaline earth metal complexes exhibit mainly ionic bonding situations with small influence of the metal on the structure of the anions. Because of the ionic nature of the $Ph_2PE_2^-$ complexes (E = O, S, Se) charge delocalization is observed within the E-P-E moieties and both chalcogen atoms bind to the same metal atom as chelate ligands (E = S, Se) or in a bridging manner to two metal atoms (E = O). This behavior is characteristic for these ligands as it is also found in complexes of indium(III)[31,36,37] and antimony(III),[36] but the radius of gallium(III) is too small and a coordination number of four is realized by one bidentate ligand and two monodentate phosphinate anions.[36] Contrary to these metal complexes, characteristic single and double bonds were found in covalently bound molecules such as $[Ph_2P(Se)]_2Se$.[38]

The diphenylphosphinite anion shows small bond angles at P suggesting a large p(P) orbital contribution in the P−O and P−C bonds. The diphenylphosphinate anions represent distorted tetrahedrally coordinated phosphorus atoms suggesting sp^3 hybridization. This higher s-orbital contribution and the higher oxidation state of P lead to a significant shortening of the P−C and P−O bonds. Because of the rather small P−O distances electrostatic repulsion between the oxygen atoms enhances the O−P−O angle. Larger P−E bond lengths reduce this intraligand repulsion and smaller E−P−E angles are observed.

An increasing oxidation of the phosphorus atom leads to a high field shift of the ^{31}P NMR resonances. As already studied by Bildstein and Sladky[26] for the lithium salts $LiEPPh_2$ substitution of oxygen by its heavier homologues also leads to a high field shift [$\delta(^{31}P)$ = 88.9 (E = O), 20.7 (S), 6.5 (Se), and −35.7 (Te)]. A comparable observation is true for the phosphinates [$\delta(^{31}P)$ = 17.1 ($Ph_2PO_2^-$), 62 ($Ph_2PS_2^-$), 44 (Ph_2PSSe^-), 23 ($Ph_2PSe_2^-$)]; however, the oxygen-based phosphinate represents an exception because of a different bonding situation. The oxygen-based phosphinates always act as bridging ligands whereas the homologous thio- and selenophosphinates occupy terminal positions. For LiS_2PPh_2 and $ClMgS_2PPh_2$ very similar chemical ^{31}P NMR shifts of $\delta(^{31}P)$ = 59.8 and 59.0, respectively, were observed verifying the small influence of the cations on the anions and emphasizing the ionic nature of all these phosphinite and phosphinate complexes.

■ EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled in an argon atmosphere, deuterated solvents were dried over sodium, degassed, and saturated with argon. The yields given are not optimized. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC 200 MHz, AC 400, or AC 600 spectrometers. Chemical shifts are reported in parts per million and referenced to $SiMe_4$ using the residual signal of the deuterated solvent as internal standard. Starting $[(thf)_4Ca(PPh_2)_2]$,[1,2] $[Ca\{N(SiMe_3)_2\}_2]$, and $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$[39−41] were prepared according to literature procedures.

Synthesis of $[(thf)_4Ca(OPPh_2)_2]$ (1). Diphenylphosphane oxide (0.37 g, 1.83 mmol) was added at −78 °C to a stirred solution of $[Ca\{N(SiMe_3)_2\}_2]$ (0.46 g, 0.91 mmol) in 10 mL of THF. The solution was slowly warmed to room temperature (r.t.) and stirred overnight. Then the volume of the reaction mixture was reduced in vacuo to half of the original volume. Storage at −20 °C yielded 0.465 g of colorless crystals of **1** (0.64 mmol, 69%).

Physical data: Elemental analysis ($C_{40}H_{52}CaO_6P_2$, 730.86): calc.: C 65.73, H 7.17; found: C 65.70, H 7.14. ^1H NMR (400 MHz, 298 K, $[D_8]$THF): δ = 1.77 (thf), 3.63 (thf), 6.98 (2H, t, $^3J_{H,H}$ = 8.4 Hz, *p*-CH), 7.09 (4H, t, $^3J_{H,H}$ = 6.5 Hz, *m*-CH), 7.54 (4H, t, $^3J_{H,H}$ = 6.9 Hz, *o*-CH). $^{13}C\{^1H\}$ NMR (101 MHz, 298 K, $[D_8]$THF): δ = 126.3 (*p*-C), 127.5 (*m*-C, $^3J_{C,P}$ = 3.8 Hz), 129.4 (*o*-C, $^2J_{C,P}$ = 20.5 Hz), 157.0 (*i*-C, $^1J_{C,P}$ = 35.5 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, 298 K, $[D_8]$THF): δ = 83.0 (s).

Synthesis of $[(dmso)_2Ca(O_2PPh_2)_2]$ (2). Diphenylphosphinic acid (0.26 g, 1.19 mmol) was added to a stirred solution of $[Ca\{N(SiMe_3)_2\}_2]$ (0.21 g, 0.59 mmol) in 8 mL of a 1:1 mixture of THF and methanol. The solution was stirred overnight at r.t. A white precipitate formed and was collected by filtration. The solid was suspended in 2 mL of DMSO and stored at r.t. for 3 weeks. This procedure led to formation of a colorless crystals of **2** (0.26 mmol, 71%).

Physical data: M.p above 300 °C. Elemental analysis ($C_{28}H_{32}CaO_6P_2S_2$, 630.68): calc.: C 53.32, H 5.11, S 10.17; found: C 53.14, H 5.04, S 10.15. IR: 1628 w, 1437 w, 1412 w, 1261 vs, 1177 m, 1097 s, 1023 s, 999 w, 954 w, 865 m, 802 vs, 755 w, 723 m, 699 m, 563 m, 540 w.

Synthesis of $[(thf)_3Ca(O_2PPh_2)I]_2$ (3). *Method A.* A suspension of diphenylphosphinic acid (0.58 g, 2.66 mmol) in 15 mL of THF was added to a suspension of KH (0.11 g, 2.66 mmol) in 5 mL of THF and

Table 2. Selected Structural Parameters (Average Values) for the Alkaline Earth Metal Complexes $[(thf)_4Ca(OPPh_2)_2]$ (1), $[(dmso)_2Ca(O_2PPh_2)_2]$ (2), $[(thf)_3Ca(O_2PPh_2)I]_2$ (3), $[(thf)_3Ca(S_2PPh_2)_2]$ (4), $[(thf)_2Ca(Se_2PPh_2)_2]$ (5), $[(thf)_3Sr(S_2PPh_2)_2]$ (6), $[(thf)_3Sr(Se_2PPh_2)_2]$ (7), and $[(thf)_2Ca(O_2PPh_2)(S_2PPh_2)]_2$ (8)[a]

comp.	M	C.N.(M)	E	ligand	M−E	M−O_{thf}	P−E	P−C	E−P−E′	C−P−C′
1	Ca	6	O		220.7	238.9	155.7	185.5		98.3
2	Ca	6	O	A1	230.5	236.0[b]	149.4	181.7	119.8	103.0
				B1	232.3	235.8[b]	149.9	181.7	119.9	101.4
3[c]	Ca	6	O		224.9	253.9	149.3	181.7	117.9	106.2
4	Ca	7	S	A1	291.7	240.5	199.2	181.9	113.8	101.2
				A2	292.7		199.4	182.1	114.4	104.4
5	Ca	6	Se	A1	297.8	234.8	215.8	182.4	114.1	103.6
				A2	297.8		215.7	182.0	114.1	103.2
				B1	297.3	233.3	215.8	182.6	114.0	104.9
				B2	299.1		215.9	182.1	114.3	103.5
6	Sr	7	S	A1	302.8	252.7	199.1	183.1	115.3	101.6
				A2	303.9		199.6	182.5	116.0	105.3
				B1	303.0	255.0	199.5	182.6	115.9	104.4
				B2	302.9		199.7	181.0	115.0	100.7
7	Sr	7	Se	A1	317.0	254.7	215.5	182.4	114.6	104.4
				A2	317.1		215.1	181.6	114.4	104.5
				B1	318.6	255.2	214.8	182.1	114.2	104.5
				B2	319.7		215.6	182.7	114.5	104.4
				C1	318.2	253.9	214.9	182.4	114.2	103.3
				C2	319.1		215.8	182.5	113.8	103.2
8	Ca	6	O	A1	222.4	236.9	149.3	180.9	117.9	105.8
			S	A2	287.6		200.0	182.5	116.0	104.6

[a] The molecules are distinguished by the letters A, B, and C, and the ligands within one molecule are numbered; thus ligand B2 addresses the second ligand of molecule B (M alkaline earth metal, E chalcogen atom, C.N. coordination number of the alkaline earth metal center). [b] Ca−O_{dmso}. [c] Structural motif due to poor crystal quality; the constitution is verified but a detailed structure discussion is impossible.

stirred for 1 h. CaI_2 (0.78 g, 2.65 mmol) was added to this solution, and the reaction mixture was stirred overnight. Insoluble KI was removed by filtration. The volume of the filtrate was reduced under vacuum to one-third of the original volume, and the resulting solution was stored at −25 °C for 1 d yielding 0.95 g of colorless crystals (30%).

Method B. Diphenylphosphinic acid (0.78 g, 3.62 mmol) was added to potassium carbonate K_2CO_3 (0.25 g, 1.81 mmol) in 10 mL of water and heated for 15 min. Then the water was removed by distillation. The residue was dried in vacuo to give 0.90 g of potassium salt (98%) which was dissolved in 10 mL of THF. After addition of calcium iodide (1.05 g, 3.57 mmol) and stirring overnight at r.t. KI was removed by filtration, and the volume of the filtrate was reduced to one-third of its original volume. This concentrated solution was stored in a freezer. After 1 d colorless crystals precipitated and were collected on a cooled frit and dried under reduced pressure (1.5 g, 36%).

Physical Data. Elemental analysis $C_{44}H_{68}Ca_2I_2O_{10}P_2$, 1200.96): Calc.: C 48.00, H 5.71; found: C 47.88, H 5.63. ^1H NMR (400 MHz, 298 K, $[D_8]$THF): δ 1.73 (thf), 3.60 (thf), 7.15 (4H, dt, m-CH), 7.33 (2H, p-CH), 7.66 (4H, o-CH), ^{13}C NMR (150.9 MHz, 298 K, $[D_8]$THF): δ 26.3 (thf), 68.2 (thf), 128.1 (m-C, $^3J_{C,P}$ = 12.5 Hz), 130.4 (p-C), 131.9 (o-C, $^2J_{C,P}$ = 9.4 Hz), 139.8 (*i*-C, $^1J_{C,P}$ = 136.9 Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, 298 K, $[D_8]$THF): δ = +17.1 (s).

Synthesis of $[(thf)_3Ca(S_2PPh_2)_2]$ (4). *Method A.* A THF solution of $KPPh_2$ (0.5 M, 6.6 mL, 3.3 mmol) was added to a suspension of S_8 (0.21 g, 6.6 mmol) in 10 mL of THF and stirred for 6 h at −35 °C. Thereafter the solution was warmed to r.t. and stirred for additional 12 h. Complete conversion to $K(S_2PPh_2)$ was controlled by ^{31}P NMR spectroscopy. CaI_2 (0.48 g, 1.65 mmol) was added to this solution at −78 °C and then the reaction was warmed to r.t. and stirred for 2 h. Precipitated KI was removed by filtration. The volume of the filtrate was reduced to half of the original volume at −25 °C. Cooling of this solution gave colorless crystals of **1** (0.98 g, 80%).

Method B. $Ca\{N(SiMe_3)_2\}_2$ (0.342 g, 0.96 mmol) was dissolved in 18 mL of THF at −78 °C, and 0.48 g (1.92 mmol) of diphenyldithiophosphinic acid in 10 mL of THF was added dropwise. The solution was stirred overnight. Then the volume was reduced to 7 mL. After addition of a few milliliters of pentane and storage of this solution at −25 °C, 0.57 g of colorless crystals formed within 2 weeks (79%).

Physical Data. Mp 254−257 °C (dec.). Elemental analysis ($C_{36}H_{44}CaO_3P_2S_4$, 755.02): calc.: C 57.27, H 5.87, S 16.99; found: C 57.04, H 5.84, S 17.25. IR: 1585 w, 1569 w, 1460 vs, 1377 vs, 1305 s, 1173 m, 1156 m, 1096 s, 1068 w, 1026 s, 999 w, 917 w, 873 m, 744 s, 703 s, 666 m, 653 s, 613 s, 566 vs, 491 m, 483 m. ^1H NMR ($[D_8]$THF, 200.13 MHz): δ 7.28 (m, Ph, m- and p-CH), 8.06 (m, Ph, o-CH), 1.74 and 3.62 (THF). ^{13}C NMR (50.32 MHz, $[D_8]$THF): δ = 143.9 d (C_i, $^1J_{PC}$ = 78.0 Hz); δ = 131.1 d (C_o, $^2J_{PC}$ = 11.5 Hz); δ = 129.8 s (C_p), δ = 127.9 d (C_m, $^3J_{PC}$ = 12.5 Hz), δ = 67.1, 25.2 (THF). $^{31}P\{^1H\}$ NMR ($[D_8]$THF, 81.013 MHz): δ 61.5. MS (EI, *m/z* (%)): 538 (15%) $[Ca(S_2PPh_2)_2]^+$, 289 (100%) $[CaS_2PPh_2]^+$, 249 (10%) $[Ph_2PS_2]^+$, 217 (4%) $[Ph_2PS]^+$, 183 (5%) $[Ph_2P - 2H]^+$.

Synthesis of $[(thf)_2Ca(Se_2PPh_2)_2]$ (5). $[(thf)_4Ca(PPh_2)_2]$ (0.17 g, 0.24 mmol) in 10 mL of THF was added dropwise to a suspension of 0.15 g of Se (1.89 mmol) in 8 mL of THF at −78 °C. The mixture was stirred for 6 h at the same temperature and then warmed to r.t. giving a clear yellow solution. Excess of selenium was removed by filtration. The volume of the solution was reduced to 5 mL, then 4 mL of toluene were added to the filtrate. At −25 °C colorless crystals of **5** precipitated within 3 days (0.17 g, 81%).

Physical Data. Mp 198−202 °C (dec.). Elemental analysis ($C_{32}H_{36}CaO_2P_2Se_4$, 755.02): calc.: C 44.15, H 4.17; found: C 42.68, H 4.44. IR: 1607 w, 1571 w, 1458 vs, 1377 vs, 1305 m, 1261 m, 1180 w, 1154 w, 1089 s, 1067 w, 1026 s, 918 m, 873 m, 800 m, 743 s, 689 s, 618 m, 543 vs, 518 vs, 472 s. ^1H NMR ($[D_8]$THF, 200.13 MHz): δ 7.25 (m, Ph, m- and p-CH), 8.06 (m, Ph, o-CH), 1.74 and 3.62 (THF). ^{13}C NMR (100.65 MHz, $[D_8]$THF): δ = 142 (C_i, very broad); δ = 131.8 d (C_o, $^2J_{PC}$ = 11.6 Hz); δ = 130.0 s (C_p), δ = 127.9 d (C_m $^3J_{PC}$ = 12.5 Hz); δ = 67.1, 25.2 (THF). $^{31}P\{^1H\}$ NMR ($[D_8]$THF, 81.013 MHz): δ 21.8 (s + d satellites, $^1J_{PSe}$ = 574.1 Hz). ^{77}Se NMR ($[D_8]$THF, 76.334 MHz): δ −17.7 (d). MS (EI, *m/z* (%)): 726 (4%)

Table 3. Crystal Data and Refinement Details for the X-ray Structure Determinations of the Compounds 1−8

	1	2	3	4
formula	$C_{40}H_{52}CaO_6P_2$	$C_{28}H_{32}CaO_6P_2S_2$	$C_{40}H_{52}Ca_2I_2O_8P_2$	$C_{36}H_{42}CaO_3P_2S_4$
fw (g mol^{-1})	730.84	630.68	1056.72	752.96
T/°C	−140(2)	−90(2)	−140(2)	−90(2)
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/ Å	9.7050(2)	5.7704(2)	11.2639(5)	20.0027(6)
b/ Å	8.5891(1)	15.4651(8)	19.4276(9)	12.9986(5)
c/ Å	23.5100(6)	16.8331(6)	12.5674(5)	15.7385(5)
α/ deg	90	89.439(3)	90	90
β/ deg	92.052(1)	88.309(3)	101.267(2)	108.126(2)
γ/ deg	90	83.633(2)	90	90
V/ Å^3	1958.47(7)	1492.23(11)	2697.1(2)	3889.0(2)
Z	2	2	2	4
ρ (g cm^{-3})	1.239	1.404	1.301	1.286
μ (cm^{-1})	2.86	4.97	14.54	4.91
measured data	12668	11416	17978	25959
data with $I > 2\sigma(I)$	4052	4328	4081	5751
unique data/R_{int}	4472/0.0246	6791/0.0541	6136/0.0475	8806/0.0582
wR_2 (all data, on F^2)[a]	0.0883	0.1333	0.3986	0.1381
R_1 ($I > 2\sigma(I)$)[a]	0.0329	0.0535	0.1176	0.0522
s[b]	1.112	0.894	1.532	1.018
res. dens./e Å^{-3}	0.298/−0.293	0.391/−0.450	1.314/−1.294	0.690/−0.385
CCDC No.	880401	880402	motif	880403

	5	6	7	8
formula	$C_{32}H_{36}CaO_2P_2Se_4$	$C_{36}H_{44}O_3P_2S_4Sr$	$C_{36}H_{44}O_3P_2Se_4Sr$	$C_{32}H_{36}CaO_4P_2S_2$, C_4H_8O
fw (g mol^{-1})	870.47	802.51	990.11	722.85
T/°C	−90(2)	−90(2)	−90(2)	−90(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1$	$P2_1/n$	$P2_1/n$
a/ Å	8.8990(18)	15.7762(4)	17.2391(3)	12.7135(3)
b/ Å	26.290(5)	13.1205(5)	32.1960(4)	17.4860(4)
c/ Å	15.472(3)	20.0254(6)	21.9626(4)	19.4052(5)
α/ deg	90	90	90	90
β/ deg	103.45(3)	108.406(2)	102.443(1)	100.702(1)
γ/ deg	90	90	90	90
V/ Å^3	3520.5(12)	3933.0(2)	11903.6(3)	4238.90(18)
Z	4	4	12	4
ρ (g cm^{-3})	1.642	1.355	1.657	1.133
μ (cm^{-1})	44.32	16.97	51.41	3.57
measured data	18541	28263	71584	28446
data with I > $2\sigma(I)$	10258	10285	13934	6729
unique data/R_{int}	12241/0.0403	16922/0.0622	26636/0.1144	9650/0.0465
wR_2 (all data, on F^2)[a]	0.0817	0.1136	0.1059	0.2440
R_1 ($I > 2\sigma(I)$)[a]	0.0389	0.0586	0.0580	0.0733
s[b]	1.038	0.948	0.924	1.057
res. dens./e Å^{-3}	0.398/−0.518	0.425/−0.344	1.331/−0.862	1.225/−0.407
Flack-parameter	0.786(7)	0.028(6)		
CCDC No.	880404	880405	880406	880407

[a] Definition of the R indices: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2)]/3$. [b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

$[Ca(Se_2PPh_2)_2]^+$, 383 (20%) $[CaSe_2PPh_2]^+$, 343 (8%) $[Ph_2PSe_2]^+$, 264 (32%) $[Ph_2PSe]^+$, 183 (85%) $[Ph_2P]^+$.

Synthesis of $[(thf)_3Sr(S_2PPh_2)_2]$ (6). A 0.5 M solution of $KPPh_2$ (2.76 mL, 1.38 mmol) in THF was added to a suspension of S_8 (0.09 g, 2.76 mmol) in 10 mL of THF and stirred for 6 h under an argon atmosphere at −35 °C. Then the solution was stirred overnight at r.t. $[(thf)_5SrI_2]$ (0.483 g, 0.688 mmol) was added to this solution at −35 °C. Thereafter the reaction mixture was warmed to r.t. and stirred for 2 h. The precipitate (KI) was removed by filtration. The volume of the filtrate was reduced to half of the original volume and then 3 mL of toluene were added. At −25 °C 0.39 g of colorless crystals of **6** formed and were collected after 24 h (78%).

Physical Data. Mp 107−110 °C (dec.). Elemental analysis ($C_{36}H_{44}SrO_3P_2S_4$, 802.56): calc.: C 53.88, H 5.53, S 15.98; found: C 53.04, H 5.48, S 15.87. IR: 1634 w, 1457 vs, 1377 vs, 1305 s, 1173 m, 1156 m, 1096 s, 1068 w, 1026 s, 998 w, 917 w, 874 m, 745 s, 721 w, 702 s, 662 m, 650 s, 612 s, 562 vs, 491 m, 482 m. ^{1}H NMR ([D_8]THF, 200.13 MHz): δ 7.25 (m, Ph, m- and p-CH), 8.02 (m, Ph, o-CH), 1.74 and 3.62 (THF). ^{13}C NMR (50.32 MHz, [D_8]THF): δ = 144.2 d (C_i, $^1J_{PC}$ = 79.2 Hz); δ = 131.1 d (C_o, $^2J_{PC}$ = 11.5 Hz); δ = 129.8 s (C_p), δ

= 127.9 d (C_m, $^3J_{PC}$ = 12.6 Hz); δ = 67.1, 25.2 (THF). $^{31}P\{^1H\}$ NMR ([D_8]THF, 81.013 MHz): δ 61.5. MS (EI, m/z (%)): 586 (36%) $[Sr(S_2PPh_2)_2]^+$, 554 (48%) $[Sr(S_2PPh_2)(SPPh_2)]^+$, 337 (60%) $[SrS_2PPh_2]^+$, 249 (4%) $[Ph_2PS_2]^+$, 217 (64%) $[Ph_2PS]^+$, 183 (100%) $[Ph_2P - 2H]^+$.

Synthesis of $[(thf)_3Sr(Se_2PPh_2)_2]$ (7). A 0.5 M solution of $KPPh_2$ (2.41 mL, 1.21 mmol) in THF was added to a suspension of Se (0.19 g, 2.42 mmol) in 10 mL of THF and stirred for 6 h under an argon atmosphere at −35 °C and then at r.t. overnight. $[(thf)_5SrI_2]$ (0.423 g, 0.603 mmol) was added to this solution at −35 °C, and then the reaction mixture was warmed to r.t. and stirred for additional 2 h. The solution was filtered to remove precipitated KI. The volume of the filtrate was reduced to half of the original volume. Addition of 3 mL of hexane and storage at −25 °C afforded 0.49 g of colorless crystals of 7 within 3 days (82%).

Physical Data. Mp 118−121 °C (dec.). Elemental analysis ($C_{36}H_{44}SrO_3P_2Se_4$, 990.14): calc.: C 43.67, H 4.48; found: C 42.40, H 4.12. IR: 1608 w, 1571 w, 1456 vs, 1378 vs, 1341 w, 1304 s, 1177 m, 1156 w, 1091 s, 1067 w, 1030 s, 998 w, 918 m, 876 m, 746 s, 689 s, 618 m, 538 m, 516 vs, 467 s. ^1H NMR ([D_8]THF, 25 °C): δ 7.23 (m, Ph, m- and p-CH), 8.03 (m, Ph, o-CH), 1.74 and 3.62 (THF). ^{13}C NMR (50.32 MHz, [D_8]THF): δ = 142.0 d (C_i, $^1J_{PC}$ = 61.4 Hz); δ = 131.8 d (C_o, $^2J_{PC}$ = 11.9 Hz); δ = 129.9 s (C_p), δ = 127.8 d (C_m $^3J_{PC}$ = 12.5 Hz); δ = 67.1, 25.2 (THF). $^{31}P\{^1H\}$ NMR ([D_8]THF, 81.013 MHz): δ 22.4 (s + d satellites, $^1J_{PSe}$ = 633.6 Hz). ^{77}Se NMR ([D_8]THF, 76.334 MHz): δ −15.9 (d). MS (EI, m/z %): 774 (8%) $[Sr(Se_2PPh_2)_2]^+$, 433 (20%) $[SrSe_2PPh_2]^+$, 343 (6%) $[Ph_2PSe_2]^+$, 264 (34%) $[Ph_2PSe]^+$, 183 (6%) $[Ph_2P - 2H]^+$.

X-ray Structure Determination. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo−K_α radiation. Data was corrected for Lorentz and polarization effects but not for absorption effects.[42,43]

The structures were solved by direct methods (SHELXS[44]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[44]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically.[44] Crystallographic data as well as structure solution and refinement details are summarized in Tables 2 and 3. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-880401 for **1**, CCDC-880402 for **2**, CCDC-880403 for **4**, CCDC-880404 for **5**, CCDC-880405 for **6**, CCDC-880406 for **7**, and CCDC-880407 for **8**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

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Notes

The authors declare no competing financial interest.

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