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Parallels between the Chemistry of Calcium(II) and Ytterbium(II). Synthesis and Crystal Structure of a Calcium Alkoxo-Phosphide Cuboidal Complex

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Metathesis between CaI_2 and $K[P\{CH(SiMe_3)_2\}(C_6H_4\text{-}2\text{-}OMe)]$ in THF yields the alkoxo-phosphide complex $[Ca\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}O)\}(THF)]_4\cdot 4THF$ (**2**) via a ligand cleavage reaction involving the migration of a methyl group from oxygen to phosphorus. X-ray crystallography shows that **2** contains a Ca_4O_4 cuboidal core with μ_2-phosphide groups bridging four of the faces of the cuboid.

Introduction

Complexes of the group 2 elements with P-donor ligands are expected to be disfavored due to the mismatch between the hard cation and the soft donor ligand. However, over the past few years the synthesis and structural characterization of several (di)organophosphide and phosphinediide complexes of the group 2 metals have been reported, including examples containing each of the accessible elements of the group (i.e., excluding radium).[1] The large size of the heavier group 2 ions (Ca^{2+}, Sr^{2+}, Ba^{2+}) has the consequence that solvation and/or aggregation of these complexes is common. Hence, alkaline earth metal phosphide complexes are typically solvated monomers of the form $[Ae(PR_2)_2L_n]$, although dimeric (e.g., $[\{(Me_2Pr^iSi)_2P\}(THF)_2Ba\{\mu\text{-}P(SiMe_2Pr^i)_2\}]_2)$,[1e] trimeric (e.g., $[[\{(Me_3Si)_2P\}Mg\{\mu\text{-}P(SiMe_3)_2\}_2]_2Mg]$),[1j] and even hexameric complexes (e.g., $[Mg\{P(SiBu^t{}_3)\}]_6)$[1m] have been reported; partial hydrolysis of $[Sr\{P(SiMe_3)_2\}_2(THF)_4]$ yields the oxo-centered cluster $[Sr_4(\mu_4\text{-}O)\{\mu_2\text{-}P(SiMe_3)_2\}_6]$,[1f] and several mixed metal alkaline earth−tin heterometallic clusters have been isolated.[1n,2]

The chemistry of the three lanthanide elements (Eu, Sm, Yb) that may be routinely isolated in the +2 oxidation state exhibits strong similarities to that of the group 2 ions since they are all hard, relatively nonpolarizable, oxophilic cations with a +2 charge.[3,4] In some cases the ionic radii of a group 2 ion is very close to that of a lanthanide(II) ion: according to Shannon, the ionic radii of Ca^{2+} and Yb^{2+} differ by only 0.02 Å, while the ionic radii of Sr^{2+} and either Eu^{2+} or Sm^{2+} differ by just 0.01−0.02 Å.[5] This often leads to striking similarities in the structures and reactions of lanthanide(II) and group 2 complexes. For example, all of the metallocene complexes $Cp^*{}_2M$ (M = Ca, Sr, Ba, Eu, Sm, Yb; Cp* = pentamethylcyclopentadienyl) are bent in both the gas phase and the solid state; the ring centroid−M−ring centroid bending angles of the complexes $Cp^*{}_2Ca$ and $Cp^*{}_2Yb$ determined by gas-phase electron diffraction are very similar, at 154(3)° and 158(4)°, respectively.[6] In the present context it may be noted that the Sm(II) complex $[(THF)_3Sm\{\mu\text{-}P(SiMe_3)_2\}_3Sm\{P(SiMe_3)_2\}]$[7] adopts an essentially identical structure to the Sr(II) complex $[(THF)_3Sr\{\mu\text{-}P(SiMe_3)_2\}_3Sr\{P(SiMe_3)_2\}]$.[1c]

We recently reported that ytterbium(II) iodide underwent a novel reaction with the potassium salt of a potentially chelating, sterically demanding phosphide ligand, $[K\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}OMe)\}]$, to give a highly unusual ytterbium(II) alkoxo-phosphide cluster $[Yb\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}O)\}(THF)]_4\cdot 4Et_2O$ (**1**).[8] The similarity sometimes observed between the chemistry of Yb(II) and Ca(II) prompted us to investigate the reaction between the same potassium phosphide and CaI_2. We herein describe this reaction and the crystal structure of the resulting calcium complex.

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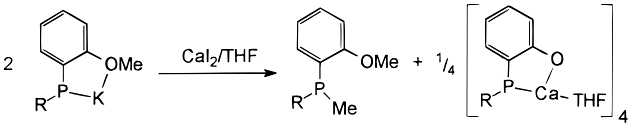
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2[a]

Ca(1)−O(1)	2.3991(13)	Ca(1)−O(1A)	2.3660(12)	Ca(1)−O(1B)	2.3661(12)
Ca(1)−O(2)	2.3874(14)	Ca(1)−P(1)	2.9612(6)	Ca(1)−P(1B)	2.9695(7)
C(1)−P(1)	1.8741(18)	C(1)−Si(1)	1.879(2)	C(1)−Si(2)	1.865(2)
P(1)−C(8)	1.8226(19)	C(13)−O(1)	1.374(2)		

Ca(1A)−O(1)−Ca(1B)	108.37(4)	Ca(1)−O(1)−Ca(1B)	95.59(4)
Ca(1)−O(1)−Ca(1A)	95.58(4)	O(1A)−Ca(1)−O(1B)	71.49(4)
O(1)−Ca(1)−O(1A)	81.49(5)	O(1)−Ca(1)−O(1B)	81.48(5)
O(1)−Ca(1)−O(2)	173.71(5)	P(1B)−Ca(1)−O(1)	78.36(3)
P(1)−Ca(1)−O(1)	64.03(3)	P(1)−Ca(1)−O(2)	115.62(4)
P(1B)−Ca(1)−O(2)	97.74(4)	O(1A)−Ca(1)−O(2)	104.70(5)
O(1B)−Ca(1)−O(2)	101.36(5)	P(1)−Ca(1)−P(1B)	126.193(13)
Ca(1)−P(1)−Ca(1A)	73.045(18)		

[a] Symmetry operators for this table and Figure 1. A: $1-y, x, -z$; B: $y, 1-x, -z$; C: $1-x, 1-y, z$.

Scheme 1



Results and Discussion

The reaction between calcium diiodide and 2 equiv of $[K\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}OMe)\}]$ in ether/THF solution gives the tetrameric alkoxo-phosphide cluster $[Ca\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}O)\}(THF)]_4\cdot 4THF$ (**2**) in high yield, according to Scheme 1. Complex **2** is insoluble in hydrocarbons and only sparingly soluble in ether solvents, but may be obtained as pale yellow needles by recrystallization from hot THF.

X-ray crystallography shows that **2** consists of a tetrameric cluster with a cuboidal Ca_4O_4 core. The molecular structure of **2** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. Each alkoxo-phosphide ligand bridges three calcium centers via its alkoxo oxygen atom at alternate corners of the Ca_4O_4 cuboid. Additionally, four of the faces of the cube are μ_2-bridged by the phosphido P atoms of the ligands. Each Ca atom is further coordinated by the oxygen atom of one molecule of THF (showing 2-fold disorder), giving each Ca an overall coordination number of 6. The overall structure of **2** therefore greatly resembles that of the analogous ytterbium(II) cluster **1**, and bond lengths and angles within the two clusters are remarkably similar (see below).

The Ca−P−Ca bridges are essentially symmetrical, with Ca−P distances of 2.9612(6) and 2.9695(7) Å; these distances lie within the range of the few Ca−P distances reported previously. For example, the Ca−P(terminal) distances in $[Ca\{P(SiMe_3)_2\}_2(TMTA)_2]$[1b] and $[Ca\{PH(SiPr^i{}_3)\}_2(THF)_4]$[1a] are 2.994(2) and 2.947(1) Å, respectively (TMTA = 1,3,5-trimethyl-1,3,5-triazinane), and the Ca−P distances in the phosphido-bridged complex $[Ca\{\mu\text{-}PH(SiPr^i{}_3)\}\{N(SiMe_3)_2\}(DME)]_2$ are 3.000(1) and 3.005(1) Å;[1a] in the heterometallic complex $[\{(Me_3Si)_2N\}Ca\{\mu\text{-}P(SiMe_3)_2\}_2Ca\{\mu\text{-}P(SiMe_3)_2\}_2Sn\{P(SiMe_3)_2\}]$ the Ca−P distances range from 2.880(2) to 2.900(2) Å.[2a]

The Ca−O(alkoxide) distances in **2** are 2.3660(12) and 2.3661(12) Å in the open faces of the cluster [Ca−O(1A)/Ca−O(1B)] and 2.3991(13) Å on the remaining edges of the faces bridged by phosphorus [Ca−O(1)]. These are similar to the internal Ca−O distances reported for the cuboidal mixed alkoxide-β-diketonate cluster $[Ca(tmhd)(\mu_3\text{-}OEt)(EtOH)]_4$ [Ca−O = 2.328(6)−2.367(6) Å][9a] and for the oxo-alkoxide double cuboidal cluster $[Ca_6(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_4(EtOH)_4]\cdot 14EtOH$ [Ca−O = 2.312−2.529(5) Å] (tmhd = tetramethylheptanedionate).[9b]

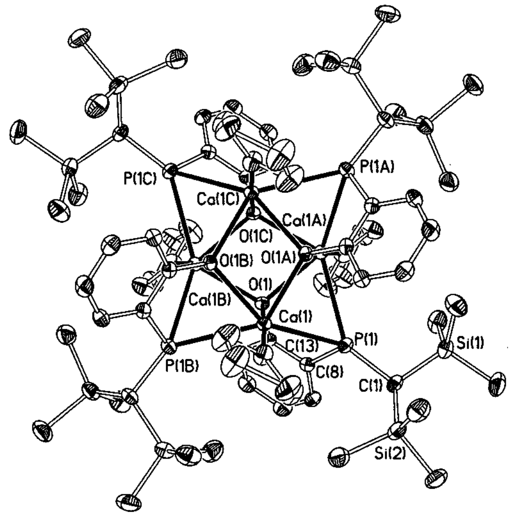


Figure 1. Crystal structure of **2** with 40% probability ellipsoids and with H atoms and one THF disorder component omitted for clarity.

The molecule as a whole possesses exact crystallographic S_4 symmetry. The two faces of the cuboidal core that are not bridged by phosphorus are essentially planar, parallel rhombuses, which are twisted through an angle of 90° with respect to each other. The internal Ca−O−Ca and O−Ca−O angles within these rhombuses are 108.37(4)° and 71.49(4)°, respectively, while the Ca−O−Ca and O−Ca−O angles in the four phosphorus-bridged faces are 95.58(4)° and 81.48(5)°, respectively. The calcium atoms are six-coordinate with a geometry that is best described as pentagonal bipyramidal, with one equatorial coordination site vacant and with THF and one μ_3-oxygen in the axial positions. Coordination by additional solvent at this vacant site is prevented by the sterically demanding $CH(SiMe_3)_2$ groups of the adjacent ligands.

Complex **2** is only the third crystallographically characterized cuboidal complex of calcium to be reported,[9] although a number of magnesium and barium alkoxides and mixed metal alkaline earth oxo-alkoxides adopt this structural motif.[10,11] The tetrameric clusters

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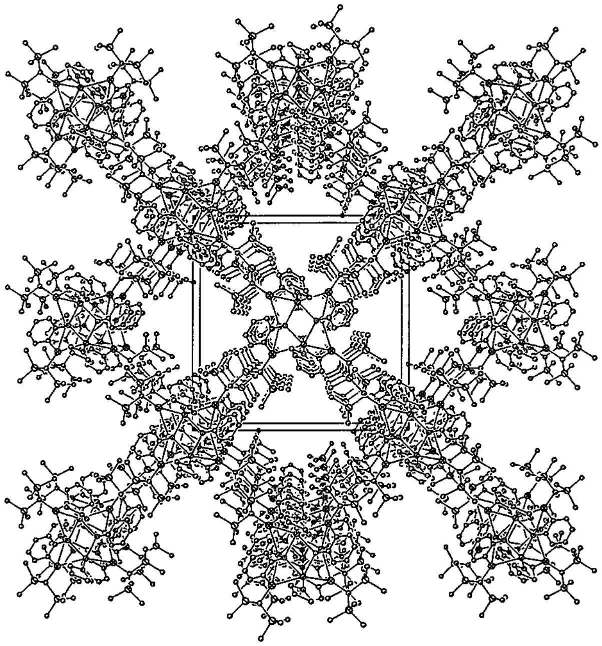

Figure 2. Packing of the molecules in **2** showing the large cavities containing disordered solvent (omitted for clarity). View along the *c* axis.

Table 2. Bond Lengths (Å) and Angles (deg) within the Core of 2 and 1

	2 (M = Ca)	**1** (M = Yb)
M−P(1)	2.9612(6)	2.9604(13)
M−P(1B)	2.9695(7)	2.9601(12)
M−O(1)	2.3991(13)	2.459(3)
M−O(1A)	2.3660(12)	2.400(3)
M−O(1B)	2.3661(12)	2.404(3)
M−O(1A)−M′	108.37(4)	110.07(10)
O(1A)−M−O(1B)	71.49(4)	69.75(10)
M−P(1)−M′	73.045(18)	75.08(3)

pack in the crystal in such a way that there are large columnar cavities aligned along the *c*-axis (Figure 2). These cavities are filled with four disordered molecules of THF per molecule of cluster.

Comparison of the bond lengths and angles within **1** and **2** is quite instructive (Table 2). It can clearly be seen that bond lengths and angles within the cores of these two complexes are remarkably similar. In general the M−P distances are slightly longer and the M−O distances are slightly shorter (by ∼0.04−0.06 Å) in **2** compared to **1**. These marginal differences serve to illustrate the strong parallels between Ca(II) and Yb(II).

The $^{31}P\{^1H\}$ NMR spectrum of **2** in THF-d_8 exhibits a single resonance at −82.7 ppm, while the ^1H and ^{13}C NMR spectra show only a single set of signals for the ligands. This suggests that, like **1**, a highly symmetrical, possibly oligomeric, structure is maintained by **2** in solution. Unfortunately, the very limited solubility of **2** prevented elucidation of its aggregation state in solution by cryoscopy. While the coordinated THF is apparently retained, the lattice solvent is readily lost under vacuum and is not observed by NMR spectroscopy or elemental analyses.

The formation of **2** is accompanied by a ligand cleavage reaction and the elimination of the tertiary phosphine $MeP\{CH(SiMe_3)_2\}(C_6H_4\text{-}2\text{-}OMe)$ (**3**). This side product was isolated and identified spectroscopically.[8] The reaction therefore involves the migration of a methyl group from oxygen on one ligand to phosphorus on another. Thus, the formation of **2** exactly parallels the reaction observed between YbI_2 and $[K\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}OMe)\}]$.[8]

Demethylation of anisole-substituted tertiary phosphines to give phenoxy-phosphine ligands has previously been noted in complexes with the soft metal centers Rh(II), Ir(II), and Pt(II).[12] These reactions typically require relatively high temperatures or are accompanied by redox at the metal center. For example, heating the complex $[PtCl_2\{PPh_2(C_6H_4\text{-}2\text{-}OMe)\}_2]$ to 270 °C gives the phenoxy-phosphine complex $[Pt\{PPh_2(C_6H_4\text{-}2\text{-}O)\}_2]$ and chloromethane,[12a] while the reaction of $IrCl_6^{3-}$ with $t\text{Bu}_2P(C_6H_4\text{-}2\text{-}OMe)$ gives the Ir(I) complex $[Ir(CO)\{P(t\text{Bu})_2(C_6H_4\text{-}2\text{-}O)\}\{P(t\text{Bu})_2(C_6H_4\text{-}2\text{-}OH)\}]$, which, upon exposure to air, gives the Ir(II) complex $[Ir\{P(t\text{Bu})_2(C_6H_4\text{-}2\text{-}O)\}_2]$ with the elimination of CO_2.[12b,c] More recently the Ni(II)-mediated desilylation of a silyl ether-substituted tertiary phosphine has been reported.[12d] In contrast, the formation of both **1** and **2** occurs rapidly at room temperature, and in both cases the demethylation reaction is mediated by a hard metal center, Yb(II) and Ca(II), respectively. The reactions leading to the formation of **1** and **2** are also the first such demethylation reactions to generate a dianionic, alkoxo-phosphide ligand, rather than an alkoxo-functionalized tertiary phosphine.

Although certain complexes of group 2 ions are known to cleave the C−O bonds of alkyl ethers, mechanistic details of these reactions are often unclear.[13] For example, the magnesium amide $Mg\{N(SiMe_3)_2\}_2$ reacts with a range of crown ethers to give magnesium alkoxide species, via an unspecified route.[13a] In contrast to the reactions giving **1** and **2**, cleavage of ethyl ethers by the bulky alkyl complex $Ca\{C(SiMe_3)_3\}_2$ proceeds by proton transfer from a methyl group of the ether to an alkyl ligand, according to eq 1.[14]

$$Ca\{C(SiMe_3)_3\}_2 + 2Et_2O \xrightarrow{\text{ether}} Ca(OEt)_2 + 2HC(SiMe_3)_3 + 2CH_2{=}CH_2 \quad (1)$$

The parallel behavior of CaI_2 and YbI_2 toward $[K\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}OMe)\}]$ suggests that it is purely

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the size/charge ratio of the cation that determines whether ligand cleavage takes place; the reaction of the larger SmI_2 with $[K\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}OMe)\}]$ yields the diphosphide complex $[Sm\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}OMe)\}_2(DME)]$ with no ligand cleavage.[15] It would therefore appear that the dominant factor influencing the formation of **1** and **2** is the Lewis acidity of the metal centers.

Conclusions

The reaction of the ether-functionalized phosphide $[K\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}OMe)\}]$ with CaI_2 yields an unusual alkoxo-phosphide complex with a cuboidal Ca_4O_4 core (**2**). This reaction proceeds via C−O cleavage of a phosphide ligand mediated by the calcium center. The work described in this paper highlights the similarities between the chemistry of calcium(II) and ytterbium(II) and suggests that the observed ligand cleavage reaction is dependent upon the Lewis acidity of the metal center.

Further research into the chemistry of sterically demanding, donor-functionalized phosphide complexes of the group 2 elements is currently underway.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or argon. Ether, THF, and light petroleum (bp 40−60 °C) were distilled from potassium or sodium/potassium alloy under an atmosphere of dry nitrogen and stored over a potassium film (with the exception of THF, which was stored over activated 4 Å molecular sieves). Deuterated THF was distilled from potassium and was deoxygenated by three freeze−pump−thaw cycles and stored over activated 4 Å molecular sieves. $K[P\{CH(SiMe_3)_2\}(C_6H_4\text{-}2\text{-}OMe)]$ was prepared according to a previously published procedure.[8] Anhydrous CaI_2 was purchased from Aldrich and used without further purification.

^{31}P NMR spectra were recorded on a Bruker WM300 spectrometer operating at 121.5 MHz, and ^1H and ^{13}C spectra on a JEOL Lambda500 spectrometer, operating at 500 and 125.7 MHz, respectively. ^1H and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane; ^{31}P chemical shifts are quoted relative to external 85% H_3PO_4. Elemental analyses were obtained by Elemental Microanalysis Ltd., Okehampton, U.K.

Preparation of $[Ca\{P(CH[SiMe_3]_2)(C_6H_4\text{-}2\text{-}O)\}(THF)]_4\cdot 4THF$ (2). To a cold (−78 °C) suspension of CaI_2 (0.35 g, 1.19 mmol) in ether (10 mL) was added, dropwise, a solution of $K[P\{CH(SiMe_3)_2\}(C_6H_4\text{-}2\text{-}OMe)]$ (0.60 g, 1.78 mmol) in THF (15 mL). This mixture was allowed to attain room temperature and was stirred for 5 h. The colorless precipitate was removed by filtration, and the filtrate was concentrated to ∼10 mL and cooled to 6 °C for 36 h, after which time the pale yellow needles of **2** were isolated. Single crystals suitable for X-ray crystallography were obtained from a slowly cooled solution of **2** in hot THF. Yield: 0.28 g, 68%. Anal. Calcd for $C_{68}H_{124}Ca_4O_8P_4Si_8$ (molecular formula without lattice solvent): C, 51.73; H, 7.93. Found: C, 51.47; H, 8.06. ^1H NMR (THF-d_8, 313 K): δ 0.13 (s, br 18H, $SiMe_3$), 0.41 (d, $J_{PH} = 4.6$ Hz, 1H, CHP), 1.77 (m, 4H, THF), 3.61 (m, 4H, THF), 6.31 (m, 1H, ArH), 6.44 (m, 1H, ArH), 6.57 (m, 1H, ArH), 6.80 (m, 1H, ArH). $^{13}C\{^1H\}$ NMR (THF-d_8, 313 K): δ 1.65 ($SiMe_3$), 3.11 (d, $J_{PC} = 52.6$ Hz, CHP), 26.32 (THF), 68.16 (THF), 114.41, 120.13, 120.48, 127.13 (Ar; *ipso*-carbons not resolved). ^{31}P NMR (THF-d_8, 320 K): δ −82.7.

Crystal Structure Determination of 2. Data were collected at 160 K on a Bruker AXS SMART CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data: $C_{84}H_{156}Ca_4O_{12}P_4Si_8$, $M = 1867.01$, tetragonal, space group $I\bar{4}$, $a = 20.4587(17)$ Å, $c = 12.6985(15)$ Å, $V = 5315.1(9)$ Å^3, $Z = 2$, $D_{calcd} = 1.167$ g cm^{-3}, $\mu = 0.404$ mm^{-1}, R (F; $F^2 > 2\sigma$) = 0.0320, R_w (F^2; all data) = 0.0626, $S = 0.962$ for 6140 unique, absorption-corrected data and 225 refined parameters; final difference map extremes +0.18 and −0.15 e Å^{-3}. Programs: Bruker AXS SMART (diffractometer control), SAINT (data integration), and SHELXTL (structure solution and refinement).

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Supporting Information Available: For **2** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

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