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Complexes of the Heavier Alkaline Earth Metals Ca, Sr, and Ba with O-Functionalized Phosphanide Ligands

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Metathesis reactions between either SrI_2 or BaI_2 and 2 equiv of the potassium phosphanide $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P]K$ yield, after recrystallization, the complexes $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}OMe)P\}_2M(THF)_n]$ [M = Sr, *n* = 2 (**5**); Ba, *n* = 3 (**6**)]. Similar metathesis reactions between MI_2 and 2 equiv of the more sterically demanding potassium phosphanide $[\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P]K$ yield the chemically isostructural complexes $[\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P\}_2M(THF)_2]$ [M = Ca (**9**), Sr (**7**), Ba (**8**)]. Compounds **5**–**9** have been characterized by multi-element NMR spectroscopy and X-ray crystallography. Complex **9** is thermally unstable and decomposes at room temperature to give the tertiary phosphane $\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P(Me)$ and an unidentified Ca-containing product. Compounds **5** and **6** also decompose at elevated temperatures to give the corresponding tertiary phosphane $\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P(Me)$ and intractable metal-containing products. The decomposition of **5**, **6**, and **9** suggests that these compounds undergo an intramolecular methyl migration from the O atom in one phosphanide ligand to the P atom of an adjacent phosphanide ligand to give species containing dianionic alkoxo-phosphanide ligands.

Introduction

Although, according to Pearson's HSAB theory,[1] bonds between the hard alkaline earth metal cations and soft phosphorus-donor ligands should be disfavored, this can be mitigated by incorporating the phosphorus donor atom into an anionic ligand; a significant number of complexes exhibiting such contacts have now been isolated and structurally characterized.[2–9] In particular, Westerhausen and co-workers have demonstrated that complexes of the ions Mg^{2+}–Ba^{2+} with sterically demanding silyl-substituted phosphanide ligands such as $(Me_3Si)_2P^-$ may be isolated readily.[4] In addition, Westerhausen has isolated a range of alkaline earth metal 1-aza-3-phosphapropenides,[5] phosphanediides,[4a,l,6] and heterometallic phosphanide and phosphanediide clusters.[4j,n,p,7] Alkaline earth metal complexes with formally tertiary phosphane centers are confined to a small number of phosphinomethanides[8] and a tertiary phosphane-substituted aryl complex.[9]

We recently reported the synthesis and molecular structures of a series of monomeric alkaline earth metal phosphanides $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2M(L)]$ [M(L) = Mg,

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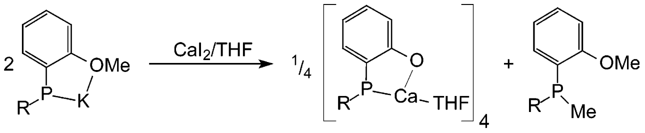
10.1021/ic048978a CCC: $27.50

Scheme 1 [a]



(**1a**) (**2**) (**3a**)

[a] R = $(Me_3Si)_2CH$.

Ca, Sr(THF), Ba(THF)].[10] The Ca, Sr, and Ba complexes are subject to an unusual monomer−dimer equilibrium in solution which is not observed when M = Mg, due to the high Lewis acidity of the Mg^{2+} ion. While these compounds may be routinely synthesized by a metathesis reaction between 2 equiv of the potassium phosphanide $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}CH_2NMe_2)P]K$ and the respective diiodide MI_2, the corresponding reaction between the closely related anisole-functionalized phosphanide $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P]K$ (**1a**) and CaI_2 yields the novel heterocubane cluster $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}O)P\}Ca(THF)]_4.4Et_2O$ (**2**) as the sole calcium-containing product (Scheme 1).[11] Compound **2** is formed via an unusual ligand cleavage reaction which yields the tertiary phosphane $\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P(Me)$ (**3a**) as the only phosphorus-containing side-product. We have also noted previously that the Grignard analogues $[\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}R)P\}MgBu]_2$ [R = H (**4a**), Me (**4b**)] are unstable in THF solution, decomposing to give the corresponding tertiary phosphines **3** and unidentified Mg-containing products.[12]

To understand better this ligand degradation reaction and the factors governing the stabilities of these complexes, we have now studied the synthesis, structures, and solution behavior of a series of related heavier alkaline earth metal phosphanides. We herein report the results of this study and provide evidence to support our contention that the formation of **2** proceeds via an intramolecular methyl transfer reaction involving the putative bis(phosphanide) intermediate $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}OMe)P\}_2Ca(THF)_n]$.

Results and Discussion

A straightforward metathesis reaction between SrI_2 or BaI_2 and 2 equiv of the potassium phosphanide $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P]K$ (**1a**) in THF (eq 1) gives the corresponding alkaline earth metal complexes $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}OMe)P\}_2M(L)]$ [M(L) = $Sr(THF)_2$ (**5**), $Ba(THF)_3$ (**6**)] in good yields as yellow, air- and moisture-sensitive powders, which are soluble in ethereal solvents but only sparingly soluble in light petroleum. Multi-element (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) NMR spectra of **5** and **6** are consistent with these formulations, although the third molecule of THF in **6** appears to be held only weakly; ^1H NMR spectra recorded on samples of **6** exposed to vacuum for 10 min correspond to the formula $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}OMe)P\}_2Ba(THF)_2]$. The sharpness of these spectra indicates that, unlike the corresponding amino-functionalized phosphanide derivatives $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}CH_2NMe_2)P\}_2M(THF)]$ [M = Sr, Ba],[10] compounds **5** and **6** do not exhibit dynamic behavior on the NMR time scale.

Whereas the reaction between CaI_2 and 2 equiv of **1a** results in rapid formation of the heterocubane cluster **2**,[11] reactions between SrI_2 or BaI_2 and **1a** show no evidence for the formation of alkoxo-phosphanide products at room temperature; samples of **5** and **6** are stable both in the solid state and in THF solution for several weeks under ambient conditions. However, ^{31}P NMR spectroscopy indicates that THF solutions of **5** and **6** decompose when heated to 50−60 °C for several hours, yielding the tertiary phosphane **3a** and unidentified phosphorus-containing products. Attempts to isolate the alkaline earth metal-containing products from these thermolysis reactions were unsuccessful.

Metathesis reactions between either SrI_2 or BaI_2 and 2 equivalents of the slightly more sterically hindered potassium phosphanide $[\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P]K$ (**1b**) in THF give the complexes $[\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P\}_2M(THF)_2]$ [M = Sr (**7**), Ba (**8**)] in good yield (eq 1).

$$MI_2 + 2[\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}R)P]K \xrightarrow{THF} [\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}R)P\}_2M(L)] + 2\,KI$$

$$[R = H,\ M(L) = Sr(THF)_2\ (\mathbf{5}),\ Ba(THF)_3\ (\mathbf{6});\quad R = Me,\ M(L) = Sr(THF)_2\ (\mathbf{7}),\ Ba(THF)_2\ (\mathbf{8})] \quad (1)$$

However, in contrast to the facile preparation of **7** and **8**, the synthesis of the calcium analogue $[\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P\}_2Ca(THF)_2]$ (**9**) proved far less straightforward. Attempts to isolate a solid product from the reaction between CaI_2 and 2 equiv of **1b** in THF under the same conditions as those used in the synthesis of **7** and **8** were unsuccessful; ^{31}P and ^1H NMR spectra of the crude reaction mixture indicated the formation of the tertiary phosphane $\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P(Me)$ (**3b**) and at least one other major phosphorus-containing product, which we were unable to isolate. However, when the reaction between CaI_2 and 2 equiv of **1b** in THF was carefully maintained at 0 °C for 8 h, a small quantity of crystalline **9** could be isolated, after a low-temperature workup. Compound **9** is stable at 0 °C for several hours; however, room-temperature solutions of **9** in THF show signs of extensive and rapid decomposition to **3b** and other unidentified phosphorus-containing products. The ^1H and ^{31}P NMR spectra of **9** are consistent with the solid-state structure (see below); these spectra were obtained by carefully maintaining the sample

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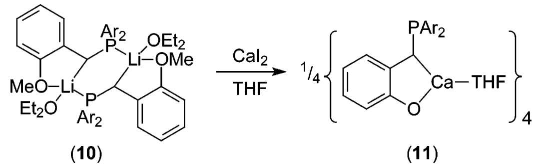
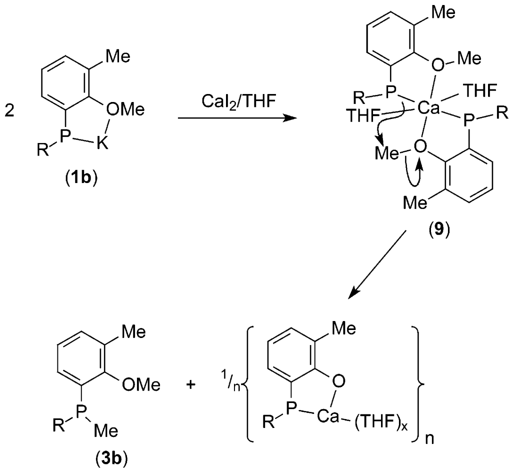
Scheme 2 [a]



[a] Ar = *p*-tolyl.

Scheme 3 [a]



[a] R = $(Me_3Si)_2CH$.

temperature below 0 °C during both sample preparation and spectra accumulation.

Metathesis reactions between MgI_2 and 2 equiv of either **1a** or **1b** also failed to yield simple magnesium phosphanide products under any conditions of temperature and solvent that we attempted. These reactions yield only the tertiary phosphanes **3** and intractable phosphorus-containing species.

The formation of the tertiary phosphanes **3** in these reactions suggests that complexes between the lighter alkaline earth metals Mg and Ca and these anisole-functionalized phosphanides are unstable at room temperature and is consistent with ligand degradation to form a dianionic alkoxo-phosphanide $[\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}O\text{-}3\text{-}R)P]^{2-}$ similar to that observed in the reaction between **1a** and CaI_2.

Müller and Knapp have previously reported that the reaction between the lithium salt of an anisole-substituted phosphinomethanide ligand (**10**) and CaI_2 yields the organocalcium heterocubane cluster (**11**) via an in situ demethylation reaction (Scheme 2).[13] The formation of **11** was attributed to nucleophilic attack by iodide at the carbon atom of a calcium-coordinated methoxy group; the other product(s) from this reaction were not identified.

In the present case, because decomposition occurs when an iodide-free sample of **9** is dissolved in THF, the decomposition of **9** cannot be mediated by nucleophilic attack by halide; instead, we propose that this reaction involves the intramolecular migration of a methyl group from the oxygen atom of one phosphanide ligand in the bis(phosphanide) complex to the phosphorus atom of the other phosphanide ligand (Scheme 3) [i.e., nucleophilic attack by a coordinated phosphorus at an adjacent, coordinated methoxy group].

The rate of decomposition appears to be dependent on both the ionic radius (Lewis acidity) of the metal center and the steric demands of the ligands: whereas decomposition is rapid for Mg and Ca, the corresponding Sr and Ba complexes are stable at room temperature. The extra steric hindrance associated with the presence of a methyl group in the 3-position of the aromatic ring appears to slow the decomposition reaction sufficiently that the bis(phosphanide) intermediate **9** may be isolated, albeit only at low temperatures and in small quantities; in comparison, the formation of **2** is too rapid for the intermediate bis(phosphanide) to be isolated.

There are frequently striking similarities between the chemistry of the heavier group 2 cations Ca(II), Sr(II), and Ba(II) and the divalent lanthanide ions Sm(II), Eu(II), and Yb(II) due to their similar hardness, the ionic nature of the bonding in their complexes, and their comparable ionic radii; the ionic radius of Sr(II) differs from those of Eu(II) and Sm(II) by approximately 0.01 Å, whereas the ionic radii of Yb(II) and Ca(II) differ by 0.02 Å.[14] In accord with this, there is a remarkable similarity between the group 2 phosphanide chemistry described here and that of the corresponding Sm(II) and Yb(II) phosphanides. The Sm(II) complexes $[\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P\}_2Sm(DME)]$ and $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}OMe)P\}_2Sm(DME)(THF)]$[15] and the Sr(II) complexes **5** and **7** are stable both in the solid state and in THF solution at room temperature. In contrast, reactions between 2 equiv of **1a** and either YbI_2 or CaI_2 yield heterocubane clusters.[11,16] Reactions between 2 equiv of **1b** and either CaI_2 or YbI_2 yield unstable bis(phosphanide) complexes which decompose to give tertiary phosphanes and, most likely, complexes of the corresponding alkoxo-phosphanide dianions.

The identities of compounds **5**−**9** were confirmed by X-ray crystallography. Single crystals of **5** and **6** were obtained from methylcyclohexane/THF (10:1) at −30 °C or hexamethyldisiloxane/THF (10:1) at 5 °C, respectively; single crystals of **7**−**9** were obtained from cold diethyl ether. Compounds **5**−**9** crystallize as discrete molecular species in which the phosphanide ligands bind the metal centers via their P and O donors to give five-membered chelate rings; the coordination spheres of the metals are completed by either two (**5**, **7**−**9**) or three (**6**) molecules of THF, depending on the size of the metal cation and the difference in ligand steric bulk associated with the presence of H or Me in the 3-position of the aromatic ring.

The molecular structures of **5** and **6** are shown in Figures 1 and 2, respectively, and details of bond lengths and angles are given in Table 1. The strontium atom in **5** adopts a distorted all-*trans*-octahedral geometry, whereas in **6** the barium atom is seven-coordinate; the geometry about the barium atom may best be described as distorted pentagonal bipyramidal with the sterically hindered phosphorus atoms

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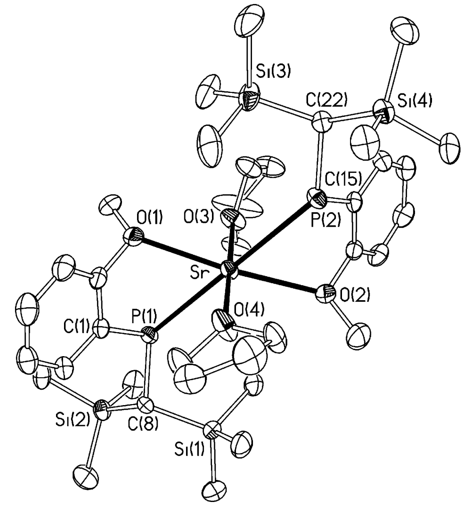

Figure 1. Molecular structure of **5** with 40% probability ellipsoids, and with H atoms and one disorder component omitted for clarity.

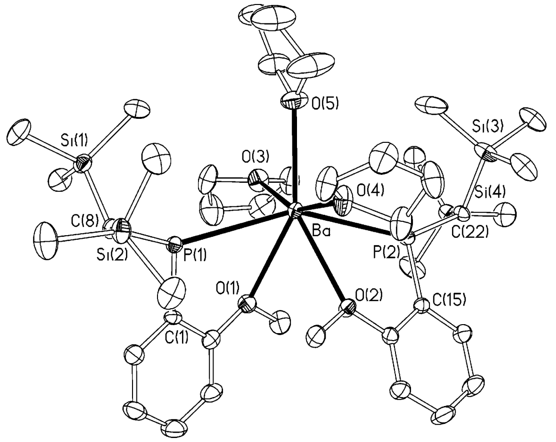

Figure 2. Molecular structure of **6** with 40% probability ellipsoids, and with H atoms omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **5** and **6**

	5		
Sr−O(1)	2.5218(17)	Sr−P(2)	3.0255(7)
Sr−O(2)	2.5504(17)	P(1)−C(8)	1.884(2)
P(1)−C(1)	1.809(2)	Sr−O(3)	2.5393(16)
P(2)−C(22)	1.890(2)	Sr−P(1)	3.0476(6)
Sr−O(4)	2.5333(17)	P(2)−C(15)	1.804(2)
O(1)−Sr−O(4)	95.52(6)	O(1)−Sr−O(3)	84.12(6)
O(4)−Sr−O(3)	179.64(7)	O(1)−Sr−O(2)	169.52(6)
O(4)−Sr−O(2)	94.96(6)	O(3)−Sr−O(2)	85.40(6)
O(1)−Sr−P(2)	117.27(4)	O(4)−Sr−P(2)	87.45(4)
O(3)−Sr−P(2)	92.70(4)	O(2)−Sr−P(2)	63.36(4)
O(1)−Sr−P(1)	63.69(4)	O(4)−Sr−P(1)	95.92(4)
O(3)−Sr−P(1)	83.93(4)	O(2)−Sr−P(1)	114.99(4)
P(2)−Sr−P(1)	176.419(17)	C(1)−P(1)−C(8)	104.52(10)
C(1)−P(1)−Sr	89.16(7)	C(8)−P(1)−Sr	133.33(8)
C(15)−P(2)−C(22)	105.05(10)	C(15)−P(2)−Sr	91.39(7)
C(22)−P(2)−Sr	135.42(8)		
	6		
Ba−O(3)	2.725(2)	P(1)−C(1)	1.808(3)
Ba−O(2)	2.794(2)	P(2)−C(22)	1.886(3)
Ba−P(1)	3.1572(8)	Ba−O(4)	2.750(2)
P(2)−C(15)	1.807(3)	Ba−P(2)	3.1529(8)
Ba−O(5)	2.749(2)	P(1)−C(8)	1.878(3)
Ba−O(1)	2.878(2)		
O(3)−Ba−O(5)	79.80(8)	O(5)−Ba−O(4)	78.68(8)
O(3)−Ba−O(2)	128.59(8)	O(4)−Ba−O(2)	70.70(8)
O(3)−Ba−O(1)	77.15(8)	O(4)−Ba−O(1)	124.20(8)
O(2)−Ba−O(1)	64.25(7)	O(3)−Ba−O(4)	158.24(9)
O(5)−Ba−O(2)	145.37(8)	O(5)−Ba−O(1)	150.17(7)
O(3)−Ba−P(2)	94.30(6)	O(5)−Ba−P(2)	105.79(6)
O(4)−Ba−P(2)	88.44(5)	O(2)−Ba−P(2)	58.62(5)
O(1)−Ba−P(2)	94.63(5)	O(3)−Ba−P(1)	86.33(6)
O(5)−Ba−P(1)	103.15(6)	O(4)−Ba−P(1)	101.69(5)
O(2)−Ba−P(1)	98.61(5)	O(1)−Ba−P(1)	56.90(5)
P(2)−Ba−P(1)	150.70(2)	C(1)−P(1)−C(8)	104.44(15)
C(1)−P(1)−Ba	105.74(11)	C(8)−P(1)−Ba	142.34(11)
C(15)−P(1)−C(22)	105.39(14)	C(15)−P(2)−Ba	107.90(10)
C(22)−P(2)−Ba	146.71(10)		

occupying the axial positions [the oxygen atoms of **6** deviate from the mean BaO_5 plane by between 0.084 and 0.675 Å]. The P−M−O bite angles are 63.69(4)° and 63.36(4)° for **5** and 56.90(5)° and 58.62(5)° for **6**, consistent with the greater ionic radius of Ba than Sr. The Sr−P distances of 3.0255(7) and 3.0476(6) Å in **5** and the Ba−P distances of 3.1572(8) and 3.1529(8) Å in **6** are typical for such contacts.[2,4] For example, the Sr−P distances in $\{(Me_3Si)_2P\}_2Sr(THF)_4$ are 3.035(6) and 3.006(6) Å,[4m] whereas the Ba−P distances in $\{(Me_3Si)_2P\}_2Ba(THF)_4$ are 3.185(6) and 3.190(6) Å.[4f] The Sr−O and Ba−O distances are also similar to previously reported examples.[4]

Compounds **7**−**9** are chemically isostructural, although only **7** and **9** are crystallographically isomorphous, and so only the structure of **7** is shown in Figure 3; details of bond lengths and angles for **7**−**9** are given in Table 2.

All three compounds **7**−**9** crystallize as centrosymmetric molecules having an all-*trans*-octahedral geometry at the metal centers. The phosphanide ligand bite angles are 63.62(9)°, 59.08(3)°, and 66.86(8)° for **7**, **8**, and **9**, respectively, and the M−P distances of 2.897(2), 3.0099(15), and 3.2516(5) Å for M = Ca, Sr, and Ba, respectively, fall, once again, within the range of previously reported M−P distances for these metals.[2,4] The THF ligands in all three compounds are each subject to disorder over two orientations.

Interestingly, despite the difference in ionic radius between Ca^{2+}, Sr^{2+}, and Ba^{2+}, complexes **7**, **8**, and **9** crystallize as chemically isostructural bis-THF adducts. This behavior parallels that of the alkaline earth metal amides $[M\{N(SiMe_3)_2\}_2]_2$ [M = Mg−Ba], which, in the absence of donor solvents, crystallize as isostructural dimers with an

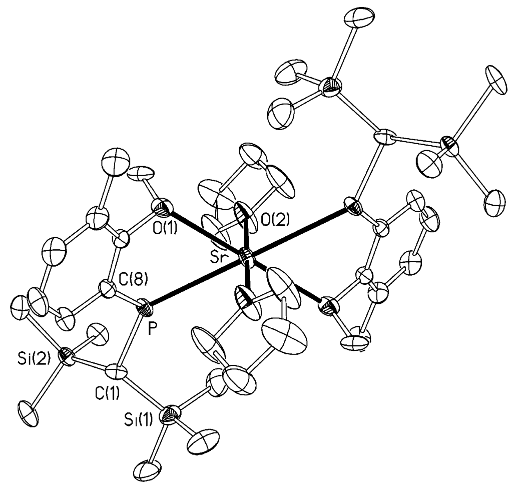

Figure 3. Molecular structure of **7** with 40% probability ellipsoids, and with H atoms and the minor disorder component omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **7**−**9**

	7		
Sr−P	3.0099(15)	P−C(8)	1.803(6)
P−C(1)	1.885(5)	Sr−O(2)	2.538(4)
Sr−O(1)	2.536(4)		
P−Sr−O(1)	63.62(9)	P−Sr−O(2)	86.96(10)
O(1)−Sr−O(2)	92.33(16)	Sr−P−C(8)	93.91(18)
Sr−P−C(1)	141.4(2)	C(1)−P−C(8)	104.9(3)
	8		
Ba−P	3.2516(5)	P−C(9)	1.8882(18)
P−C(1)	1.817(2)	Ba−O(2)	2.7461(16)
Ba−O(1)	2.7103(14)		
P−Ba−O(1)	59.08(3)	P−Ba−O(2)	97.20(4)
O(1)−Ba−O(2)	93.30(5)	Ba−P−C(9)	124.41(6)
Ba−P−C(1)	86.37(6)	C(1)−P−C(9)	104.01(9)
	9		
Ca−P	2.897(2)	P−C(9)	1.812(5)
P−C(1)	1.883(4)	Ca−O(2)	2.412(3)
Ca−O(1)	2.393(3)		
P−Ca−O(1)	66.86(8)	P−Ca−O(2)	87.95(10)
O(1)−Ca−O(2)	93.83(12)	Ca−P−C(8)	104.7(2)
Ca−P−C(1)	143.98(14)	C(1)−P−C(8)	104.7(2)

M_2N_2 core, irrespective of the ionic radius of the metal center.[2]

Experimental Section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Ether, THF, methylcyclohexane, and light petroleum (bp 40−60 °C) were distilled under nitrogen from sodium, potassium, or sodium/potassium alloy. With the exception of THF, which was stored over activated 4 A molecular sieves, all solvents were stored over a potassium film. Hexamethyldisiloxane was distilled under nitrogen from CaH_2 and was stored over activated 4 A molecular sieves. Deuterated THF was distilled from potassium and deoxygenated by three freeze−pump−thaw cycles and was stored over activated 4 A molecular sieves. The compounds $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P]K$ (**1a**) and $[\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P]K$ (**1b**) were prepared by previously published procedures.[11] All other compounds were used as supplied by the manufacturer.

^1H and ^{13}C NMR spectra were recorded on a JEOL Lambda 500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a Bruker Avance 300 spectrometer operating at 300.13 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. ^{31}P NMR spectra were recorded on a Bruker WM300 spectrometer operating at 121.5 MHz, and chemical shifts are quoted relative to external 85% H_3PO_4. Where possible, elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University; due to the exceptional air sensitivity of **6** and **8** and the thermal instability of **9**, satisfactory elemental analyses of these compounds could not be obtained.

Preparation of $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}OMe)P\}_2Sr(THF)_2]$ (5). To a suspension of SrI_2 (0.19 g, 0.56 mmol) in diethyl ether (5 mL) was added, dropwise, a solution of $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P]K$ (0.37 g, 1.10 mmol) in THF (20 mL). This mixture was stirred for 5 h, and solvent was removed in vacuo. The sticky solid was extracted into ether (15 mL) and filtered. Solvent was removed in vacuo from the filtrate to give **5** as a bright yellow solid. Single crystals of **5** were obtained from cold (−30 °C) methylcyclohexane/THF (10:1 mL). Yield: 0.32 g, 69%. Found: C, 51.41; H, 8.27. $C_{36}H_{68}O_4P_2Si_4Sr$ requires: C, 52.29; H, 8.29. ^1H NMR (d_8-THF, 22 °C): δ 0.12 (s, 36H, $SiMe_3$), 0.41 (s, 2H, CHP), 1.76 (m, 8H, THF), 3.61 (m, 8H, THF), 4.01 (s, 6H, OMe), 6.36−6.91 (m, 8H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 22 °C): δ 1.88 ($SiMe_3$), 5.32 (d, J_{PC} = 51.6 Hz, CHP), 26.63 (THF), 56.52 (OMe), 68.50 (THF), 109.25, 116.38, 122.97, 127.16 (Ar), 149.11 (d, J_{PC} = 49.5 Hz, Ar), 156.27 (Ar). $^{31}P\{^1H\}$ NMR (d_8-THF, 22 °C): δ −61.8.

Preparation of $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}OMe)P\}_2Ba(THF)_3]$ (6). To a stirred suspension of BaI_2 (0.50 g, 1.29 mmol) in THF (15 mL) was added, dropwise, a solution of $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P]K$ (0.87 g, 2.85 mmol) in THF (25 mL). This mixture was stirred for 16 h, and then solvent was removed in vacuo. The sticky solid was extracted into ether (20 mL) and filtered, and solvent was removed from the filtrate in vacuo to give a sticky yellow solid, which was washed with hexamethyldisiloxane (2 × 20 mL). Single crystals of **6** were obtained from cold (5 °C) hexamethyldisiloxane/THF (10:1 mL). These crystals rapidly lose THF under vacuum to give a compound of approximate composition from NMR data $[\{([Me_3Si]_2CH)(C_6H_4\text{-}2\text{-}OMe)P\}_2Ba(THF)_2]$. Yield: 0.72 g, 59%. ^1H NMR (d_8-THF, 22 °C): δ 0.11 (s, 36H, $SiMe_3$), 0.42 (s, 2H, CHP), 1.77 (m, ~8H, THF), 3.62 (m, ~8H, THF), 4.00 (s, 6H, OMe), 6.33−6.89 (m, 8H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 22 °C): δ 1.52 ($SiMe_3$), 5.00 (d, J_{PC} = 41.3 Hz, CHP), 26.32 (THF), 56.11 (OMe), 68.17 (THF), 109.45, 115.95, 122.69, 126.82, 130.53 (Ar), 135.55 (d, J_{PC} = 18.6 Hz, Ar). $^{31}P\{^1H\}$ NMR (d_8-THF, 22 °C): δ −44.8.

Preparation of $[\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P\}_2Sr(THF)_2]$ (7). To a suspension of SrI_2 (0.29 g, 0.85 mmol) in THF (5 mL) was added a solution of $[\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P]K$ (0.57 g, 1.69 mmol) in THF (15 mL), and this mixture was stirred for 16 h. Solvent was removed in vacuo, and the solid was extracted into ether and filtered. Solvent was removed from the filtrate in vacuo, and the solid was washed with hexamethyldisiloxane (2 × 15 mL) to give **7** as a yellow powder. Yellow blocks of **7** were obtained from cold (5 °C) ether. Yield: 0.49 g, 67%. Found: C, 53.17; H, 8.52%. $C_{38}H_{72}O_4P_2Si_4Sr$ requires: C, 53.29; H, 8.52. ^1H NMR (d_8-THF, 22 °C): δ 0.14 (s, 36H, $SiMe_3$), 0.32 (s, 2H, CHP), 1.76 (m, 8H, THF), 2.24 (s, 6H, Me), 3.58 (m, 8H, THF), 4.12 (s, 6H, OMe), 6.18−6.71 (m, 6H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 22 °C): δ 1.52 ($SiMe_3$), 3.98 (d, J_{PC} = 61.2 Hz, CHP), 16.13 (Me), 26.25 (THF), 59.24 (OMe), 68.10 (THF), 118.86, 125.77, 127.51, 132.41, 132.50 (Ar), 153.04 (d, J_{PC} = 53.2 Hz, Ar). $^{31}P\{^1H\}$ NMR (d_8-THF, 22 °C): δ −68.3.

Preparation of $[\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P\}_2Ba(THF)_2]$ (8). To a suspension of BaI_2 (0.23 g, 0.59 mmol) in THF (5 mL) was added, dropwise, a solution of $[\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P]K$ (0.42 g, 1.20 mmol) in THF (15 mL). This mixture was allowed to stir for 24 h, and then solvent was removed in vacuo. The solid was extracted into ether (20 mL) and filtered. Solvent was removed from the filtrate in vacuo, and the solid was washed with hexamethyldisiloxane (2 × 15 mL). Yellow needles of **8** were obtained from cold (5 °C) ether. Yield: 0.27 g, 51%. ^1H NMR (d_8-THF, 22 °C): δ 0.10 (s, 36H, $SiMe_3$), 0.27 (s, 2H, CHP), 1.77 (m, 8H, THF), 2.14 (s, 6H, Me), 3.61 (m, 8H, THF), 4.06 (s, 6H, OMe), 6.13−6.71 (m, 6H, ArH). $^{13}C\{^1H\}$ NMR (d_8-THF, 22 °C): δ 1.40 ($SiMe_3$), 3.88 (d, J_{PC} = 48.5 Hz), 16.11 (Me), 26.22 (THF), 59.14 (OMe), 68.11 (THF), 117.46, 125.14, 127.49, 127.84, 129.26, 135.12 (Ar). $^{31}P\{^1H\}$ NMR (d_8-THF, 22 °C): δ −50.3.

Preparation of $[\{([Me_3Si]_2CH)(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P\}_2Ca(THF)_2]$ (9). To a cold (0 °C) suspension of CaI_2 (0.27 g, 0.92 mmol) in THF (10 mL) was added, dropwise, a cold (0 °C) solution of $[\{(Me_3Si)_2CH\}(C_6H_3\text{-}2\text{-}OMe\text{-}3\text{-}Me)P]K$ (0.65 g, 1.85 mmol) in THF (15 mL). The mixture was stirred at this temperature for 8 h, and then solvent was removed in vacuo, while maintaining the temperature below 0 °C. The sticky solid was extracted into cold

Table 3. Crystallographic Data for **5**−**9**

	5	**6**	**7**	**8**	**9**
formula	$C_{36}H68O_4P_2Si_4Sr$	$C_{40}H_{76}BaO_5P_2Si_4$	$C_{38}H_{72}O_4P_2Si_4Sr$	$C_{38}H_{72}BaO_4P_2Si_4$	$C_{38}H_{72}CaO_4P_2Si_4$
fw	826.8	948.7	854.9	904.6	807.3
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	$Pca2_1$	Cc	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	20.7600(16)	14.0099(5)	12.2184(18)	9.4765(6)	12.259(8)
b, Å	12.3207(9)	18.5854(7)	17.818(3)	11.7093(8)	17.560(10)
c, Å	18.0165(14)	20.2378(8)	12.5916(18)	12.9960(8)	12.588(14)
α, deg				107.935(2)	
β, deg		103.401(2)	118.471(2)	100.147(2)	118.796(18)
γ, deg				111.752(2)	
V, Å^3	4608.2(6)	5126.0(3)	2409.7(6)	1203.59(13)	2375(3)
Z	4	4	2	1	2
ρ_{calcd}, g cm^{-3}	1.192	1.229	1.178	1.248	1.129
μ, mm^{-1}	1.38	0.97	1.32	1.02	0.33
reflns collected	36 861	21 230	10 214	10 075	4113
independent reflns (R_{int})	10 542 (0.0358)	11 036 (0.0212)	10 214	5316 (0.0210)	4113
reflns with $F^2 > 2\sigma$	8819	10 701	7400	4800	3827
min., max. transmission	0.596, 0.734	0.700, 0.729	0.779, 0.827	0.579, 0.629	0.878, 0.936
R, R_w $[F^2 > 2\sigma]^a$	0.0291, 0.0580	0.0295, 0.0627	0.0782, 0.1942	0.0282, 0.0700	0.0616, 0.1590
R, R_w (all data)^a	0.0411, 0.0607	0.0309, 0.0631	0.1070, 0.2113	0.0339, 0.0730	0.0763, 0.1721
S^a	0.954	1.145	1.000	1.076	1.072
largest diff. peak and hole, e Å^{-3}	0.41, −0.36	0.69, −1.28	1.58, −1.56	0.73, −0.51	0.96, −0.33
absolute struct. param.^{b}	0.018(4)	0.530(7)			

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2/(\text{no. data} - \text{no. params})]^{1/2}$ for all data. [b] Reference 17.

(0 °C) ether (20 mL) and filtered. The filtrate was concentrated to a volume of ∼5 mL and cooled to −30 °C for 48 h to give **9** as yellow blocks. Yield: 0.20 g, 27%. ^{1}H NMR (d_8-THF, −10 °C): δ 0.12 (s, 36H, $SiMe_3$), 0.28 (s, 2H, CHP), 1.75 (m, 8H, THF), 2.15 (s, 6H, Me), 3.59 (m, 8H, THF), 4.23 (s, 6H, OMe), 6.23−6.74 (m, 6H, ArH). ^{31}P{^{1}H} NMR (d_8-THF, −10 °C): δ −74.2.

Crystal Structure Determinations of 5−9. For **5**−**9**, measurements were made at 150 K on a Bruker AXS SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and narrow (0.3° in ω) frame exposures. For all compounds, cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods or Patterson synthesis and were refined on F^2 values for all unique data. Table 3 gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Disorder was resolved and refined for coordinated THF in **5** and **7**−**9**. Crystals of **7** and **9** were nonmerohedrally twinned, so equivalent data could not be merged before the refinement. Compounds **5** and **6** crystallize in polar space groups; the absolute polarity of **5** was confirmed in the refinement, and **6** was found to be inversion-twinned. Programs were Bruker AXS SMART (control) and SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics.[18]

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Supporting Information Available: For **5**−**9**, 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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