Inorg. Chem. **2007**, *46*, 10410–10415

Inorganic Chemistry
Article

Bis(diphenylphosphido) Derivatives of the Heavier Group 2 Elements

Mark R. Crimmin,[†] Anthony G. M. Barrett,*[,†] Michael S. Hill,*[,†] Peter B. Hitchcock,[‡] and Panayiotis A. Procopiou[§]

Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, U.K., The Chemistry Laboratory, University of Sussex, Falmer, Brighton, East Sussex BN1 9QJ, U.K., and GlaxoSmithKline Medicines Research Centre, Gunnels Wood Road, Stevenage, Hertfordshire SG1 2NY, U.K.

Received August 13, 2007

A number of heavier alkaline-earth (Ae) diphenylphosphides have been prepared by protonolysis of the corresponding bis(trimethylsilyl)amides and completely characterized in the solid state and in solution. Through careful control of the reaction and workup conditions, preparations performed with tetrahydrofuran (THF) as the only donor solvent crystallize as octahedral tetrakis-solvated THF adducts $[Ae(PPh_2)_2(THF)_4]$ when Ae = Ca and Sr. Both structures are similar and contain the two diphenylphosphide substituents in a trans disposition. In contrast, the analogous reaction performed upon the barium amide yielded a one-dimensional polymeric complex containing both five- and six-coordinated Ba centers in which the polymer is propagated via bridging diphenylphosphide units. Further strictly mononuclear derivatives of the Ca and Ba diphenylphosphides may be straightforwardly prepared by treatment of the THF adducts with 18-crown-6. Although the THF-solvated species are evidently labile to loss of solute, solution (diffusion-ordered spectroscopy NMR, THF-d_8) studies indicate that, under catalytically relevant conditions, a similar mononuclear constitution is most likely retained.

Introduction

Although the organometallic and coordination chemistry of the heavier alkaline-earth (Ae) elements (Ae = Ca, Sr, Ba) has been studied for the best part of a century, it is only with the advent of modern analytical and experimental techniques that a well-defined and potentially useful chemistry of this under-represented series has finally begun to emerge. Indeed it is only in the very recent past that Westerhausen has provided the first complete (X-ray) analyses of calcium analogues of magnesium Grignard species, standard workhorse reagents of innumerable organic and organometallic syntheses.[1] It was precisely this deficiency that attracted our own attention to the chemistry of these elements. On the basis of an, admittedly, naive conjecture that well-defined complexes of these redox inactive and electropositive elements would yield a catalytic chemistry comparable to that of the trivalent lanthanide elements, we have recently reported that the heteroleptic calcium amide **1** (Scheme 1) acts as a highly competent reagent for the catalytic intramolecular hydroamination and intermolecular hydrophosphination of unsaturated carbon−carbon bonds.[2] Although we and others have described further chemistries based upon these inexpensive and biologically benign elements,[3] this latter process in particular (Scheme 1) indicates that the elaboration of a distinct (i.e., rather than simply “lanthanide mimetic”) catalytic reaction chemistry for these elements is an exciting and distinctly

---

* To whom correspondence should be addressed. E-mail: m.s.hill@bath.ac.uk.

[†] Imperial College London.

[‡] University of Sussex.

[§] GlaxoSmithKline Medicines Research Centre.

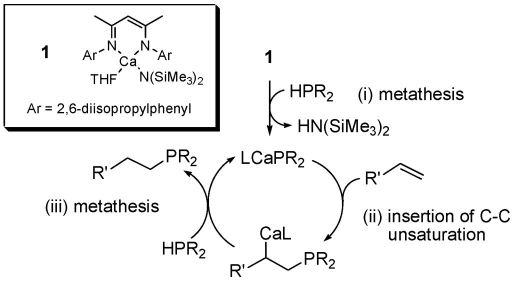
(1) (a) Fischer, R.; Gärtner, M.; Westerhausen, M. *Inorg. Chem. Commun.* **2005**, *8*, 1159. (b) Langer, J.; Fischer, R.; Gärtner, M.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2007**, *10*, 1001. (c) Langer, J.; Görls, H.; Westerhausen, M. *Inorg. Chem. Commun.* **2007**, *10*, 853. (d) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J.; Yu, L.; Reiher, M. *Chem.*−*Eur. J.* **2007**, *13*, 6292. (e) Gärtner, M.; Görls, H.; Westerhausen, M. *Organometallics* **2007**, *26*, 1077. (f) Fischer, R.; Gärtner, Görls, H.; Yu, L.; Reiher, M.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1618. (g) Westerhausen, M.; Gärtner, M.; Fischer, R.; Langer, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 1950. (h) Fischer, R.; Gärtner, M.; Görls, H.; Westerhausen, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 609. (i) Fischer, R.; Gärtner,; M.; Görls, H.; Westerhausen, M. *Organometallics* **2006**, *25*, 3496.

(2) (a) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042. (b) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Hitchcock, P. B.; Procopiou, P. A. *Organometallics*, **2007**, *26*, 2953.

(3) (a) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Procopiou, P. A. *Org. Lett.* **2007**, *9*, 331. (b) Buch, F.; Brettar, J.; Harder, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2741.

10.1021/ic701608x CCC: $37.00

Scheme 1



achievable undertaking.[4] We have reported previously that the homoleptic amide $[\mathrm{Ca\{N(SiMe_3)_2\}_2(THF)_2}]$ (THF = tetrahydrofuran), **2**, displays only a limited capacity for the catalytic (10% loading) hydrophosphination of styrene with diphenylphosphine, taking 36 h at 75 °C to near completion. This reaction is accompanied by the precipitation of a small amount of a yellow insoluble solid, assumed to be the catalytic intermediate $[\mathrm{Ca(PPh_2)_2(THF)_2}]n$ (?).[2b] Although a number of homoleptic heavy group 2 phosphides have been reported previously, these are restricted to PR_2 units containing either sterically demanding (e.g., R = Me_3Si, $^i Pr_3Si$)[5] substituents and/or substituents containing donors capable of intramolecular coordination (e.g., R = C_6H_4-2-CH_2NMe_2, C_6H_4-2-OMe).[6,7] In order to improve our understanding of the initial precatalyst activation step of the catalytic cycle illustrated in Scheme 1 and to enhance our appreciation of the solution molecularity of these simple species, we report here the synthesis and solid- and solution-state characterization of a series of homoleptic group 2 diphenylphosphides, $[\mathrm{Ae(PPh_2)_2(L)}_n]$ (Ae = Ca, Sr, Ba, L = THF or 18-crown-6).

Experimental Section

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of dinitrogen. All solvents were distilled under dinitrogen and dried with conventional drying agents (toluene and THF/sodium benzophenone, hexane/NaK). THF-d_8 was distilled from sodium benzophenone and stored under an inert atmosphere. Diphenylphosphine was purchased from Strem chemicals and used without further purification. The homoleptic amides $[\mathrm{Ae\{N(SiMe_3)_2\}_2(THF)_2}]$ (Ae = Ca, Sr, Ba) were synthesized by the literature procedures.[8] Repeated attempts to acquire satisfactory elemental analysis upon compounds $[\mathrm{Ae(PPh_2)_2(THF)}_n]$ were complicated by not only their highly moisture sensitive nature but also their propensity to decoordinate and lose THF under vacuum. NMR data were collected on either Bruker AV-400 (^{13}C, 100.6 MHz) or AV-500 spectrometers (^{13}C, 125.8 MHz). The molecular volumes for compounds **5** and **6** quoted in Table 5 were calculated by single-point energy calculations (HF, 3-21G) performed upon coordinates provided by the single-crystal X-ray experiments. The use of the "vol" keyword implemented in the *Gaussian 03* suite of programs and an assumption that the tumbling molecules are "spherical" (i.e., volume = $^4/_3\pi r^3$) allowed the calculation of the expected hydrodynamic radii, r_{mono}.[17]

Synthesis of $[\mathrm{Ca(PPh_2)_2(THF)_4}]$, 5. To an unstirred solution of $[\mathrm{Ca\{N(SiMe_3)_2\}_2(THF)_2}]$ (500 mg, 1 mmol) in THF (20 mL) was added diphenylphosphine (327 mg, 1.8 mmol) as a solution in hexane (10 mL). The addition was carried out so as to layer the two solutions, and the reaction was left undisturbed. The reaction

---

(4) Lanthanocene catalysts of the form Cp_2LnX (X = H, $CH(SiMe_3)_2$, (Ln = La, Sm, Y, Lu) have been applied to the intramolecular hydrophosphination/cyclization of a variety of phosphinoalkenes. (a) Douglass, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 1824. (b) Douglass, M. R.; Stern. C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221. (c) Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4630. (d) Motta, A.; Fragalà, I. L.; Marks, T. J. *Organometallics* **2005**, *24*, 4995. Conversely, the intermolecular hydrophosphination of alkenes with such catalysts has not been achieved; rather, a lanthanocene phosphide-mediated polymerization of ethylene has been reported. (e) Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 12764. (f) Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 6311.

(5) (a) Westerhausen, M.; Löw, R.; Schwarz, W. *J. Organomet. Chem.* **1996**, *513*, 213. (b) Westerhausen, M.; Schwarz, W. *J. Organomet. Chem.* **1993**, *463*, 51. (c) Westerhausen, M. *J. Organomet. Chem.* **1994**, *479*, 141. (d) Westerhausen, M.; Hartmann, M.; Schwarz, W. *Inorg. Chem.* **1996**, *35*, 2421. (e) Westerhausen, M.; Lang, G.; Schwarz, W. *Chem. Ber.* **1996**, *129*, 1035. (f) Westerhausen, M.; Digeser, M. H.; Nöth, H.; Knizek, J. *Z. Anorg. Allg. Chem.* **1998**, *624*, 215. (g) Westerhausen, M.; Digeser, M. H. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1237. (h) Hey, E.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 81. (i) Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 304. (j) Westerhausen, M.; Digeser, M. H.; Wieneke, B.; Nöth, H.; Knizek, J. *Eur. J. Inorg. Chem.* **1998**, 517. (k) Westerhausen, M.; Pfitzner, A. *J. Organomet. Chem.* **1995**, *487*, 187. (l) Atwood, J. L.; Bott, S. G.; Jones, R. A.; Koschmieder, S. U. *Chem. Commun.* **1990**, 692. (m) Westerhausen, M.; Krofta, M.; Pfitzner, A. *Inorg. Chem.* **1999**, *38*, 598. (n) Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 903. (o) Westerhausen, M.; Digeser, M. H.; Krofta, M.; Wiberg, N.; Nöth, H.; Knizek, J.; Ponikwar, W.; Seifert, T. *Eur. J. Inorg. Chem.* **1999**, 743. (p) Westerhausen, M.; Birg, C.; Krofta, M.; Mayer, P.; Seifert, T.; Nöth, H.; Pfitzner, A.; Nilges, T.; Deiseroth, H.-J. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1073. (q) Westerhausen, M.; Krofta, M.; Mayer, P. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2307.

(6) (a) Izod, K; Clegg, W.; Liddle, S. T. *Organometallics* **2000**, *19*, 3640. (b) Blair, S; Izod, K; Clegg, W. *Inorg. Chem.* **2002**, *41*, 3886. (c) Blair, S; Izod, K; Clegg, W.; Harrington, R. W. *Inorg. Chem.* **2004**, *43*, 8526.

(7) For examples of mixed-metal Ae−tin heterometallic phosphido clusters, see: (a) Westerhausen, M.; Enzelberger, M. M.; Schwarz, W. *J. Organomet. Chem.* **1995**, *491*, 83. (b) Westerhausen, M.; Hausen, H.-D.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 877. (c) Recent review of heterobimetallic Ae compounds: Westerhausen, R. *Dalton Trans.* **2006**, 4755.

(8) Westerhausen, M. *Inorg. Chem.* **1991**, *30*, 96.

(9) Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(10) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(11) Gärtner, M.; Fischer, R.; Langer, J.; Görls, H.; Walther, D.; Westerhausen, M. *Inorg. Chem.* **2007**, *46*, 5118.

(12) For, a review, see: Westerhausen, M.; Birg, C.; Krofta, M.; Makropoulos, N.; Schneiderbauer, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **2001**, *168*, 173.

(13) Alexander, J. S.; Ruhlandt-Senge, K. *Chem.*−*Eur. J.* **2004**, *10*, 1274.

(14) Crimmin, M. R.; Barrett, A. G. M.; Hill, M. S.; Procopiou, P. A., unpublished results.

(15) Batchelor, R.; Birchall, T. *J. Am. Chem. Soc.* **1982**, *104*, 674.

(16) Pregosin, P. S.; Anil, Kumar, P. G.; Fernández, I. *Chem. Rev.* **2005**, *105*, 2977.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford CT, 2004.

Table 1. Selected Crystallographic and Data Collection Parameters for Compounds **5**−**9**

	5	**6**	**7**	**8**	**9**
chemical formula	$C_{40}H_{52}CaO_4P_2$	$C_{40}H_{52}O_4P_2Sr$	$C_{88}H_{92}Ba_3O_4P_6$	$C_{36}H_{44}CaO_6P_2$	$C_{36}H_{44}BaO_6P_2$
fw	698.84	746.38	1811.46	674.73	771.99
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst size (mm^3)	0.35 × 0.30 × 0.25	0.25 × 0.15 × 0.10	0.25 × 0.2 × 0.15	0.30 × 0.30 × 0.15	0.25 × 0.25 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
a (Å)	10.0836(2)	11.7671(2)	35.9158(6)	11.2163(3)	16.7496(3)
b (Å)	17.6001(4)	16.0751(4)	13.0999(2)	20.0617(4)	12.5808(2)
c (Å)	10.8606(2)	20.9647(5)	21.9088(3)	15.4639(3)	17.1857(3)
β (deg)	101.386(1)	104.127(1)	127.420(1)	90	93.159(1)
Z	2	4	4	4	4
V (Å^3)	1889.52(7)	3845.69(15)	8186.6(2)	3479.66(13)	3615.93(11)
d_c (Mg m^{-3})	1.23	1.29	1.47	1.29	1.42
μ (mm^{-1})	0.29	1.52	1.59	0.32	1.23
θ range (deg)	3.42 to 26.02	3.45 to 26.01	3.40 to 27.48	3.63 to 26.03	3.45 to 26.05
R1, wR2 [$I > 2\sigma(I)$]	0.0375, 0.0983	0.038, 0.079	0.030, 0.070	0.044, 0.104	0.028, 0.060
R1, wR2 all data	0.0447, 0.1025	0.059, 0.087	0.042, 0.077	0.056, 0.110	0.037, 0.064
measd/indep rflns/*R*(int)	28015/3712/0.039	30554/7533/0.048	63294/9331/0.063	31994/3417/0.039	31051/7111/0.039
rflns with $I > 2\sigma(I)$	3264	5905	7524	2855	6103

mixture gradually changed from colorless to bright orange, and after 16 h, the product crystallized as orange needles suitable for X-ray diffraction analysis. Crystallographic analysis of this material revealed the complex $[Ca(PPh_2)_2(THF)_4]$, while isolation by filtration and drying under vacuum gave $[Ca(PPh_2)_2(THF)_2]$ (218 mg, 0.39 mmol, 44%, based upon two THF molecules being removed upon drying) as an orange semicrystalline solid. Mp: 110−115 °C (dec). ^{1}H NMR (THF-d_8, 400 MHz, 298 K): δ 1.77−1.84 (m, 8H), 3.63−3.69 (m, 8H), 6.67 (t, 4H, $J = 7.0$ Hz), 6.90 (m, 8H), 7.40−7.44 (m, 8H). ^{13}C NMR (THF-d_8, 100 MHz, 298 K): δ 26.5, 68.3, 121.2, 127.9 (d, $^3J_{PC} = 3.7$ Hz), 131.4 (d, $^2J_{PC} = 16.2$ Hz), 153.2 (d, $^1J_{PC} = 30.1$). ^{31}P NMR (THF-d_8, 298 K): δ −17.3.

Synthesis of $[Sr(PPh_2)_2(THF)_4]$, 6. To an unstirred solution of $[Sr\{N(SiMe_3)_2\}_2(THF)_2]$ (500 mg, 0.91 mmol) in THF (20 mL) was added diphenylphosphine (337 mg, 1.81 mmol) as a solution in hexane (10 mL). The addition was carried out so as to layer the two solutions, and the reaction was left undisturbed. The reaction gradually changed from colorless to a bright yellow. Cooling to −20 °C resulted in the formation of yellow crystals of $[Sr(PPh_2)_2(THF)_4]$ suitable for X-ray diffraction analysis. Isolation by filtration gave the product as a yellow crystalline solid. Following drying under dynamic vacuum, NMR data were consistent with the isolation of $[Sr(PPh_2)_2(THF)]$ (341 mg, 0.64 mmol, 71%). Mp: 237−239 (dec). ^{1}H NMR (THF-d_8, 400 MHz, 298 K): δ 1.75 (m, 4H), 3.61 (m, 4H), 6.57 (t, 4H, $J = 7.2$ Hz), 6.82 (dd, 8H, $J_{HH} = 7.5$ Hz), 7.36 (dd, 8H, $J_{HH} = 7.5$ and 7.2 Hz). ^{13}C NMR (THF-d_8, 100 MHz, 298 K): δ 26.5, 68.4, 121.0, 128.0 (d, $^3J_{PC} = 5.8$ Hz), 131.0 (d, $^2J_{PC} = 17.2$ Hz), 153.6 (d, $^1J_{PC} = 37.0$ Hz). ^{31}P NMR (THF-d_8, 298 K): δ −11.9.

Synthesis of $[Ba_3(PPh_2)_6(THF)_4]_n$, 7. To an unstirred solution of $[Ba\{N(SiMe_3)_2\}_2(THF)_2]$ (500 mg, 0.91 mmol) in THF (20 mL) was added diphenylphosphine (337 mg, 1.8 mmol) as a solution in hexane (10 mL) so as to layer the two solutions. The reaction was left to sit overnight and yielded a yellow microcrystalline solid. The product was isolated by filtration and recrystallized by redissolving in THF and layering with hexane to give $[Ba_3(PPh_2)_6(THF)_4]_n$ (324 mg, 0.18 mmol, 59%) as a yellow crystalline solid. ^{1}H NMR (THF-d_8, 400 MHz): δ 1.79−1.83 (m, 16H), 3.64−3.66 (m, 16H), 6.60 (m, 12 H), 6.88 (m, 24 H), 7.42 (m, 24H). ^{13}C NMR (THF-d_8, 100 MHz): δ 26.5, 68.4, 120.6, 128.2, 130.7 (d, $^2J_{PC} = 14.9$ Hz), 155.0 (d, $^1J_{PC} = 42.4$ Hz). ^{31}P NMR (THF-d_8): δ +1.6.

Synthesis of $[(18\text{-crown-}6)Ca(PPh_2)_2]$, 8. A mixture of compound **5** (200 mg, 0.29 mmol) and 18-crown-6 (95 mg, 0.36 mmol) was dissolved in THF (10 mL). The solution was stirred for 20 min, left to settle, and then layered with hexane (20 mL). The product crystallized as orange crystals, and isolation by filtration gave $[(18\text{-crown-}6)Ca(PPh_2)_2]$ (45 mg, 0.07 mmol, 23%). Mp: 74−78 °C (dec); ^{1}H NMR (THF-d_8, 400 MHz, 193 K): δ 3.81 (s, 24H), 6.50−6.58 (broad s, 4H), 6.75−6.87 (broad s, 8H), 7.44−7.51 (broad s, 8H). ^{31}P NMR (THF-d_8, 298 K): δ −17.6. Satisfactory ^{13}C NMR data were not acquired. Anal. Calcd for $C_{36}H_{44}CaO_6P_2$: C, 64.07; H, 6.57. Found: C, 63.95; H, 6.61.

Synthesis of $[(18\text{-crown-}6)Ba(PPh_2)_2]$, 9. To an unstirred solution of $[Ba\{N(SiMe_3)_2\}_2(THF)_2]$ (500 mg, 0.91 mmol) in THF was added a solution of 18-crown-6 (219 mg, 0.79 mmol) and diphenylphosphine (337 mg, 1.8 mmol) in hexane (10 mL). Slow diffusion of the two solutions over a 48 h period resulted in the formation of orange/red crystals. Isolation by filtration gave **9** (210 mg, 0.27 mmol, 34%). Mp: 135−138 °C (dec). ^{1}H NMR (THF-d_8, 500 MHz, 193 K): δ 3.54 (s, 24H), 7.25−7.55 (broad multiplets, 20 H). ^{13}C NMR (THF-d_8, 125 MHz, 193 K): δ 71.3, 118.7, 129.4 (apparent d), 129.4 (d, $^2J_{PC} = 16.4$ Hz), C_{ipso} not observed. ^{31}P NMR (THF-d_8, 193 K): δ −3.9. Anal. Calcd for $C_{36}H_{44}BaO_6P_2$: C, 56.03; H, 5.74. Found: C, 55.92; H, 5.67.

Crystal Structure Determinations. Data were collected at 173 K on a Nonius KappaCCD diffractometer, with λ(Mo Kα) = 0.71073 Å; details are given in Table 1. An absorption correction (multiscan) was applied in all cases. For **6**, the disordered C atoms of the THF ligands were left isotropic. For **7**, one THF ligand was disordered and was included with isotropic C atoms and geometry restraints. The structures were solved by direct methods (*SHELXS-97*) and refined by full matrix least squares (*SHELXL-97*) with non-H atoms anisotropic and H atoms included in riding mode.[9,10]

Results and Discussion

Synthesis. The metalation of secondary and primary organo- and organosilylphosphines with group 2 bis(trimethylsilyl)amides is a well-established method for the preparation of phosphido derivatives of this series of elements.[5] An initial NMR scale reaction between 2 equiv of $HPPh_2$ and $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$, **2**, in C_6D_6 resulted in an instant color change of the solution to orange and the slow precipitation of a fine yellow/orange solid, consistent with that observed under the catalytic conditions for the hydrophosphination of styrene.[2b] The heavier Ae phosphide could be isolated as a crystalline solid by changing the

Table 2. Selected Bond Lengths (Å) for **5**−**9**

	5[a,i]	**6**[b]	**7**[d,g]	**8**[a,i]	**9**[d]
M/M(1)−P/P(1)	2.9882(4)	3.1427(7)[c]	3.2958(7)[e]	2.9789(6)	3.3484(7)[h]
M/M(1)−O(1)	2.3784(11)	2.511(2)	2.686(2)	2.6883(14)	2.7853(17)
M/M(1)−O(2)	2.3762(12)	2.541(2)	2.711(2)[f]	2.6700(15)	2.7840(17)
P/P(1)−C(1)	1.8235(18)	1.826(2)	1.810(3)	1.824(2)	1.817(3)
P/P(1)−C(7)	1.8121(17)	1.817(3)	1.822(3)	1.837(2)	1.821(3)

[a] M = Ca. [b] M = Sr. [c] Sr−P(2), 3.1453(7). [d] M = Ba. [e] Ba(1)−P(1)′, 3.3627(7). [f] Ba(2)−O(2). [g] Ba(1)−C(29), 3.182(2). [h] Ba−P(2), 3.3230(8). [i] Symmetry transformations to generate equivalent atoms (noted with ′): $-x + 1, -y + 1, -z + 1$.

Table 3. Selected Bond Angles (deg) for **5**−**9**

	5[a]	**6**[b]	**7**[c]	**8**[a]	**9**[c]
P/P(1)−M/M(1)−P′/P(2)	180	177.476(19)	90.281(17)[d]	180	160.825(19)
O(2)−M/M(1)−O(1)	87.44(5)	90.26(6)		60.30(5)	60.56(5)
O(1)−M/M(1)−P/P(1)	87.26(3)	86.63(4)	77.19(5)	96.91(4)	94.19(4)
O(1)−M/M(1)−P(2)		91.65(4)	98.95(5)		94.31(4)
O(2)−M/M(1)−P/P(1)	85.68(3)	88.64(4)	114.68(5)[e]	97.95(4)	94.90(4)
O(2)−M/M(1)−P(2)		93.23(4)	91.62(5)[f]		104.24(4)
C(1)−P/P(1)−C(7)	103.29(8)	107.05(11)	104.84(11)	103.25(10)	105.34(12)

[a] M = Ca. [b] M = Sr. [c] M = Ba. [d] P(2)−Ba(1)−P(3), 68.194(16); P(1)−Ba(1)−P(3), 150.501(17); P(3)−Ba(1)−P(1)′, 101.781(16); P(2)−Ba(1)−P(1)′, 112.705(18); P(1)−Ba(1)−P(1)′, 67.151(19); Ba(2)−P(2)−Ba(1), 112.245(19); Ba(1)−P(3)−Ba(2), 111.314(18). [e] O(2)−Ba(2)−P(2). [f] O(2)−Ba(2)−P(3).

reaction solvent and further slowing the rate of the reaction. Thus, the layered addition of a solution of diphenylphosphine in hexane to a solution of **2** in THF provided $[Ca(PPh_2)_2(THF)_4]$, **5**, as a crystalline orange solid. Similarly, $[Sr(PPh_2)_2(THF)_4]$, **6**, and $[Ba_3(PPh_2)_6(THF)_4]_n$, **7**, could be isolated by using $[Sr\{N(SiMe_3)_2\}_2(THF)_2]$, **3**, and $[Ba\{N(SiMe_3)_2\}_2(THF)_2]$, **4**, respectively, as starting materials (eq 1). This slow diffusion technique yielded well-formed single crystals suitable for single-crystal X-ray diffraction analysis in all three cases, details of which are provided in Table 1.

$$[Ae\{N(SiMe_3)_2\}_2(THF)_2] + 2HPPh_2 \xrightarrow[\text{rt, 12 h}]{\text{THF/hexane}} [Ae(PPh_2)_2(THF)_n] + 2HN(SiMe_3)_2 \quad (1)$$

$$\mathbf{5},\ Ae = Ca,\ n = 4$$
$$\mathbf{6},\ Ae = Sr,\ n = 4$$
$$\mathbf{7},\ Ae = Ba,\ n = 1.5$$

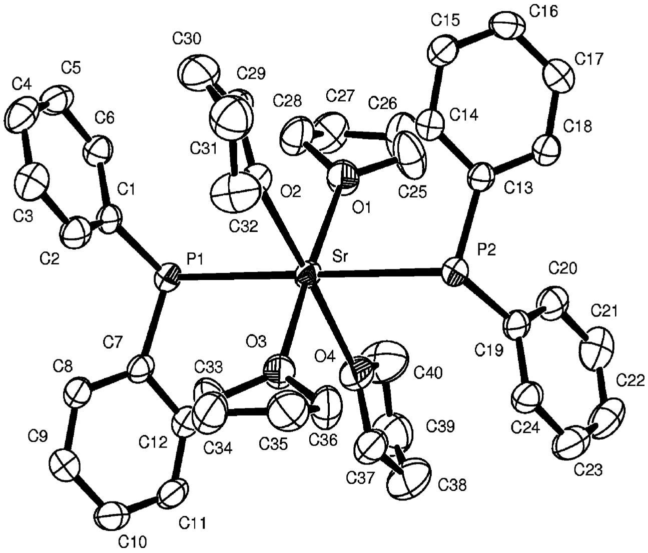


Figure 1. Thermal ellipsoid plot of compound **6** (50% probability). H atoms are omitted for clarity.

Molecular Structures of the THF Adducts 5−7. Selected bond length and angle data are provided in Tables 2 and 3, respectively, while the molecular structures of compounds **6** and **7** are shown in Figures 1 and 2 (the structure of compound **5** is similar to that of **6** and is illustrated in the Supporting Information for this paper). The crystallographic analyses revealed that, while the calcium and strontium derivatives are both isolated as monomeric hexacoordinate complexes in the solid state, the barium compound is polymeric and aggregates via μ_2-bridging phosphide ligands. While not isostructural, both compounds **5** and **6** are octahedral at the group 2 metal centers and display approximate D_{4h} symmetry with respect to the metal centers. In both cases, four molecules of THF occupy the equatorial planes and axial ligation is provided by two monoanionic diphenylphosphide moieties. The structures of compounds **5** and **6** thus feature a *trans*-P_2O_4 coordination sphere identical to those of the previously reported bis[bis(trimethylsilyl)phosphido] derivatives $[Ae\{P(SiMe_3)_2\}_2(THF)_4]$ (Ae = Sr,[5c] Ba[5b]). Although we do not attribute any electronic significance to the observation, this bonding situation contrasts with that within the recently reported and similarly six-coordinate diphenylamides, $[Ae(NPh_2)_2(THF)_4]$ (Ae = Sr, Ba), in which the two amide moieties adopt a mutual cis orientation and are effectively planar (i.e., sp^2 hybridized) at the amide nitrogen centers (vide infra).[11] The metal−oxygen bond lengths within **5** and **6** are completely normal for compounds of the type $[AeX_2(THF)_4]$ and are similar to those within the previously characterized hexacoordinate compound $[Ca\{PH(Si^iPr_3)\}_2(THF)_4]$.[5a] In both centrosymmetric complex **5** and complex **6** there is little deviation from ideal octahedral geometry and O−M−O bond angles approach 90° while the P−M−P bond angles are near 180° (Figure 1). As with the heteroleptic calcium phosphide **1**, both homoleptic phosphides demonstrate a degree of pyramidalization (DP, where DP(%) = $[(360 - \Sigma\text{angles subtended at P})/360]100$) at phosphorus (**5**, DP = 29.8%; **6**, DP = 52.4%) that contrasts with that of the planar nitrogen centers in the series of diphenylamides $[Ae\{N(Ph)_2\}L_x]$ (Ae

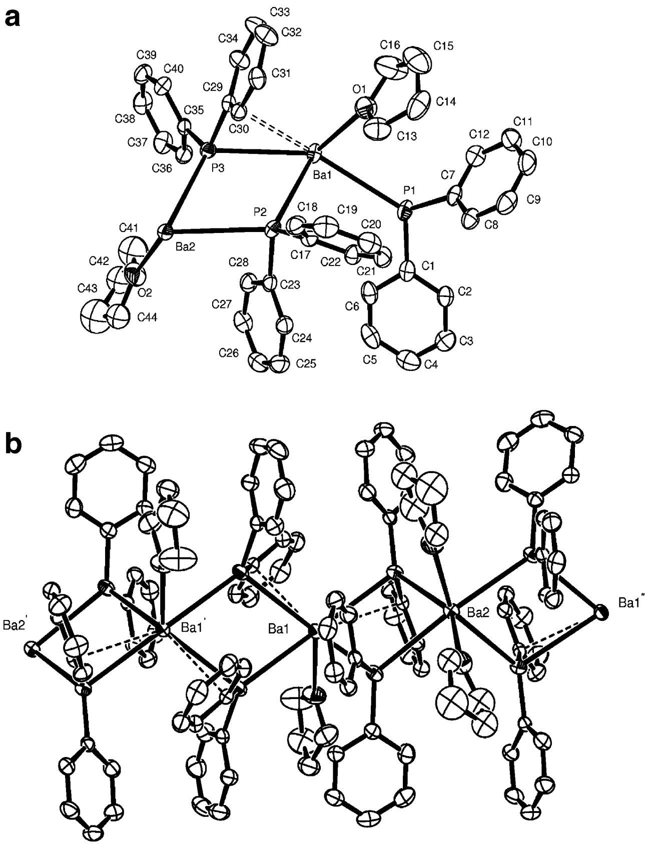


Figure 2. (a) Thermal ellipsoid plot of the asymmetric unit of compound **7** (50% probability). H atoms are omitted for clarity. (b) The polymeric structure of compound **7**.

= Ca Sr, Ba) recently reported by Westerhausen and coworkers.[11] These latter complexes also differ in that both structures feature notable distortions about the M−N−C bonds caused by pronounced attractive interactions between the metal centers and the π system of one of the N-bound phenyl rings of both diphenylamide substituents.

In contrast to these mononuclear structures, the barium phosphide **7** presents a polymeric array in the solid state (Figure 2a). Previous crystallographic analyses of group 2 phosphides have identified the propensity of coordinatively unsaturated complexes to oligomerize through bridging phosphide units, and a number of oligomeric and cagelike structural motifs have been identified.[12] Despite this, to the best of our knowledge, compound **7** represents the first polymeric derivative of such compounds. The crystal structure consists of infinite chains. The Ba(2) atom lies on a two-fold rotation axis, and Ba(1) is related to Ba(1)′ by an inversion center. Thus, the chain sequence is Ba(2)·Ba(1)·Ba(1)·Ba(2),Ba(1),Ba(1), etc. (Figure 2b). Although coordination of the Ba(1) centers is provided by four bridging phosphide groups and a single molecule of THF to provide a P_4O heteroatom donor array, the coordination sphere is also augmented by an additional C···Ba contact to the *ipso*-carbon (Ba(1)−C(29), 3.182 Å) of one of the P(3)-bound phenyl rings. Conversely, the Ba(2) centers are coordinated by an additional molecule of THF and thus may be described as unambiguously six-coordinate. The various bridging Ba−P interactions lie in the narrow range of 3.2785(7)−3.3627(7) Å and are comparable to the endocyclic Ba−P distances

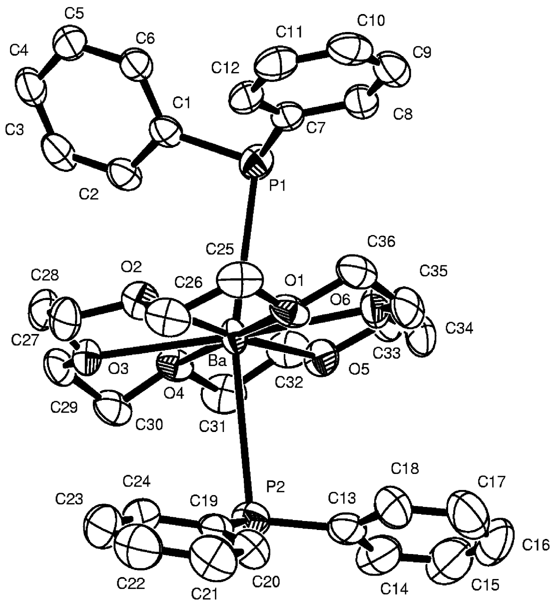


Figure 3. Thermal ellipsoid plot of compound **9** (50% probability). H atoms are omitted for clarity.

within the dimeric compounds $[\{(Me_3Si)_2N\}Ba(dme)\{\mu\text{-}P(SiMe_3)_2\}Ba(dme)\{N(SiMe_3)_2\}]$ (3.340(2) Å)[7b] and $[(THF)_2Ba\{P(SiMe_2{}^iPr)_2\}_2]_2$ (3.313(2) and 3.325(2) Å).[5e]

The mononuclear crown ether derivatives $[Ae(PPh_2)_2(18\text{-crown-6})]$ (**8**, Ae = Ca; **9**, Ae = Ba) were easily synthesized by treatment of the respective THF complexes, **5** and **7**, with 18-crown-6 and crystallization from a layered THF/hexane mixture. Although not isostructural, the compounds are very similar. Details of the X-ray analyses are given in Table 1, and while selected bond length and angle data are provided in Tables 2 and 3, only the structure of the barium derivative is illustrated in Figure 3. In both cases an eight-coordinate geometry is imposed upon the group 2 metal cation. The hexadentate crown ether ligands occupy the equatorial plane in both molecules and show only minor variations within the ranges of the various Ae−O contacts (Table 2), which are again commensurate with previously reported Ae structures containing the 18-crown-6 ligand (for example, the average Ba−O bond distance within the diphenylmethanide $[Ba(CHPh_2)_2(18\text{-crown-6})]$ is 2.778(2) Å).[13]

Solution-State Behavior. Our recent report describing the calcium-catalyzed intermolecular hydrophosphination of a variety of activated alkenes and alkynes employed the heteroleptic species **1** as a stabilized and lipophilic reaction platform. Although the use of the homoleptic calcium amide **2** was less successful under similar catalytic conditions, we have since discovered that both the homoleptic amides **2**−**4** and phosphides **5**−**7** are highly competent catalysts for the hydrophosphination of *N*-alkyl carbodiimides to form the corresponding phosphaguanidines.[14] Since this latter reaction may be expected to occur via a mechanism similar to that outlined in Scheme 1 with the formation of the homoleptic phosphides as likely intermediate species, an assessment of the solution-state molecularity of the simple series of Ae diphenylphosphides described above was undertaken.

Compounds **5**−**7** demonstrated very limited solubility in hydrocarbon solvents, such as C_6D_6, an observation consis-

Table 4. Multinuclear NMR Data for **5**−**9**

compound	$\delta_{31\mathrm{P}}$	δ_{Cipso}	δ_{Cortho}	δ_{Cmeta}	δ_{Cpara}	$^{1}J_{31\mathrm{P}-13\mathrm{C}}$	$^{2}J_{31\mathrm{P}-13\mathrm{C}}$	$^{3}J_{31\mathrm{P}-13\mathrm{C}}$
[$NaPPh_2$][a]	−22.5(1)	155.5	130.8	127.79	120.21	44.1(8)	17.7(8)	4.4(8)
5	−17.3	153.2	131.4	127.9	121.2	30.1	16.2	3.7
6	−11.9	153.6	131.0	128.0	121.0	37.0	17.2	5.8
7	+1.6	155.0	130.7	128.2	120.6	42.4	14.9	[c]
9	−3.9	[c]	134.6	129.4	118.7	[c]	16.4	[c]

[a] Reference 15. [b] Data collected at 193 K. [c] Not observed.

Table 5. Diffusion Coefficients (THF-d_8) and Calculated Radii of **5**−**7**[a]

compound	diff coefficient, D, $m^2\ s^{-1}$	PGSE hydrodynamic radius, r_H, Å	calculated radius, r_{mono}, Å
5	6.91×10^{-10}	5.2	5.5
6	6.61×10^{-10}	5.5	5.6
7	$6.3 - 9.1 \times 10^{-10}$	5.1−7.5	[b]

[a] Data measured in THF-d_8 using tetrakis(trimethylsilyl)silane or THF-d_8 as an internal standard. Due to poor resolution of the data, the barium compound did not provide an accurate diffusion coefficient. [b] Crystallographic coordinates of mononuclear species not available.

tent with that during the attempted hydrophosphination of styrene with diphenylphosphine catalyzed by [$Ca\{N(SiMe_3)_2\}_2(THF)_2$], which was accompanied by the production of an insoluble yellow solid assumed to be the intermediate homoleptic calcium phosphide.[2b] Indeed, the propensity for such compounds to form aggregates is illustrated by the barium derivative **7**, which is polymeric in the solid state. All three heavier Ae phosphides were, however, soluble in aprotic coordinating solvents such as THF. Although low-temperature experiments provided no obvious evidence dynamic behavior, it is likely that any ligand exchange equilibria would be so rapid as to be unobservable to the low-temperature limits of the solutions and cannot, therefore, be discounted. ^{31}P NMR spectroscopy of THF-d_8 solutions of **5**−**7** displayed a single phosphorus resonance for each heavier Ae phosphide, consistent with a time-averaged molecular environment in solution. The ^{31}P chemical shifts for the series shift upfield with increasing Ae atomic weight, taking values of −17,3, −11.9, and 1.6 ppm for compounds **5**, **6**, and **7**, respectively (Table 4). The $^{1}J_{31\mathrm{P}-13\mathrm{C}}$ coupling constants between the phosphorus center and the *ipso*-carbon of the aromatic rings ($P-C_{ipso}$) reflect a similar trend and increase in the order Ca < Sr < Ba (Table 4). These data are similar to those reported previously for heavier alkali and Ae phosphides[5,15] and suggest an increased electron density upon the phosphorus moiety and a resulting enhancement of the ionicity of the Ae−P bond with increasing the electropositive nature (and ionic radius) of the group 2 metal. These data are also comparable to those reported for sodium diphenyphosphide and are suggestive of an increasing s orbital (i.e., decreasing p orbital) character in the individual $P-C_{ipso}$ bonds as the group is descended and may be considered as a manifestation of Bent's rule.[15]

The solution molecularity of all three compounds in THF-d_8 solution was assessed by the application of pulse gradient spin echo (PGSE) techniques to the direct measurement of molecular diffusion coefficients, D, in solution. Once values of D have been determined for the species of interest, these may be related directly to the hydrodynamic radii via the Stokes−Einstein equation.[16] Table 5 lists the experimentally determined values of D for each of the three complexes along with the calculated hydrodynamic radii. Also listed for comparison are the radii of compounds **5** and **6**, determined from the molecular volumes calculated from the crystallographic coordinates and through use of the "vol" keyword of the *Gaussian 03* suite of programs to determine the molecular volume and a subsequent assumption that the tumbling molecules are "spherical" with regard to their apparent radii in THF solution.[17]

Examination of the data in Table 5 shows that the r_H values from the diffusion-ordered spectroscopy measurements for all three compounds show an acceptable agreement with those calculated for the solid-state species, r_{mono}, for compounds **5** and **6**. Although the absolute values obtained from the solution measurements should be viewed with caution, it is clear that species (at least on a time-averaged basis) similar to those depicted from the solid-state analyses also predominate in solution irrespective of any transient intermolecular contacts and ligand transfer reactions.

We are continuing to elaborate the reactivity of these well-defined species and will report the results of further stoichiometric and catalytic applications in subsequent publications.

Acknowledgment. We thank GlaxoSmithKline for the generous endowment (to A.G.M.B.), the Royal Society for a University Research Fellowship (M.S.H.) and a Royal Society Research Merit Award (A.G.M.B.), and the Engineering and Physical Sciences Research Council for the generous support of our studies.

Supporting Information Available: Crystallographic data (CIF files) for compounds **5**−**9** and ORTEP plots of the structures of compounds **5** and **8** (PDF file). This material is available free of charge at http://pubs.acs.org.

IC701608X