Syntheses and Structures of [(THF)$_n$M{(NSiMe$_3$)$_2$PPh$_2$}$_2$] Complexes (M = Be, Mg, Ca, Sr, Ba; n = 0−2): Deviation of Alkaline Earth Metal Cations from the Plane of an Anionic Ligand[†]

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Received October 31, 1996[⊗]

The syntheses and solid-state structures of [(THF)$_n$M{(NSiMe$_3$)$_2$PPh$_2$}$_2$] (M = Be, n = 0, **1**; M = Mg, n = 0, **2**; M = Ca, n = 1, **3**; M = Sr, n = 2, **4**; M = Ba, n = 2, **5**) are presented. Comparison of the geometric parameters within the homologous series and to related systems uncovers the dication-induced alterations of coordination to, as well as bonding within, the anionic fragment. The coordination number increases from 4 (Be, Mg) *via* 5 (Ca) to 6 (Sr, Ba). Two of the Ph$_2$P(Me$_3$SiN)$_2$ anions cover the coordination sphere of beryllium and magnesium, while with calcium one single THF molecule and with strontium and barium two additional THF molecules are required to complete the metal coordination sphere. Against steric considerations the two THF molecules in **4** and **5** are coordinated to the same hemisphere of the metal leaving the two anions cisoid. Even against sterical strain the alkaline earth metals leave the plane of one of the Ph$_2$P(Me$_3$SiN)$_2$ anions with increasing mass demonstrating the preference of Sr and Ba to interact with π electron density. This effect can also be found in related systems. It might be small and counterbalanced by steric requirements, but it is significant. The metal π interaction rises continually with the mass of the metal and decreasing bulk of the anion but is independent from cisoid or transoid arrangement of the anions. From the homologous series of complexes presented three structure determining factors can be deduced: (i) dicationic size; (ii) bent X−M−X (M = Sr, Ba) arrangement; (iii) increasing π interaction with increasing mass of the alkaline earth metal cation.

Introduction

Up to now most effort in the chemistry of alkaline earth metal organometallic chemistry still is focused on organomagnesium compounds,[1] because since the 1900s they became a well-established synthetic tool in organic and organometallic chemistry. It is only very recently that not only Grignard reagents but also the compounds containing the heavier alkaline earth metals have attracted the interest of both synthetically[2] and theoretically[3] oriented chemists. Alkaline earth metal compounds are promising precursors to metal oxides for the chemical vapor deposition (CVD) process. Volatile and soluble complexes of these metals are required in the CVD or sol−gel process to facilitate materials synthesis like high-temperature super conductors.[4,5]

Furthermore, the structures of MX$_2$ molecules (M = alkaline earth metal; X = halides, hydride, organic substituents) are vigorously discussed: Is the deviation from linearity an intrinsic structural feature or is the bending induced by additionally present donor bases in the metal coordination sphere?[6,7] Because bonding to alkaline earth metals is regarded predominantly ionic, simple electrostatic models as well as the first VSEPR approach[8] predicted a linear structure for MX$_2$ species. However, the bent geometry of, for instance, CaF$_2$ and many complexes of the heavier group 2 dihalides represent the most prominent exceptions from the VSEPR theory and, among others, lead to its present extended form.[9−11]

This paper is concerned with the synthesis and structural investigation of the aminoiminophosphoranate complexes [(THF)$_n$M{(NSiMe$_3$)$_2$PPh$_2$}$_2$] (M = Be, n = 0, **1**; M = Mg, n = 0, **2**; M = Ca, n = 1, **3**; M = Sr, n = 2, **4**; M = Ba, n = 2, **5**). The aminoiminophosphoranate ligand is a versatile building block in transition and main group metal chemistry.[12,13] The chelating [Ph$_2$P(Me$_3$SiN)$_2$] bidentate anion provides sufficient bulk to prevent the resulting alkaline earth metal complexes from aggregation. Two of this substituents cover the coordination sphere of beryllium and magnesium, while with calcium

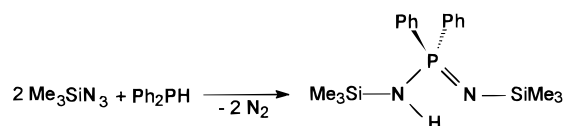† Dedicated to Prof. Dr. W. Adam, Würzburg, on the occasion of his 60th birthday.

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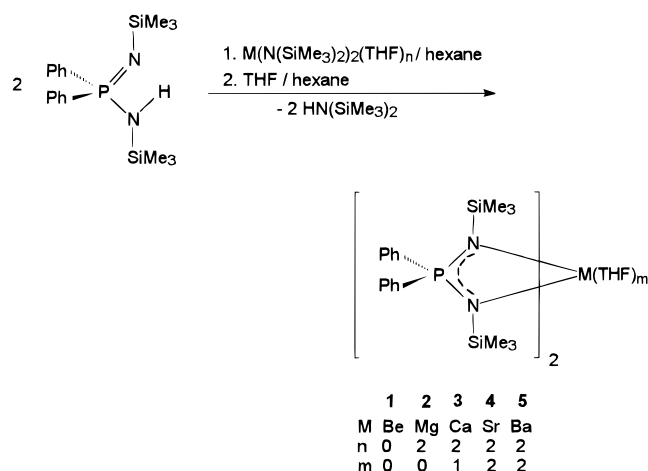⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

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Scheme 1

$$2\ Me_3SiN_3 + Ph_2PH \xrightarrow{-\ 2\ N_2} Me_3Si-N \cdots P \cdots N-SiMe_3$$

(Ph Ph on P; H below left N)

Scheme 2

(Reaction of the aminoiminophosphorane with)
1. $M(N(SiMe_3)_2)_2(THF)_n$ / hexane
2. THF / hexane
$- 2\ HN(SiMe_3)_2$

	1	2	3	4	5
M	Be	Mg	Ca	Sr	Ba
n	0	2	2	2	2
m	0	0	1	2	2

one single THF molecule and with strontium and barium two additional THF molecules are required to complete the metal coordination sphere. All complexes **1**–**5** are quite soluble in apolar hydrocarbons; hence, synthesis in homogeneous phase is facilitated. Gels containing $M(OH)_2 \cdot xH_2O$ (M = Be, Mg, Ca, Sr, Ba) can readily be made by hydrolyzation of the homogeneous solution of the related complex in toluene with water in methanol or ethanol.

Results and Discussion

Preparation of 1–5. The three chemically active sites in the *N,N'*-bis(trimethylsilyl)aminoiminodiphenylphosphorane are (i) the acidic NH function (ii) the donating imino nitrogen atom, and (iii) the potential cleavage of the Si−N or P−N bond, leading to anionic chelating ligands.[14] These properties of the aminoimino-phosphoranes hastened them to be widely used ligands in the synthesis of metallacycles.[13] The starting materials are obtained in the reaction of trimethylsilyl azide with diphenylphosphane in a Staudinger-type reaction.[15] The amino function of the *N,N'*-bis(trimethylsilyl)aminoiminodiphenyl-phosphorane can be deprotonated by strong bases. In the syntheses presented here the alkaline earth metal bis[bis-(trimethylsilyl)amides] have been used as bases. They can readily be obtained from the tin bis[bis(trimethylsilyl)amide].[16] The beryllium bis[bis(trimethylsilyl)amide] was obtained by a transmetalation reaction of the lithium derivative with beryllium dichloride.[17] The barium bis[bis(trimethylsilyl)amide] was obtained by the reaction of bis(trimethylsilyl)amine with elemental barium.[18] After 1–2 h of stirring of the starting materials in hexane at room temperature the crude product was obtained as a white precipitate. The solution was decanted and the product washed twice with hexane. Crystallization from hexane/THF (1:1) yielded pure alkaline earth metal complexes (Scheme 2).

Crystal Structure of [Be{(NSiMe₃)₂PPh₂}₂] (1). Although **1** crystallizes from pure hexane at 0 °C, those crystals are not

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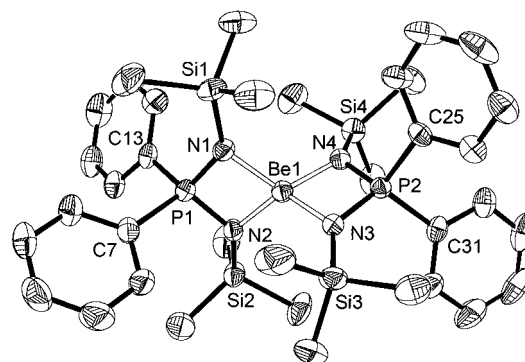(18) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 121

Figure 1. Structure of [Be{(NSiMe₃)₂PPh₂}₂] (**1**) in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level.

Table 1. Selected Bond Lengths (pm) and Angles (deg) for **1**–**5**

	compound				
	1	**2**	**3**	**4**	**5**
M−N1	177.1(4)	208.3(2)	255.1(2)	268.9(3)	279.6(2)
M−N2	175.3(4)	206.8(2)	239.7(2)	261.0(2)	273.7(2)
M−N3	177.7(3)	207.2(2)	254.6(2)	263.9(3)	284.9(2)
M−N4	176.0(3)	207.8(2)	239.3(2)	260.5(2)	274.8(2)
M−O1			235.3(1)	264.7(2)	281.1(2)
M−O2				259.8(2)	277.7(2)
M···P1	231.2(4)	262.8(1)	302.02(7)	321.73(9)	335.20(8)
M···P2	232.1(4)	262.2(1)	303.92(7)	319.60(9)	337.27(8)
P1−N1	159.0(2)	159.6(2)	158.9(2)	158.2(3)	157.9(2)
P1−N2	160.1(2)	159.6(2)	166.4(2)	158.8(3)	158.9(2)
P2−N3	158.9(2)	159.2(2)	159.0(2)	158.4(3)	157.7(3)
P2−N4	159.5(2)	159.3(2)	164.6(2)	158.8(3)	158.3(2)
N1−P1−N2	99.1(1)	104.3(1)	109.38(8)	109.1(1)	110.00(1)
N3−P2−N4	99.1(1)	104.5(1)	108.29(8)	109.5(1)	109.86(1)
C7−P1−C13	103.0(1)	104.2(1)	104.4(1)	102.4(1)	103.14(1)
C25−P2−C31	105.6(1)	103.4(1)	103.05(9)	102.4(1)	102.98(1)
P1−N1−Si1	136.1(1)	133.5(1)	134.8(2)	134.3(1)	135.0(2)
P1−N2−Si2	133.8(1)	137.2(1)	134.5(1)	131.2(1)	136.6(2)
P2−N3−Si3	135.7(1)	136.8(1)	135.1(1)	132.7(2)	136.9(2)
P2−N4−Si4	132.7(1)	135.1(1)	131.4(1)	135.1(2)	134.0(2)
P1···M···P2	175.8(2)	176.11(4)	144.29(2)	132.54(2)	131.52(1)

suitable for cryogenic structural determination. At lower temperatures they suffer from solid−solid phase transition, and at higher temperatures they decompose in the X-ray beam. However, recrystallization of the high-temperature phase from a THF/hexane mixture at −22 °C yielded crystals of the low-temperature phase which could be studied at −120 °C. **1** is a monomer in the solid state (Figure 1).

The central beryllium dication is coordinated to two chelating Ph₂P(Me₃SiN)₂ monoanions resulting in an almost undistorted tetrahedral BeN₄ arrangement in the core of the complex. The orthogonals of the two PN₂ planes intersect at an angle of 89°. The average Be−N distance in **1** of 176.5 pm (Table 1) is 6.5 pm longer than the related distance in the recent structure of the diazadien beryllium complex [Be(NPh=CPhCPh=NPh)₂], which adopts the same tetrahedral BeN₄ arrangement.[19] The elongation of the Be−N distance in **1** by about 20 pm compared to the gas-phase structure of Be{N(SiMe₃)₂}₂[20] (Be−N 157 pm) testifies to either the considerable steric requirements of the two Ph₂P(Me₃SiN)₂ ligands or the increase of the coordination number. The four independent P−N bond distances are of equal length within their estimated standard deviation, indicating ideal charge delocalization in the PN₂ fragment of the anion as observed earlier.[21]

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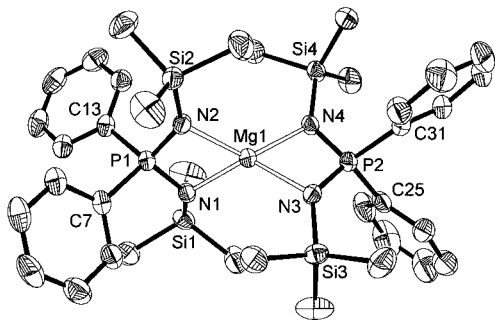(20) Clark, A. H.; Haaland, A. *J. Chem. Soc., Chem. Commun.* **1969**, 912.

Figure 2. Structure of [Mg{(NSiMe$_3$)$_2$PPh$_2$}$_2$] (**2**) in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level.

Crystal Structure of [Mg{(NSiMe$_3$)$_2$PPh$_2$}$_2$] (2). Unlike the crystals of the isotype structure of **1**, the crystals of **2** grown from THF/hexane at room temperature show no phase transition at low temperature. In the monomeric structure the single magnesium cation is tetrahedrally coordinated by the four nitrogen atoms of the two anions (Figure 2).

The almost linear P1···Mg···P2 arrangement (176.1°, Table 1) minimizes steric repulsion. Like in **1** the orthogonals of the two PN$_2$ planes intersect at an angle of 89°. The average Mg−N distance is 207.5 pm. The increase of 44 pm in the cationic radius of Mg^{2+} (78 pm) versus Be^{2+} (34 pm)[22] is not quite reflected in the increase of the metal−nitrogen distances, but the distances of 202 pm in monomeric [Mg{N(SiMe$_3$)$_2$}$_2$· 2THF][23] and of 198/215 pm in Mg{N(SiMe$_3$)$_2$}$_2$,[24] respectively, are in the same order of magnitude.

Crystal Structure of [(THF)Ca{(NSiMe$_3$)$_2$PPh$_2$}$_2$] (3). Crystals were grown from a THF/hexane mixture at room temperature. Exposure to air cause the colorless blocks to turn opaque. Different from those of **1** and **2**, the structure of **3** shows an additional THF molecule coordinated to the calcium dication. Apparently the radius of 106 pm [22] for Ca^{2+} is sufficient to accommodate two Ph$_2$P(Me$_3$SiN)$_2$ ligands and a solvent molecule (Figure 3a).

The coordination polyhedron of the central metal can be described as a distorted trigonal bipyramid (Figure 3b). The equatorial positions are occupied by two nitrogen atoms (N2 and N4) and the oxygen atom of the THF molecule, while N1 and N3 are located at the axial positions. The P1···Ca···P2 vector is clearly bent (144.3°, Table 1), and the orthogonals of the two PN$_2$ planes intersect at an angle of 68°. Neither the Ca−N nor the P−N distances are equally long (**a** and **b** in Scheme 4). They can be classified into two different groups. The shorter Ca−N distances of the equatorial positions (239.3(2) and 239.7(2) pm) are correlated to the longer P−N distances (164.6(2) and 166.4(2) pm), while the shorter P−N distances (158.9(2) and 159.0(2) pm) give rise to the longer axial Ca−N distances (255.1(2) and 254.6(2) pm). The long ≡P−N̄− bonds indicate that the electron density is mostly located at the nitrogen atom; hence, they are attractive to strong electrostatic interactions with the metal. Compared with that in the shorter ≡P=N̄− bonds the electron density is more located in a partial double bond and the nitrogen atom is less attractive to the calcium cation. The Ca−N distances of 227 pm in [Ca-

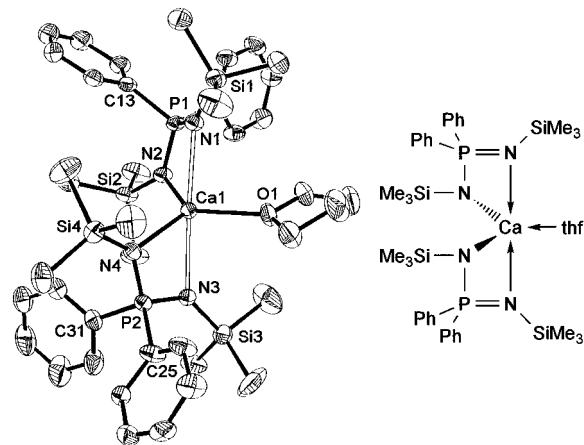(21) (a) Schmidbaur, H.; Schwirten, K.; Pickel; H.-H. *Chem. Ber.* **1969**, *102*, 564. (b) Witt, M.; Roesky, H. W.; Stalke, D.; Pauer, F.; Henkel, T.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1989**, 2173.
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Figure 3. (a) Left: Structure of [(THF)Ca{(NSiMe$_3$)$_2$PPh$_2$}$_2$] (**3**) in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level. (b) Right: Related mesomeric resonance form visualizing the bonding in the trigonal bipyramid.
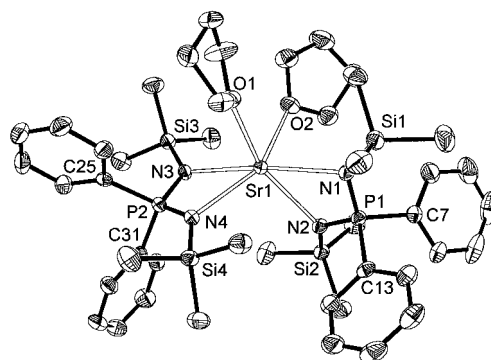

Figure 4. Structure of [(THF)$_2$Sr{(NSiMe$_3$)$_2$PPh$_2$}$_2$] (**4**) in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level.

{N(SiMe$_3$)$_2$}$_2$·dme][25] (dme = dimethoxyethane) are considerably shorter, but the average Ca−N distance in the Ca$_2$N$_2$ four-membered ring of donor-free [Ca{N(SiMe$_3$)$_2$}$_2$]$_2$[25] (μ_2-N, 249.5; terminal N, 228 pm) is almost identical to the average Ca−N distance in **3**.

Crystal Structure of [(THF)$_2$Sr{(NSiMe$_3$)$_2$PPh$_2$}$_2$] (4). The strontium complex crystallizes from a THF/hexane mixture at room temperature within a few hours. The solid decomposes instantaneously when exposed to air. Again, the increased ionic radius of Sr^{2+} to 127 pm [22] causes an extension of the coordination number. In addition to the four nitrogen atoms of the two aminoiminophosphorane ligands two THF molecules are coordinated to the metal.

The P1···Sr···P2 vector is even more acute than in **3** (132.5°, Table 1) while the orthogonals of the two PN$_2$ planes like in **1** and **2** intersect at an angle of 87°. The coordination sphere of the strontium metal can be rationalized as a distorted octahedron with two nitrogen atoms (N2 and N4, Figure 4) and both oxygen atoms in the equatorial positions and N1 and N3 at the axial positions. However, the differences in the Sr−N distances in relation to their positions are not as striking as in the trigonal bipyramidal coordination of **3** (Sr−N1,3$_{axial}$, 268.9(3) and 263.9(3) pm; Sr−N2,4$_{eq}$, 261.0(2) and 260.5(2) pm). Compared to the Sr−N distance of 244 pm in [Sr{N(SiMe$_3$)$_2$}$_2$·2dme][26] they are remarkably long. In agreement with that, the four

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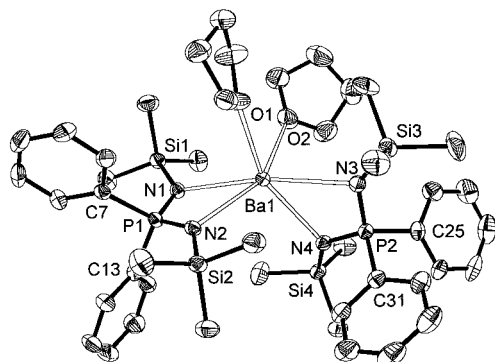
Figure 5. Structure of [(THF)₂Ba{(NSiMe₃)₂PPh₂}₂] (**5**) in the solid state. Anisotropic displacement parameters are depicted at the 50% probability level.

independent P—N bonds are identical within their estimated standard deviations (Table 1), indicating ideal charge delocalization in the PN₂ fragment. Unlike the calcium derivative **3** the different metal—nitrogen distances in **4** are attributed to steric crowding. The longer Sr—N bonds result from sterical interaction of the two THF molecules and the N-bonded trimethylsilyl groups.

Crystal Structure of [(THF)₂Ba{(NSiMe₃)₂PPh₂}₂] (5). The barium complex is very similar to the strontium derivative. It crystallizes from THF/hexane within hours as colorless cubes. Like in **4**, the metal in **5** is coordinated by two THF molecules, apart from the two Ph₂P(Me₃SiN)₂ anions. The increase in the Ba²⁺ radius to 143 pm [22] apparently is not sufficient to accommodate a third THF molecule.

The bending of the P1···Ba···P2 vector and the intersection of the orthogonals of the two PN₂ planes in **5** (131.5 and 88°, respectively; Table 1) is almost identical to the values of **4**. There is no obvious difference in the Ba—N distances for the equatorial and axial positions in the distorted octahedral Ba coordination polyhedron. The comparison of the mean Ba—N and Ba—O bond lengths to the related distances in **4** reflect the expected increase of about 16 pm due to the bigger cationic radius. However, the mean Ba—N distance of 278.3 pm in **5** is notably longer than the related distance in [Ba{N(SiMe₃)₂}₂· 2THF][18] (259 pm) but shorter than in Ba[(pz*)₃Ge]·¹/₂dioxane[27] (pz* = 3,5-dimethylpyrazol-1-yl; Ba—N(σ), 280; Ba—N(η), 293 and 297 pm). The four equally long P—N bonds in **5** indicate ideal charge delocalization in the PN₂ moiety.

Structural Comparison

Structural Comparison of 1—5 Among Themselves. The most obvious common structural feature of **1**—**5** is their monomeric molecular state. This fact seems not surprising in view of the considerable steric demand of the two anions. They shield the dication quite well. There is only room for one or two THF molecules but not for oligomerization. Hence they are soluble even in apolar organic solvents. As a consequence of the increasing cationic radius the coordination number increases from 4 (Be, Mg) via 5 (Ca) to 6 (Sr, Ba). All M—N distances are within the range of known alkaline earth metal-nitrogen distances.

However, there are some remarkable structural trends to be discussed along this homologous series of alkaline earth metal compounds summarized in Table 2. While in the Be and Mg derivatives **1** and **2** the two anions are located strictly trans and orthogonal with respect to each other to minimize sterical strain,

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Table 2. Comparison of Geometrical Features of **1**—**5**

	compound				
	1	**2**	**3**	**4**	**5**
metal	Be	Mg	Ca	Sr	Ba
coord no.	4	4	5	6	6
dicationic radius (pm)	34	78	106	127	143
av M—N (pm)	176.6	207.5	254.9 (239.6)[a]	263.8	278.3
av P—N (pm)	159.4	159.4	159.0 (165.5)[a]	158.6	158.2
deviation from	0.2	4.3	16.8	2.7	3.8
best anionic planes (pm)[a]	9.8	14.1	36.4	51.1	55.7

[a] Two values are quoted due to symmetry-independent anions.

Scheme 3. Arrangement of the PN₂M Units[a]
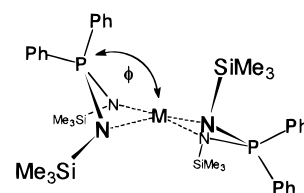
M=Sr, φ=167.2°; M=Ba, φ=167.0°

[a] While the alkaline earth metals are located in the plane of *one* Ph₂P(Me₃SiN)₂ anion (right; see also Figure 6A), the central phosphorus atom of the *second* ligand is bent toward the Ba and Sr metal center (left; see also Figure 6B).

in the Ca compound with one additional THF molecule the orientation of the two anions clearly needs to be cisoid. In the series of the alkaline earth metal aminoiminophosphinates **1**—**5**, this compound occupies a special position. In the trigonal bipyramidal coordination polyhedron the presence of partial P=N double bonds imply long N→M donor bonds in the apical positions. An ideal trans configuration of the anions could be realized by coordination of a second THF molecule, e.g. with Sr (**4**) and Ba (**5**), but the cisoid configuration is retained and even more pronounced along the homologous metals (P1···M···P2; M = Ca 144.3, Sr 132.5, Ba 131.5°; Table 1). Kaupp, Schleyer, and co-workers found by high-level *ab initio* MO calculations the MCp₂ metallocenes (M = Ca, Sr, Ba; Cp = C₅H₅) to be bent (Cp···Ba···Cp 147°) but described them as "quasilinear" due to the low linearization energy (less than 1.5 kcal/mol).[6] For the barium amides, however, they expected a bent arrangement because of small but significant covalent σ-bonding contributions involving metal d-orbitals[28] and polarization of the metal cation by the anions.[29] For the Ba(NH₂)₂-(HF)₄ system they calculated the linearization energy to be ca. 3 kcal/mol.[30] From these calculations the bending of **4** and **5** is an intrinsic feature and not induced by solvent coordination. The cisoid arrangement of the anions leaves a vacant coordination site which is filled by two THF molecules.

The most surprising structural feature of the alkaline earth metal complexes presented here is the different coordination of the two anions in the strontium and barium derivatives **4** and **5** compared to the lighter alkaline earth metal compounds **1**—**3**. Figure 6 shows the least-squares fit of the best planes of both moieties (see also Table 2). While the metals remain nearly in the plane of *one* Ph₂P(Me₃SiN)₂ anion (Figure 6A), the deviation from the plane of the second anion increases gradually from 9.8 for Be to 55.7 pm for Ba (Figure 6B).

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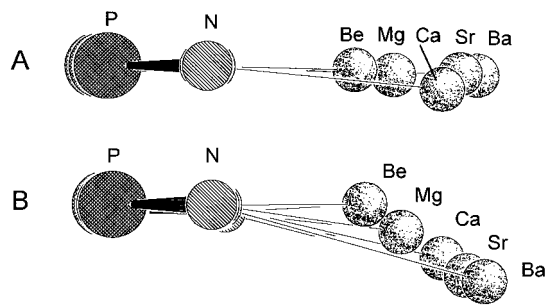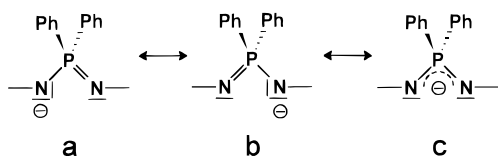
Figure 6. Superposition of the two best PN$_2$ anionic planes in **1**−**5**. While the metals remain nearly in the plane of *one* Ph$_2$P(Me$_3$SiN)$_2$ anion (A), the deviation from the plane of the *second* anion increases gradually from 9.8 for Be to 55.7 pm for Ba (B).

Scheme 4. Resonance Structures of the Ph$_2$P(Me$_3$SiN)$_2$ Anion^a

^{a} While the more localized P−N double bond of **a** and **b** is detected in the Ca complex **3**, the delocalized structure of **c** was found in the Be (**1**), Mg (**2**), Sr (**4**), and Ba (**5**) complexes.

At first sight this out-of-plane bending along the N···N vector is surprising, because it increases anion repulsion. The phenyl group of the one anion interacts with the trimethylsilyl group of the second anion. To minimize steric strain one would expect a planar arrangement for both PN$_2$M units similar to the situation found in **1** and **2**. Therefore one would expect the angle ϕ in Scheme 3 to be close to 180° for both anions, in particular, since there are no obvious packing effects which cause the bending of the central phosphorus atom of one ligand toward the Ba and Sr metal center. Therefore the angle ϕ of 167.2° in the Sr complex and of 167.0° in the Ba complex (this corresponds to a deviation of the position of the metal from the PN$_2$ plane by 51.1 (Sr) and 55.7 pm (Ba), respectively; Figure 6b) may be taken as an indication of increasing metal π-interaction of the heavier alkaline earth metals to the delocalized electron density of the PN$_2$ moiety (**c** in Scheme 4). A similar trend was observed in the homologous series of the related alkali metal derivatives [(THF)$_n$M{(NSiMe$_3$)$_2$PPh$_2$}$_2$]$_m$ (M = Li, Na, K, Rb, Cs; n = 1, 2, 4, m = 1, 2, ∞),[31] although this appeared not as so systematically as in the structures discussed here. The change of the coordination environment and the degree of oligomerization does not progress as gradually as in **1**−**5** (deviation from the PN$_2$ best plane (pm): Li, 6.4; Na, 4.9 and 19.2; K, 10.5; Rb, 71.7; Cs, 15.5).

Apart from the structure of **3**, which is a special case, the electron density is delocalized within the PN$_2$ moiety (**c** in Scheme 4). In tune with the increasing ordering number of the metal the average P−N bond length decreases (Table 2), indicating electron accumulation on the anion along the line Be to Ba. The barium dication obviously is more easy to polarize than the beryllium dication. This is supported by the NMR chemical shifts and coupling constants (Table 4). Both the signal for the central phosphorus atom as well as the signal for the silicon atoms in the ligand are detected more and more upfield as the metal gets heavier. The $^2J_{Si,P}$ coupling constant increases constantly. Since the Ph$_2$P(Me$_3$SiN)$_2$ anion in **5** (Ba) is more electron rich than in **1** (Be) and the barium dication is easy to polarize, **5** is the best candidate to observe metal

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Table 3. Deviation from Anionic Best Plane (pm)

metal	RC(NR)$_2^{-\,a}$		carbazolate	
Mg	5.4			
Ca	20.6		73.8	19.4
Sr	32.0		136.9	136.9
Ba	81.6	24.0	135.5	98.2

^{a} If only one number is quoted, the two anionic planes are symmetry related.

Table 4. NMR Spectroscopic Data for **1**−**5** from Solution

	compound				
	1	**2**	**3**	**4**	**5**
^{31}P−NMR (H$_3$PO$_4$) (δ)	33.46	22.48	14.13	11.10	8.02
^{29}Si−NMR (SiMe$_4$) (δ)	−3.23	−7.71	−11.40	−13.14	−14.44
^2J(Si,P) (Hz)	3.9	7.5	11.5	13.7	15.7

Scheme 5. Coordination of One Ge(pz*)$_3$ Anion to the Central Metal in Ba[(pz*)$_3$Ge]$_2$
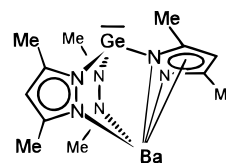
π-electron-density interaction. Like the heavier alkaline metals the higher alkaline earth metals were found to prefer the multihapto mode of bonding to delocalized anions rather than monohapto bonding.[30] This makes the out-of-plane arrangement of the metals energetically attractive even against steric requirements. The heavier (i.e. the easier to polarize) the metals get the more they want to interact with the (nondirected) electron density of the π system. In Ba[(pz*)$_3$Ge]$_2$ multihapto bonding of an heteroaromatic ring to barium was observed for the first time. Four of the six present 3,5-dimethylpyrazol-1-yl groups were exclusively N σ-bonded to the barium while two were η^2-coordinated (Scheme 5).

Structural Comparison of 1−5 to Related Homologous Systems. To test this theory we looked for related complexes and compared them to the complexes discussed here. The benzamidinate PhC(Me$_3$SiN)$_2$ anion is very similar to the Ph$_2$P(Me$_3$SiN)$_2$ anion. Only the central Ph$_2$P unit is substituted by a PhC group. The solvated magnesium to barium benz-amidinates have been synthesized and structurally characterized by Westerhausen et al.[32] The out-of-plane arrangement of the metals should even be more pronounced because of the smaller anion compared to the Ph$_2$P(Me$_3$SiN)$_2$ anion. Even though the plane of the phenyl ring is more or less perpendicular to the CN$_2$ π-system, this anion is quite flat compared to the latter. Hence the weak π-interaction to the CN$_2$ moiety is not as much counterbalanced by steric requirements. And in fact the out-of-plane deviation increases from 5.4 pm in [(C$_6$H$_5$C≡N)Mg-{(NSiMe$_3$)$_2$CPh}$_2$][32a] to 81.6 pm in [(dme)(THF)Ba{(NSiMe$_3$)$_2$-CPh}$_2$].[32d] Even the deviation of the Ba atom from the plane of the second benzamidinate anion (24.0 pm) is much higher than in **5** (Table 3).

Figure 7 shows the least-squares fit of the best planes of the CN$_2$ fragments. Clearly the same structural variations found in **1**−**5** can be seen in the alkaline earth metal benzamidinates. The lithium and sodium benzamidinate exhibit dimeric struc-

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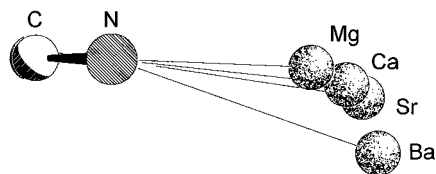
Figure 7. Superposition of the best CN_2 anionic plane in the solvated alkaline earth metal benzamidinates [(donor)$_n$M{(NSiMe$_3$)$_2$CPh}$_2$] (M = Mg, Ca, Sr, Ba) illustrating the increasing out-of-plane coordination with increasing ordering number of the metals.

tures.[33] The structures of the solvated alkaline earth carbazolate complexes of Ca, Sr, and Ba with two unsubstituted $C_{12}H_8N$ anions are known.[30] The coordinating nitrogen atom in the anions is integrated in a NC_5 aromatic ring. Unlike in the structures of the heavier alkali metal carbazolates,[34] in the structures of the alkaline earth derivatives there are no short metal–carbon distances observed. They are regarded as exclusively monohapto σ-bonded without any multihapto π-bonding to the metal,[30] but the deviation of the position of the metals from the plane of the anions is even more striking than in the benzamidinate complexes. Table 3 summarizes the deviations of the metal from the best planes of the central NC_5 perimeters in the structures of the alkaline earth metal carbazolate structures. Obviously the flat carbazole anion allows even more significant deviation from the anionic plane than the benz-amidinate ions. In the strontium and barium derivative the metal is more than 135 pm out of the plane of the anion (Table 3). Like in the other structures, a careful inspection of possible short inter- and intramolecular distances, which may account for the out-of-plane deviation, did not support the hypothesis that packing forces might cause this effect. In the alkaline earth metal mercaptobenzoxazolate[35] and aminothiatriazolate[36] complexes reported by Snaith et al. the deviation from the plane is prevented by additional M–S side arm donation. However, the following statement can be made: The higher deviation of the alkaline earth metals from the plane of the anion with increasing mass demonstrates their rising preference to interact with π-electron density, even against steric strain.

Conclusion

The question of what factors govern the coordination geometry of the alkaline earth metal has to be answered in three parts:

(i) Like in most compounds, as well the coordination geometry of the alkaline earth metals is governed by anion cation size (miss)match. Not surprisingly, the coordination number increases from 4 (Be, Mg) *via* 5 (Ca) to 6 (Sr, Ba). Two of the Ph$_2$P(Me$_3$SiN)$_2$ anions cover the coordination sphere of beryllium and magnesium, while with calcium one single THF molecule and with strontium and barium two additional THF molecules are required to complete the metal coordination sphere.

(ii) Like in many other heavier alkaline earth metal complexes, the anions in **3**−**5** were found to be cisoid with respect to each other. Against sterical considerations the two THF molecules in **4** and **5** are coordinated to the same hemisphere of the metal. Apart from the *ab initio* MO computational prediction (significant covalent σ-bonding contributions involving metal d-orbitals and polarization of the metal cation by the anions) there is now experimental evidence of a bent arrangement presented here (structural strain, shortening of the average P–N distance and NMR upfield shift).

(iii) Although multihapto π interaction with an anion has been calculated to be favorable for the heavier alkaline earth cations, this effect has not yet been reported experimentally. While the π interaction of the central Ba dication and one pyrazolyl ring in Ba[(pz*)$_3$Ge]$_2$ might be sterically induced, this is clearly not the case in the systems presented here. Even against steric strain the heavier alkaline earth metals Sr and Ba leave the plane of one anion, demonstrating their preference to interact with π electron density. This effect can also be found in related systems. Certainly the π-interaction is smaller than in the alkaline earth metallocenes and counterbalanced by steric requirements, but it is significant. The metal π-interaction rises with the mass of the metal and decreasing bulk of the anion but is independent from cisoid or transoid arrangement of the anions.

Experimental Section

All manipulations were performed under inert gas atmosphere of dry N$_2$ with Schlenk techniques or in an argon glovebox. All solvents were dried over Na/K alloy and distilled prior to use. NMR spectra were obtained in benzene-d_6 as solvent with SiMe$_4$ or H$_3$PO$_4$ as external reference on a Bruker AM 250. Mass spectra were recorded on a Finnigan Mat 8230 or Varian Mat CH5 spectrometer. Elemental analyses were performed by the Analytische Laboratorium des Instituts für Anorganische Chemie der Universität Göttingen.

Hazards. *Beryllium compounds are extremely toxic and supposed to cause cancer.*[37] *Handle with care!*

N,N′-bis(trimethylsilyl)aminodiphenylphosphinimine[15] and alkaline earth metal bis[bis(trimethylsilyl)amides][16,17] were prepared according to known literature procedures. The alkaline earth metal *N,N′*-bis[bis-(trimethylsilyl)aminodiphenylphosphinimides)] were obtained using the following general procedure: A solution of alkaline earth metal bis-[bis(trimethylsilyl)amide] (2.5 mmol) in 10 mL of hexane is added to a solution of *N,N′*-bis(trimethylsilyl)aminodiphenylphosphinimine (5 mmol, 1.8 g) in 10 mL of hexane and stirred overnight. After the precipitate has settled, the reaction solution is decanted. Recrystallization of the precipitate from THF/hexane give colorless crystals, suitable for X-ray structure analysis.

Be[(NSiMe$_3$)$_2$PPh$_2$]$_2$ (1): M = 28.13 g/mol; yield 31%; mp 53 °C; ^{1}H (C$_6$D$_6$) δ 0.06 (s, 18H), 7.05 (m, 12H), 7.75 (m, 8H); ^{29}Si (C$_6$D$_6$) δ −3.23 (d, $^2J_{Si,P}$ = 3.9 Hz); ^{31}P (C$_6$D$_6$) δ 33.46; MS (70 eV) m/z 727 (100%, M$^+$), 368 (46%, M$^+$ − C$_{18}$H$_{28}$N$_2$PSi$_2$). No elemental analysis was attempted because of the extreme toxicity of beryllium compounds.

Mg[(NSiMe$_3$)$_2$PPh$_2$]$_2$ (2): M = 743.43 g/mol; yield 93%; mp 268 °C; ^{1}H (C$_6$D$_6$) δ 0.130 (s, 18H), 7.15 (m, 12H), 7.92 (m, 8H); ^{29}Si (C$_6$D$_6$) δ −7.71 (d, $^2J_{Si,P}$ = 7.5 Hz); ^{31}P (C$_6$D$_6$) δ 22.48. MS (70 eV) m/z 742 (42% M$^+$), 383 (12% M$^+$ − C$_{18}$H$_{28}$N$_2$PSi$_2$), 356 (100% C$_{15}$H$_{34}$N$_2$PSi$_3$$^+$). Anal. Calcd (found): C, 58.2 (55.78); H, 7.60 (7.80); N, 7.5 (7.01).

Ca[(NSiMe$_3$)$_2$PPh$_2$]$_2$·THF (3): M = 831.30 g/mol; yield 88%; mp 240 °C; ^{1}H (C$_6$D$_6$) δ 0.17 (s, 18H), 1.29 (m, 4H), 3.67 (m, 4H), 7.17 (m, 12H), 7.94 (m, 8H); ^{29}Si (C$_6$D$_6$) δ −11.40 (d, $^2J_{Si,P}$ = 11.5 Hz); ^{31}P (C$_6$D$_6$) δ 14.13; MS (70 eV) m/z 758 (38% M$^+$ − THF), 399 (69% M$^+$ − C$_{22}$H$_{36}$N$_2$OPSi$_2$), 364 (100% M$^+$ − [Ph$_2$P(NHPh)(NSiMe$_3$)$^+$]. Anal. Calcd (found): C, 57.8 (57.54); H, 7.8 (7.77); N, 6.7 (6.52).

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Table 5. Crystal Data of **1**–**5** at $T = 153(2)$ K

	compound				
	1	**2**	**3**	**4**	**5**
formula	C$_{36}$H$_{56}$BeN$_4$P$_2$Si$_4$	C$_{36}$H$_{56}$N$_4$MgP$_2$Si$_4$	C$_{40}$H$_{64}$CaN$_4$OP$_2$Si$_4$	C$_{44}$H$_{72}$N$_4$O$_2$P$_2$Si$_4$Sr	C$_{44}$H$_{72}$BaN$_4$O$_2$P$_2$Si$_4$
fw	728.16	743.46	831.33	950.98	1000.70
cryst size (mm)	0.6 × 0.6 × 0.5	0.7 × 0.6 × 0.4	0.8 × 0.8 × 0.8	0.3 × 0.2 × 0.2	0.8 × 0.7 × 0.2
space group	Cc	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (pm)	1884.5(8)	1275.9(3)	1133.00(10)	1119.50(10)	1131.80(10)
b (pm)	1147.4(3)	1803.0(4)	1156.40(10)	2429.9(3)	2519.8(2)
c (pm)	1983.6(8)	1939.2(4)	1994.8(2)	1838.8(2)	1831.40(10)
α (deg)	90	90	104.162(7)	90	90
β (deg)	100.92(3)	106.21(2)	97.393(6)	92.829(8)	93.106(6)
γ (deg)	90	90	97.258(6)	90	90
V (nm^3)	4.211(3)	4.284(2)	2.4790(4)	5.1255(9)	5.2153(7)
Z	4	4	2	4	4
ρ_c (Mg m^{-3})	1.148	1.153	1.114	1.232	1.274
μ (mm^{-1})	0.246	0.257	0.320	1.245	0.951
$F(000)$	1560	1592	892	2016	2088
2θ range (deg)	8–45	8–45	8–45	8–45	8–45
no. of reflns measd	7910	5670	6353	7174	6842
no. of unique reflns	5515	5608	6217	6701	6838
no. of restraints	2	0	437	279	0
refined params	436	436	595	564	526
$R1^a$ [I > 2σ(I)]	0.026	0.037	0.032	0.035	0.028
w$R2^b$ (all data)	0.067	0.094	0.087	0.100	0.068
$g1$; $g2^c$	0.039; 1.40	0.042; 3.08	0.048; 1.29	0.031; 5.47	0.033; 4.10
highest diff peak (10^{-6} e pm^{-3})	0.16	0.38	0.27	0.29	0.35

^{a} $R1 = \sum ||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^{c} $w = 1/[\sigma^2(F_o^2) + (g1P)^2 + g2P]$; $P = (F_o^2 + 2F_c^2)/3$.

Sr[(NSiMe$_3$)$_2$PPh$_2$]$_2$·2THF (4): M = 970.94 g/mol; yield 80%; mp 155 °C; ^{1}H (C$_6$D$_6$) δ 0.16 (s, 36H), 1.33 (m, 8H), 3.59 (m, 8H), 7.16 (m, 12H), 7.93 (m, 8H); ^{29}Si (C$_6$D$_6$) δ −13.14 (d, $^2J_{Si,P}$ = 13.7 Hz); ^{31}P (C$_6$D$_6$) δ 11.10; MS (70 eV) m/z 806 (40% M$^+$ − 2THF], 447 (84% M$^+$ − C$_{26}$H$_{44}$N$_2$O$_2$PSi$_2$], 387 (100% M$^+$ − C$_{26}$H$_{48}$N$_2$OPSi$_2$]. Anal. Calcd (found): C, 54.4 (54.11); H, 7.5 (7.59); N, 5.8 (5.95).

Ba[(NSiMe$_3$)$_2$PPh$_2$]$_2$·2THF (5): M = 1000.65 g/mol; yield 78%; mp 148 °C; ^{1}H (C$_6$D$_6$) δ 0.17 (s, 18H), 1.35 (m, 8H), 3.581 (m, 8H), 7.16 (m, 12H), 7.93 (m, 8H); ^{29}Si (C$_6$D$_6$) δ −14.44 (d, $^2J_{Si,P}$ = 15.7 Hz); ^{31}P (C$_6$D$_6$) δ 8.02; MS (70 eV) m/z 856 (2% M$^+$ − 2THF), 497 (11% M$^+$ − C$_{26}$H$_{44}$N$_2$O$_2$PSi$_2$]. Anal. Calcd (found): C, 52.8 (51.99); H, 7.3 (7.29); N, 5.6 (5.61).

X-ray Measurements of 1–5. Crystal data for the five structures are presented in Table 5. All data were collected at low temperatures using oil-coated shock-cooled crystals[38] on an Stoe-Siemens AED using monochromated Mo Kα radiation (λ = 0.710 73 Å). A semiempirical absorption correction was applied.[39] The structures were solved by Patterson or direct methods with SHELXS-86.[40] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL-93.[41] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions.

In **3** the disordered trimethylsilyl moiety (Si1−C3) was refined to a split occupancy of 0.7/0.3, while the disordered phenyl ring (C7−C12) was refined to a split occupancy of 0.5/0.5 and the disordered donating THF molecule (O1−C40) was refined to a split occupancy of 0.9/0.1, using bond length and similarity restraints.

The two disordered THF molecules in **4** were refined to split occupancy of 0.7/0.3 (O1−C40) and 0.5/0.5 (O2−C44). Selected bond lengths and angles are presented in Table 1. Further details on the structure investigation can be obtained from the Director of the Cambridge Crystallographic Data Center, 12 Union Road, GB-Cambridge CB2 1EZ, U.K., by quoting the full journal citation.

Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**−**5** are available on the Internet only. Access information is given on any current masthead page.

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