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1,3-Bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide Anions as Bidentate Ligands for the Alkaline Earth Metals Magnesium, Calcium, Strontium, and Barium

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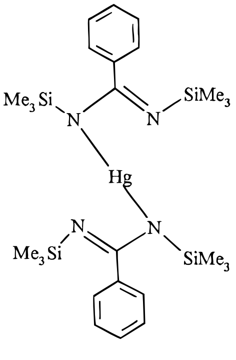
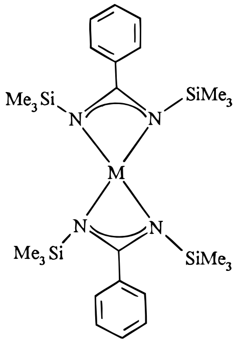
The tetrahydrofuran complexes of the alkaline earth metal bis[bis(trimethylsilyl)phosphanides] react with 2 equiv of benzonitrile to the bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenides] of magnesium (**1**), calcium (**2**), strontium (**3**), and barium (**4**). Whereas **1** and **2** crystallize as bis(tetrahydrofuran) adducts, the heavier homologous derivatives **3** and **4** precipitate as tris(tetrahydrofuran) complexes. The bidentate trans/trans-isomeric 1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide ligands of all these compounds display very similar spectroscopic data; however, the influence of the alkaline earth metal is observed in the silicon NMR. The nitrogen atoms of these anions have trigonal planar geometry, whereas the phosphorus atoms are coordinated trigonal pyramidal. Crystallographic data: **1**, monoclinic, $P2_1/c$, $a = 1505.3(3)$ pm, $b = 1259.0(2)$ pm, $c = 2278.4(5)$ pm, $\beta = 91.91(2)°$, $Z = 4$, wR2 = 0.1279; **2**, monoclinic, $P2_1/c$, $a = 1522.8(7)$ pm, $b = 1279.2(5)$ pm, $c = 2314.0(10)$ pm, $\beta = 92.53(2)°$, $Z = 4$, wR2 = 0.1513; **3**, triclinic, $P\bar{1}$, $a = 1144.8(3)$ pm, b = 1579.4(6) pm, c = 1670.6(6) pm, $\alpha = 98.02(3)°$, $\beta = 109.67(3)°$, $\gamma = 104.18(3)°$, $Z = 2$, wR2 = 0.1745; **4**, triclinic, $P\bar{1}$, $a = 1245.2(4)$ pm, $b = 1907.1(4)$ pm, $c = 2212.3(7)$ pm, $\alpha = 76.46(2)°$, $\beta = 76.45(2)°$, $\gamma = 89.31(2)°$, $Z = 4$, wR2 = 0.1409.

Introduction

The *N*,*N*′-bis(trimethylsilyl)benzamidinates of the main group and transition metals as well as f elements are well investigated compounds.[1] Besides the possibility to coordinate as a mono-[2] (**I**) as well as a bidentate ligand[1,3] (**II**) dependent on the nature of the metal atom the steric demand of this ligand allowed the characterization and structural investigation of numerous derivatives. The *N*,*N*′-bis(trimethylsilyl)benzamidinates of the alkaline earth metals are easily accessible by the addition reaction of benzonitrile to the alkaline earth metal bis[bis(trimethylsilyl)amides].[4] In contrast to this well-investigated compound class the heavier homologous ligand modified by a formal substitution of one nitrogen by a phosphorus atom could attract only scarce attention so far.



I



II

Very few examples for 1-aza-3-phosphapropenides bonded to alkaline metals exist, but as far as we know there are no investigations concerning the other transition or main group metal derivatives. Although Issleib and co-workers[5] characterized a potassium salt 20 years ago by a chemical ^{31}P NMR shift of −102 ppm, no singly substituted lithium 1-aza-3-phosphapropenides have been structurally characterized so far. Solid state structures of these lithium complexes reveal the delocalization of the anionic charge. However, the lithium atom is bonded to the nitrogen atom of this monodentate ligand. Niecke and co-workers[6] isolated the lithium complex **III** of a cis/cis isomeric 1-aza-3-phosphapropenide anion, whereas Becker and co-workers[7] synthesized (lithio(trimethylsilyl)amido]benzylidene)-phenylphosphane, **IV**, with a lithium−phosphorus contact of 292.4 pm. The cis configuration at the phosphorus carbon multiple bond is stabilized by interaction of the metal atom with the phenyl substituent indicated by a lithium ipso-carbon distance of 240.4 pm.[7]

In contrast to these derivatives, where a phenyl substituent at the phosphorus atom enhances the stability of the 1-aza-3-phosphaallylic fragment, the 3-trimethylsilyl substituted 1-aza-3-phosphapropenide undergoes further reactions as summarized in eq1.[7] Nevertheless, the ^{13}C and ^{31}P NMR spectroscopic data confirm the formation of the 1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphaallyl anion **V** as an intermediate. Even at −50

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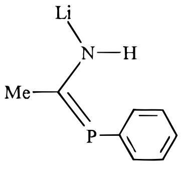
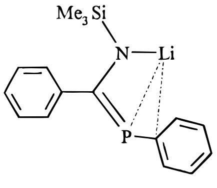
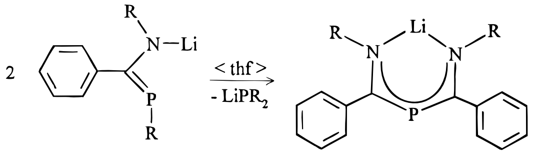


III



IV

°C this compound rearranges under loss of lithium bis(trimethylsilyl)phosphanide to yield lithium bis((trimethylsilylimino)benzoyl)phosphanide, **VI**.[7]



(1)

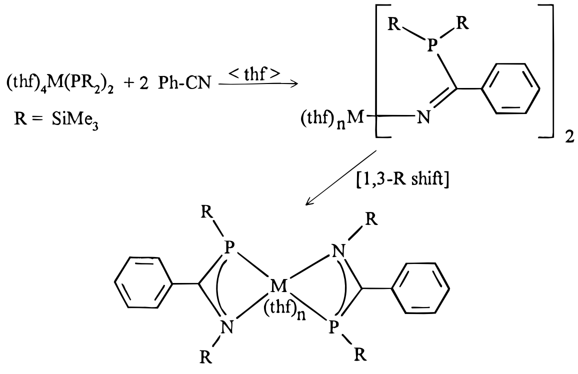
V **VI**

R = SiMe$_3$

The use of the alkaline earth metal bis[bis(trimethylsilyl)phosphanides] now offers us the opportunity to compare the reactivity of these compounds with lithium bis(trimethylsilyl)phosphanide. On the other hand, the comparison of the *N,N′*-bis(trimethylsilyl)benzamidinates with the homologous 1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenides of the alkaline earth metals shows the influence on the spectroscopic and structural parameters by a formal substitution of the nitrogen by the heavier phosphorus atom.

Results and Discussion

Preparation. The addition reaction of the tetrahydrofuran complexes of the alkaline earth metal bis[bis(trimethylsilyl)phosphanides][8] to benzonitrile in tetrahydrofuran followed by a 1,3-trimethylsilyl shift from the phosphorus to the nitrogen atom yields quantitatively the tetrahydrofuran adducts of the alkaline earth metal bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenides] of magnesium (**1**), calcium (**2**), strontium (**3**), and barium (**4**) according to eq 2. If the alkaline earth metal bis(imide) is the initial intermediate, the 1,3-trimethylsilyl shift seems to be characteristic for the benzamidinates as well as the phophabenzamidinates. All these derivatives are stable under an inert gas atmosphere for an extended time period, and a rearrangement to the above-mentioned anion of molecule **IV** was not observed at room temperature. These slightly orange-yellow 1-aza-3-phosphapropenides are air- and moisture-sensitive.



(2)

M/n = Mg/2 (1), Ca/2 (2), Sr/3 (3), Ba/3 (4)

Spectroscopic Data. The $\delta(^{13}C\{^1H\})$ values of the allylic NCP fragments lie around 222 ppm (Table 1) and show a stronger deshielding than the phenyl P-substituted lithium 1-aza-3-phosphapropenides with chemical shifts between 199 and 212 ppm.[6,7] The $^1J(P-C)$ coupling constants of approximately 50 Hz are smaller than those in the PhP=C(R)N(R) anions[6,7] bonded via the nitrogen atom to lithium. The $\delta(^{31}P\{^1H\})$ values are shifted toward higher field due to the coordinated trimethylsilyl group instead of the phenyl ligand at the phosphorus atom.

On the other hand the comparison with the alkaline earth metal bis[*N,N′*-bis(trimethylsilyl)benzamidinates][4] clearly shows the influence of the formal replacement of a nitrogen by a heavier phosphorus atom. The *N,N′*-bis(trimethylsilyl)benzamidinate substituents coordinate as bidentate ligands; however, the NMR spectroscopic parameters display nearly no dependency on the size of the alkaline earth metal. The carbon atom of the 1,3-diazaallyl moiety displays a chemical shift of 180 ppm.[4] In contrast to the missing sensitivity toward the alkaline earth metal atom the $\delta(^{29}Si\{^1H\})$ values of the trimethylsilyl substituents bonded to the nitrogen atoms show a shift toward higher field with increasing size of the metal center. The $^{13}C\{^1H\}$ resonance of the 1-aza-3-phosphapropenide moiety is shifted to lower field of approximately 40 ppm compared to the NCN fragment. Furthermore, the influence of the alkaline earth metal atom on the chemical $^{29}Si\{^1H\}$ NMR shift decreases on replacement of the nitrogen by a phosphorus atom. The influence of the alkaline earth metal is marginal since the lithium derivative displays similar $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data. This

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Table 1. NMR Data of the thf Complexes of the Alkaline Earth Metal Bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenides] Moieties of the Type $(thf)_nM[Me_3SiNC(Ph)PSiMe_3]_2$, Recorded in $[D_8]$Tetrahydrofuran at 30 °C (Chemical Shifts [ppm], Coupling Constants [Hz])

	1	**2**	**3**	**4**
M/*n*	Mg/2	Ca/2	Sr/3	Ba/3
	^{1}H NMR			
δ(NSiMe$_3$)	−0.08	−0.08	−0.15	−0.17
δ(PSiMe$_3$)	−0.12	−0.15	−0.23	−0.25
^{3}J(P-H)	4.4	4.4	4.0	3.3
δ(Ph)	7.0−7.3	7.0−7.3	7.0−7.3	7.0−7.3
	^{13}C{^{1}H} NMR			
δ(NSiMe$_3$)	3.00	2.95	2.57	2.22
δ(PSiMe$_3$)	4.13	3.37	3.19	3.31
$\lvert ^2J(P-C) + ^4J(P'-C)\rvert^a$	11.3	13.1	12.9	13.0
δ(NCP)	223.11	223.32	222.33	221.63
$\lvert ^1J(P-C) + ^3J(P'-C)\rvert^a$	42.5	50.6	49.7	53.1
δ(i-C,Ph)	150.31	151.66	151.56	151.95
$\lvert ^2J(P-C) + ^4J(P'-C)\rvert^a$	6.6	<1.5	4.6	<1.5
δ(o-C,Ph)	127.97	128.26	127.75	127.76
δ(m-C,Ph)	127.30	127.38	126.82	126.77
δ(p-C,Ph)	127.26	127.98	126.82	126.55
	^{29}Si{^{1}H} NMR			
δ(NSi)	−2.26	−5.36	−8.06	−9.40
$\lvert ^3J(P-Si) + ^3J(P'-Si)\rvert^{a,b}$	18.1	17.0	19.6	19.2
δ(PSi)	−3.05	−3.59	−4.15	−4.51
$\lvert ^1J(P-Si) + ^3J(P'-Si)\rvert^a$	44.7	43.5	45.9	50.8
	^{31}P{^{1}H} NMR			
δ(P)	−7.76	−13.09	−9.13	−1.33

[a] Evaluation of a X-part of a AA′X coupling system; the phosphorus nuclei of the regarded and the other ligand are distuingished by P and P′, respectively. [b] Intraligand (*Si*−N−C−*P*) and interligand (*Si*−N−M−*P′*) coupling routes.

lack of sensitivity toward the size and nature of the central metal atom states the mainly ionic bonding situation of these compounds.

The interpretation of the coupling between phosphorus and the carbon and silicon nuclei is somewhat complicated due to the observation of a X-part of an AA′X coupling system. The easily obtainable sum of the coupling constants $|^1J(P-Si) + ^3J(P'-Si)|$ varies with the size of the alkaline earth metal atom within a small region (Table 1). The values between 43.5 Hz for the calcium derivative **2** and 50.8 Hz for the barium compound **4** (Table 1) are even greater than in the tetrahydrofuran complexes of the alkaline earth metal bis[bis(trimethylsilyl)phosphanides], although the P−Si bond length of the 1-aza-3-phosphapropenide ligand is increased. An explanation for this observation offers the enhanced phosphorus s orbital participation at the P−Si bond. This fact is supported by the enhanced Si−P−C bond angles discussed later compared to the rather small Si−P−Si angles of the bis(trimethylsilyl)phosphanides of the alkaline earth metals.[8] The $^2J(P-P')$ coupling constants of the alkaline earth metal 1-aza-3-phosphapropenides are, with values around 4 Hz, rather small; the $^2J(P-P')$ values of the starting alkaline earth metal bis[bis(trimethylsilyl)phosphanides] are larger presumingly due to smaller metal phosphorus distances.

Molecular Structures. The molecular structures of the derivatives **1** to **4** are dominated by the steric bulk of the 1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide moiety. Figures 1 and 2 show the molecular structures of the isotypic magnesium (**1**) and calcium (**2**) derivatives, respectively. Both these compounds are bis(tetrahydrofuran) adducts. The heavier homologous derivatives contain three tetrahydrofuran molecules coordinated at the metal center. Figure 3 displays the molecular structure of **3**. Compound **4** shows a unique crystallization behavior since the cis and trans isomer cocrystallize from tetrahydrofuran at −20 °C. The presentation of the molecular

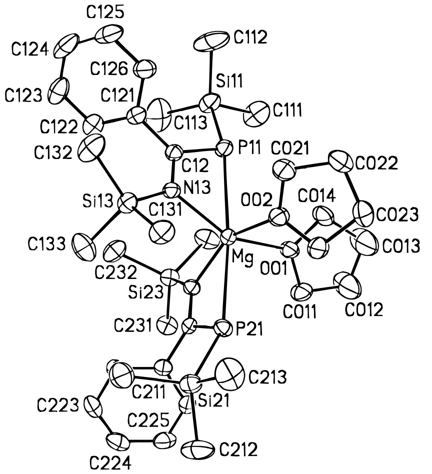

Figure 1. Molecular structure and numbering scheme of **1**. The ellipsoids represent a 50% probability. The hydrogen atoms are omitted for clarity.

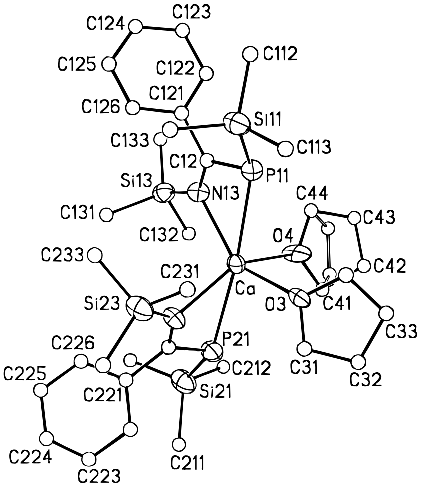

Figure 2. Molecular structure and numbering scheme of **2**. The ellipsoids represent a 50% probability. The hydrogen atoms are omitted for clarity and the carbon atoms drawn with arbitrary radii. The disordering within one of the tetrahydrofuran molecules is shown.

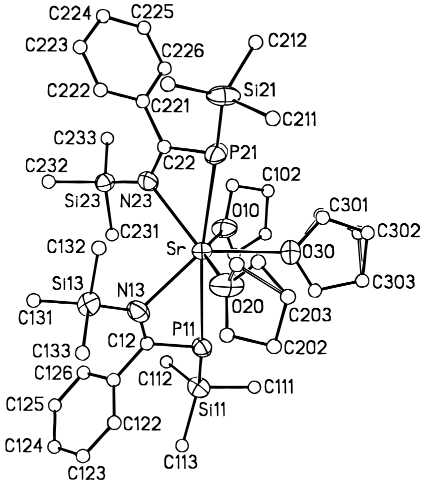

Figure 3. Molecular structure and numbering scheme of **3**. The ellipsoids represent a 50% probability. The hydrogen atoms are omitted for clarity and the carbon atoms drawn with arbitrary radii. The disordering of some methylene groups within two of the tetrahydrofuran molecules is shown.

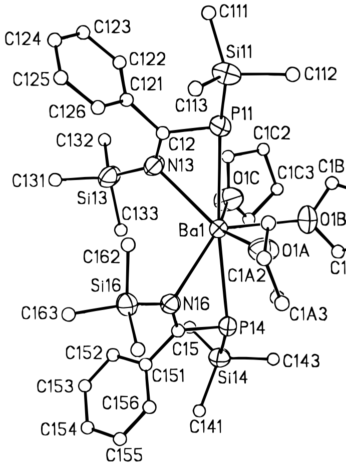

Figure 4. Molecular structure and numbering scheme of cis-isomeric barium derivative **4**. The ellipsoids represent a 50% probability. The hydrogen atoms are omitted for clarity and the carbon atoms drawn with arbitrary radii.

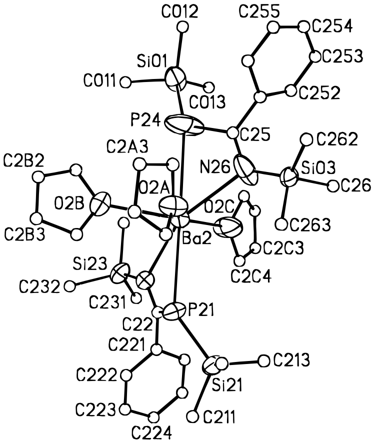

Figure 5. Molecular structure and numbering scheme of the trans-isomer of **4**. The ellipsoids represent a 50% probability. The hydrogen atoms are omitted for clarity and the carbon atoms drawn with arbitrary radii. The disordering of the upper 1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide ligand is not shown.

structures in Figures 4 and 5 clearly show the differences of these isomeres discussed later in detail. The numbering schemes of these compounds can be seen in the Figures 1−5. A remarkable common ground of these derivatives is the trans-orientation of the phosphorus atoms with a linear P−M−P arrangement. A cis or trans configuration of the ligands at the alkaline earth metals is caused by a rotation of the allylic system around the M−P bond.

The distorted octahedral environment of the magnesium and calcium atoms both presented in Figure 6 are very similar. The small bite (intraligand N···P distance) of the bidentate ligand leads to an elongation of the nitrogen atoms out of the MO_2 plane. The larger van der Waals radii of the heavier alkaline earth metals allow the coordination of the third tetrahydrofuran molecule. The environments of the metal centers Sr and Ba1 in **3** and *cis*-**4**, respectively, are very similar and best described as pentagonal bipyramids with trans-configurated phosphorus atoms in the apical positions, distorted due to the small bites of the bidentate heteroallyl ligands. The large barium atom and the resulting small NBaP angles of 52.3 and 53.7° lead also for Ba2 to a strong distortion of the pentagonal bipyramide with the apical positioned phosphorus atoms. The difference between the two molecules *cis*-**4** and *trans*-**4** is best seen in the arrangement of the nitrogen atoms. The cis-orientated molecule contains two neighboring nitrogen atoms in the equatorial plane,

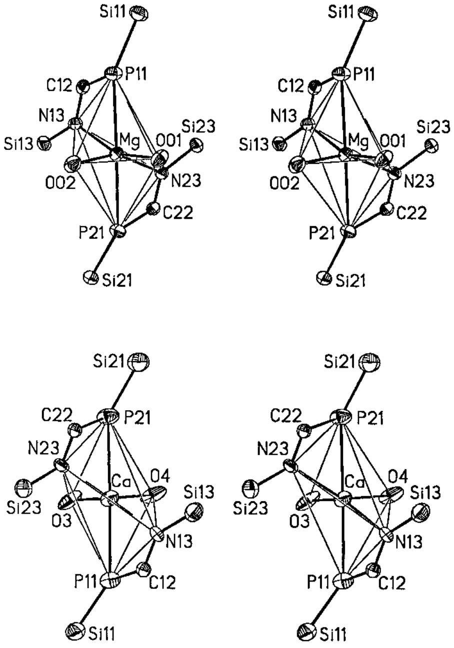

Figure 6. Stereoscopic representation of the coordination sphere of magnesium in **1** (above) and of the calcium atom in **2** (below). Thick lines represent bonds; thin lines serve to clarify the polyhedron.

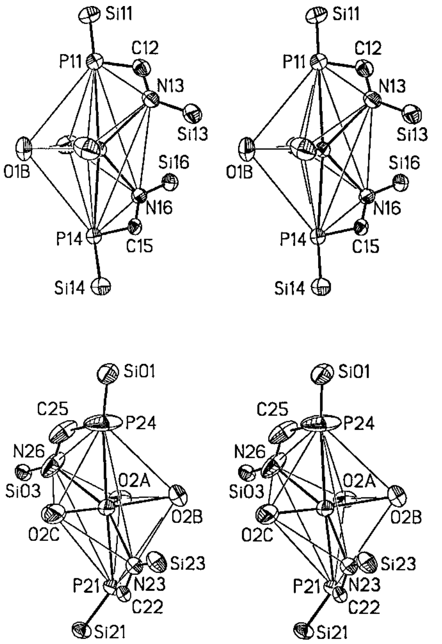

Figure 7. Comparison of the stereoscopically drawn coordination polyhedra of Ba1 (above) and Ba2 (below) of the two isomers of **4**.

whereas the other one shows a tetrahydrofuran molecule between the coordination sites of the nitrogen atoms. One of the two propenide ligands of *trans*-**4** shows a two-site disordering of both the trimethylsilyl groups and is therefore not taken into account for the discussion of the structural parameters.

In accord with the NMR spectroscopic characterization the allyl ligands of all these compounds look almost alike (Table 2) and are discussed together. The NC and PC bond lengths lie between a single and a double bond, clearly stating the delocalization of the anionic charge. In contrast to the only known 1-aza-3-phosphapropenide systems so far where lithium atoms bond to the nitrogen atoms,[6,7] the 1,3-bis(trimethylsilyl) substituted allyl ligands coordinate in a bidentate fashion to the alkaline earth metals. Three different configurations are observed for 1-aza-3-phosphaallyl ligands so far: Niecke and

Table 2. Selected Bond Lengths (pm) and Angles (deg) of the Tetrahydrofuran Complexes of the Alkaline Earth Metal Bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide] Moieties of the Type $(thf)_nM[Me_3SiNC(Ph)PSiMe_3]_2$

	1	**2**	**3**	*cis*-**4**	*trans*-**4**
M/*n*	Mg/2	Ca/2	Sr/3	Ba/3	Ba/3
M−O	213.5(2)	233(1)	260.9(9)	276.0(5)	276.5(5)
	212.0(2)	235(1)	259.6(7)	278.6(5)	274.8(5)
			261.7(6)	277.0(5)	274.6(6)
M−N	218.8(2)	245(1)	263.1(7)	277.2(5)	278.9(5)
	219.4(2)	246(1)	266.3(8)	277.6(5)	279.0(6)
M−P	274.4(1)	288.7(5)	308.8(3)	324.3(2)	321.6(2)
	271.5(1)	289.8(5)	306.2(4)	323.4(2)	320.4(2)
N−Si	175.3(2)	174(1)	175(1)	173.0(5)	173.1(6)
	175.3(2)	174(1)	174.8(6)	172.7(5)	173(1)/173(1)[a]
P−Si	222.5(1)	221.6(6)	220.2(5)	221.5(3)	222.4(3)
	222.2(1)	220.1(6)	220.4(6)	222.4(3)	214.7(5)/218.6(5)[a]
N−C	132.3(3)	130(1)	127(2)	130.7(8)	131.0(7)
	131.9(3)	129(1)	131(1)	131.0(7)	135(1)
P−C	176.8(3)	175(1)	181(1)	179.4(7)	177.5(7)
	177.9(3)	178(1)	179.2(7)	178.6(6)	177.2(10)
Si−N−C	127.9(2)	133.3(9)	128.9(7)	131.8(4)	131.8(5)
	128.1(2)	132.5(9)	128.9(7)	130.6(4)	120.9(6)/141.7(6)[a]
N−C−P	116.8(2)	120.8(10)	119.3(7)	118.0(5)	119.2(5)
	116.4(2)	120.5(10)	119.2(8)	119.5(4)	121.3(5)
C−P−Si	110.5(1)	110.3(5)	110.3(4)	110.5(2)	110.4(2)
	110.5(1)	111.0(5)	109.9(5)	109.2(2)	99.9(4)/118.9(3)[a]
ΣXNX	359.9	359.0	359.6	358.7	359.4
	359.9	358.9	359.8	357.5	356.2/359.9[a]
ΣXPX	336.5	328.8	334.3	336.3	330.5
	333.3	333.6	346.1	326.1	346.8/358.2[a]
P−M−P	174.49(4)	174.6(2)	171.23(6)	173.92(4)	169.08(8)
N−M−N	104.86(9)	109.7(4)	97.5(3)	102.9(2)	152.3(2)

[a] The trimethylsilyl substituents are disordered in two positions.

Table 3. Calculated Planes and Distances of Selected Atoms (pm, in Parentheses) Where Atoms Marked with an Asterisk Are Used for the Calculation of the Planes

plane	atoms and distances	angle φ[a]
1/A	P11*, C12*, C121*, N13*, Mg (−42), Si11 (−70), Si13 (20)	
1/B	P21*, C22*, C221*, N23*, Mg (−28), Si21 (−93), Si23 (15)	98
2/A	P11*, C12*, C121*, N13*, Ca (55), Si11 (94), Si13 (−10)	
2/B	P21*, C22*, C221*, N23*, Ca (−67), Si21 (−69), Si23 (18)	76
3/A	P11*, C12*, C121*, N13*, Sr (−73), Si11 (−68), Si13 (29)	
3/B	P21*, C22*, C221*, N23*, Sr (4), Si21(76), Si23 (−15)	54
cis **4**/A	P11*, C12*, C121*, N13*, Ba1 (106), Si11 (46), Si13 (−27)	
cis **4**/B	P14*, C15*, C151*, N16*, Ba1 (−127), Si14 (−65), Si16 (25)	36
trans **4**/A	P21*, C22*, C221*, N23*, Ba2 (99), Si21 (74), Si23 (−34)	
trans **4**/B	P24*, C25*, C251*, N26*, Ba2 (−12), Si01 (93), Si03 (−45)	50

[a] Intramolecular angles φ of intersection (deg) between the normals of the calculated planes.

co-workers isolated the cis/cis-$PhP{=}C(Me)N(H)$ anion,[6] whereas Becker and co-workers characterized the cis/trans isomeric $PhP{=}C(Ph)N(SiMe_3)$ anion;[7] the compounds presented here crystallize with trans/trans isomeric ligands. The bidentate alkaline earth metal bis[*N*,*N*′-bis(trimethylsilyl)benzamidinates] show a strictly planar SiN−C−NSi moiety, whereas the exchange of one nitrogen atom against a phosphorus atom alters the environment of the heavier pnicogen atom: in contrast to the trigonal planar CN(Si)M fragment, the CP(Si)M substructure adopts a trigonal pyramidal coordination at the phosphorus atom (Table 2). Furthermore, the SiPC bond angles with values around 110° are a lot smaller than the SiNC angles of approximately 130°. Due to rather short NSi and CN bond lengths the steric repulsion between the phenyl substituent and the trimethylsilyl group enforces the enlargement of the CNSi bond angle and a nearly orthogonal orientation of the normals of the phenyl and allyl planes.

Table 3 summarizes some of these relations and also shows the distances of the silicon atoms to the planes of the NCP−allyl moieties. The deviation from the NCP planes has to be explained differently for the N- and P-bonded silicon atoms: whereas the phosphorus atoms are surrounded pyramidically the M(Si)NC planes are slightly twisted against the allyl plane. Moreover, with increasing size of the alkaline earth metal atoms and consequently of the M−N and M−P bond lengths, the repulsion between the trimethylsilyl groups of the two 1-aza-3-phosphapropenide ligands diminishes, and the interligand twisting decreases as can be seen from the angles φ of intersection between the normals of the calculated NCP planes.

Conclusion

The size of the alkaline earth metal determines the content of tetrahydrofuran molecules coordinated to the metal center, but there is nearly no significant influence on the spectroscopic and structural parameters of the 1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide ligands, thus proving the mainly ionic appearance of these compounds. In contrast to this observation the *N*,*N*′-bis(trimethylsilyl)benzamidinate ligand and the homologous 1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide substituent show characteristic differences. The formal replacement of the nitrogen by a phosphorus atom leads to a strong low field shift of the allyl carbon atom. However, the most striking feature is the pyramidal coordination at the phosphorus, whereas the nitrogen atoms display angle sums of around 360°.

The bidentate coordination of these ligands to the alkaline earth metals leads to a kinetic stabilisation since the lithium derivative reacts to lithium bis(trimethylsilyl)phosphanide and lithium bis((trimethylsilylimino)benzoyl)phosphanide. Therefore the reduced reactivity of the alkaline earth metal derivatives compared to the lithium compounds could be due to the higher steric shielding of the vacant site at the phosphorus atom by coordination to the metal dication. Similar spectroscopic data exclude other factors such as electronic effects of the metal centers.

Experimental Section

All operations were carried out under an oxygen-free argon atmosphere by using standard Schlenk techniques, with all solvents rigorously dried and distilled under argon by standard methods. The deuterated solvents were degassed by three consecutive freeze−pump−thaw cycles and saturated with argon prior use. The synthesis of the alkaline earth metal bis[bis(trimethylsilyl)phosphanides] followed the reported procedures.[8] The measurement of the NMR spectra succeeded on Bruker AM200 and Bruker AC250 instruments. The IR spectra were recorded on Perkin-Elmer spectrophotometers; the listing of the bands around 2900 and 1450 cm^{-1} was omitted due to overlapping with the CH stretching and deformation frequencies of Nujol. The melting points were measured under argon in sealed capillaries and are uncorrected. The low carbon values at the elemental analysis result from carbide formation and loss of tetrahydrofuran during handling of the compounds.

Synthesis of Bis(tetrahydrofuran)magnesium Bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide], 1. To a solution of 0.96 g of $(dme)Mg[P(SiMe_3)_2]_2$ (2.04 mmol) in 4 mL of tetrahydrofuran was added 0.42 mL of benzonitrile (4.08 mmol) slowly at room temperature. The colorless solution turned orange-red im-

Table 4. Summary of Crystallographic Data of **1**−**4** as Well as Details of the Structure Solution and Refinement Procedures

	1	**2**	**3**	**4**
empirical formula	$MgP_2Si_4O_2N_2C_{34}H_{62}$	$CaP_2Si_4O_2N_2C_{34}H_{62}$	$SrP_2Si_4O_4N_2C_{42}H_{78}$	$BaP_2Si_4O_3N_2C_{38}H_{70}$
fw (g mol^{-1})	729.47	745.24	936.98	914.60
temp T (°C)	−90	−90	−90	−90
space group[9]	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
unit cell dimens				
a (Å)	15.053(3)	15.228(7)	11.448(3)	12.452(4)
b (Å)	12.590(2)	12.792(5)	15.794(6)	19.071(4)
c (Å)	22.784(5)	23.140(10)	16.706(6)	22.123(7)
α (deg)	90	90	98.02(3)	76.46(2)
β (deg)	91.91(2)	92.53(2)	109.67(3)	76.45(2)
γ (deg)	90	90	104.18(3)	89.31(2)
V (nm^3)	4316(1)	4503(3)	2675(2)	4960(3)
Z	4	4	2	4
ρ_{calcd} (g cm^{-3})	1.123	1.099	1.163	1.225
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (cm^{-1}, Mo-K$_\alpha$)	2.56	3.45	11.93	9.94
abs corr	none	none	Y-scan	none
no. of data collcd	8809	1935	5717	15580
no. of indep data (R_{int})	8483 (0.1009)	1817 (0.1131)	5698 (0.0639)	15558 (0.0164)
no. of params	530	245	543	952
no. of restraints	0	42	0	32
goodness-of-fits on F^2 [a]	1.029	1.068	1.210	1.298
R indices [all data]				
R1[b]	0.0896	0.1060	0.1282	0.0946
wR2[b]	0.1279	0.1513	0.1745	0.1409
R indices				
[$I > 2\sigma(I)$, data]	5791	1259	3703	11109
R1[b]	0.0511	0.0644	0.0746	0.0590
wR2[b]	0.1092	0.1372	0.1563	0.1309

[a] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$. [b] Definition of the R indices:[10] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

mediately. After 3 h of stirring, the reaction solution was concentrated to approximately 1 mL. Cooling to −20 °C yielded 1.08 g of **1** (1.48 mmol, 72.5%) as slightly yellow crystals.

Mp: 109°C dec. NMR data are listed in Table 1. IR (Nujol, CsBr): 1304 m, 1248 m, 1209 m, 1170 w, 1152 w, 1073 m, 1030 w, 1001 w, 961 w, 908 w, 862 sh, 839 vs, 759 m, 700 m, 683 w, 659 w, 625 w, 544 w, 476 w, 457 w. Anal. Found (calcd for $MgP_2Si_4O_2N_2C_{34}H_{62}$, 729.47 g mol^{-1}): C, 52.43 (55.98); H, 8.11 (8.57), N 4.01 (3.84).

Synthesis of Bis(tetrahydrofuran)calcium Bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide], 2. To a solution of 1.23 g of tris(tetrahydrofuran)calcium bis[bis(trimethlysilyl)phosphanide] (2.01 mmol) in 10 mL of tetrahydrofuran was added 0.415 g of benzonitrile (4.02 mmol) slowly. The color of the solution changed from yellow to red. After 12 h of stirring, the solution was concentrated. At −65 °C, small red crystals separated from this solution. The isolated solid was dried in vacuum. Yield: 0.86 g (1.15 mmol), 57%.

Mp: 125−131°C dec. NMR data are summarized in Table 1. IR (Nujol, CsBr): 3087 m, 3072 m, 3043 s, 1594 w, 1573 w, 1504 sh, 1456 vs, 1427 vs, 1322 m, 1304 sh, 1294 m, 1255 s, 1244 vs, 1237 vs, 1206 vs, 1172 m, 1151 m, 1113 w, 1069 m, 1040 vs, 998 w, 983 w, 956 vs, 906 vs, 864 vs, 833 vs, 784 vs, 757 vs, 746 vs, 703 vs, 680 vs, 652 m, 627 vs, 611 s, 543 m, 472 s. MS (70 eV, sample temperature 410 K): 424 (0.2%), 384 (0.3%), 321 (0.3%, $HCa(Me_3SiNCPhPSiMe_3)$), 281 (1.5%, $Me_3SiN(H)CPhPSiMe_3$), 266 (1.1%), 250 (2.0%, $P(SiMe_3)_3$), 178 (12%), 176 (17%), 103 (8%), 73 (34%, $SiMe_3$), 72 (37%, thf), 42 (100%, $SiCH_2$). Anal. Found (calcd for $CaP_2Si_4ON_2C_{30}H_{54}$, 673.13 g mol^{-1}): C, 52.13 (53.53), H, 8.12 (8.19), N, 3.84 (4.16).

Synthesis of Tris(tetrahydrofuran)strontium Bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide], 3. 1.78 mL of aliquot bis(trimethylsilyl)phosphane (8.18 mmol) was added to 2.26 g of $(thf)_2Sr[N(SiMe_3)_2]_2$ (4.09 mmol) in 10 mL of tetrahydrofuran. After formation of strontium bis[bis(trimethylsilyl)phosphanide], 0.83 mL of benzonitrile was dropped into this solution, which turned red immediately. At room temperature, three-fourths of the solution was distilled off in vacuum. Cooling of the remaining mother liquor to −20 °C led to precipitation of 1.67 g of **3** (1.78 mmol, 43.5%) as slightly yellow plates.

Mp: 83 °C dec. NMR parameters are listed in Table 1. IR (Nujol, CsBr): 1307 w, 1246 m, 1204 m, 1172 w, 1154 w, 1073 m, 1039 m, 1001 w, 955 w, 903 w, 863 sh, 835 vs, 782 w, 740 m, 699 m, 673 w, 626 m, 609 w, 545 w, 469 w, 431 m. Anal. Found (calcd for $SrP_2Si_4ON_2C_{30}H_{54}$, 720.67 g mol^{-1}): C, 48.68 (50.00); H, 7.52 (7.55), N 3.76 (3.89).

Synthesis of Tris(tetrahydrofuran)barium Bis[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenide], 4. To a solution of barium bis[bis(trimethylsilyl)phosphanide] prepared from 3.80 g of bis(tetrahydrofuran)barium bis[bis(trimethylsilyl)amide] (6.31 mmol) and 2.25 g of bis(trimethylsilyl)phosphane (12.62 mmol) in 15 mL of tetrahydrofuran was added 1.3 g of benzonitrile (12.62 mmol) slowly at room temperature. After being stirred overnight, the red solution was concentrated to half of the amount. Red crystals precipitated at −20 °C and were dried in vacuum at room temperature. Yield: 3.18 g (3.48 mmol), 55%.

Mp: 97−103 °C dec. NMR data are listed in Table 1. IR (Nujol, CsBr): 3057 w, 1594 w, 1416 vs, 1373 m, 1244 s, 1205 s, 1070 w, 1037 w, 998 w, 957 m, 931 w, 906 m, 866 sh, 836 vs, 776 m, 755 m, 745 m, 701 s, 676 m, 629 s, 613 w, 544 w, 467 m, 429 m. Anal. Found (calcd for $BaP_2Si_4ON_2C_{30}H_{54}$, 770.35 g mol^{-1}): C, 45.21 (46.77); H, 6.89 (7.07), N 3.68 (3.64).

X-ray Structure Analysis. Suitable single crystals of the derivatives **1**−**4** were covered with Nujol and sealed in thin-walled glas capillaries. The crystal structure analysis were performed on the diffractometers Syntex P2$_1$ (**3** and **4**) and Siemens P4 (**1** and **2**) with graphite-monochromated Mo Kα radiation. Only for the strontium derivative **3** was a semiempirical absorption correction (Ψ-scan) applied. A semiempirical absorption correction for **4** did not lead to an improvement of the R values nor to smaller standard deviations of the molecular parameters and therefore, no Ψ-scan correction was taken into consideration. The crystals of the calcium compound **2** showed poor diffraction properties, in the region of $2\theta > 35°$ nearly no intensities were recorded. The crystallographic data as well as details of the structure solution and refinement procedures are summarized in Table 4.

The crystal structures were solved by direct methods (**1** and **2**) or Patterson methods (**3** and **4**) with the program SHELXTL Plus.[10] The refinement of the structures succeeded with the program packages

SHELXL-93 and SHELXTL PC, version 5.03,[10] where the function $\sum[w(F_o^2 - F_c^2)^2]$ was minimized. All non-hydrogen atoms were refined anisotropically with the exception of those for compound **2**, where the carbon atoms were taken into consideration isotropically. For the calculations the atom form factors of the neutral atoms were used.[11] The hydrogen atoms of **2** and **4** were taken into account in idealized positions by the riding model with fixed *U* values and a C−H distance of 96 pm. For derivative **3** the C−H bond lengths were refined groupwise, whereas the H atoms of **1** were refined isotropically with restriction to the idealized geometry at the corresponding carbon atoms.

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Supporting Information Available: For compounds **1**−**4**, tables of positional coordinates, bond distances, bond angles, fractional parameters of all H atoms, and thermal parameters of all non-H atoms and stereoscopic views of the molecular structures and unit cells (43 pages). Ordering information is given on any current masthead page.

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