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Synthesis of Tris(1,2-dimethoxyethane-O,O′)barium Bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide) and the Monomer−Dimer Equilibrium in Toluene Solution

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(1,2-Dimethoxyethane-O,O′)lithium phosphanide (dme)$LiPH_2$ reacts with 1,2-bis(chloro-dimethylsilyl)ethane to give 2,2,5,5-tetramethyl-2,5-disilaphospholane, **1**, as well as 1,1,4,4-tetramethyl-1,4-bis(2,2,5,5-tetramethyl-2,5-disilaphospholanyl)-1,4-disilabutane, **2** ($P_2Si_6C_{18}H_{48}$, space group $P\bar{1}$, $a = 943.3(2)$ pm, $b = 1278.3(3)$ pm, $c = 1413.3(2)$ pm, $\alpha = 72.45(1)°$, $\beta = 78.13(1)°$, $\gamma = 70.83(1)°$, $d = 1.081$ g cm^{-3}, $Z = 2$, wR2 = 0.1553 at 6548 F^2 values). The reaction of 2,2,5,5-tetramethyl-2,5-disilaphospholane **1** and barium bis[bis(trimethylsilyl)amide] in 1,2-dimethoxyethane yields nearly quantitatively tris(1,2-dimethoxyethane-O,O′)barium bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide), **3A**, which crystallizes in the monoclinic space group $C2/c$ ($BaP_2Si_4O_6C_{24}H_{62}$, $a = 2152.3(1)$ pm, $b = 1381.5(1)$ pm, $c = 1459.7(1)$ pm, $\beta = 113.73(1)°$, $d_{calc} = 1.268$ g cm^{-3}, $Z = 4$, wR2 = 0.0989 at 5220 F^2 values). Due to the high coordination number of eight of the barium center, rather long Ba−P distances of 333 pm are observed. With loss of the complexating ether solvent this compound forms a dimer **3B** of the type R(dme)Ba(μ-R)$_3$Ba(dme)$_2$ in toluene or benzene solution as can be proven by $^{31}P\{^1H\}$-NMR spectroscopy (^2J(P−P) = 6.7 Hz) and by X-ray structure analysis ($Ba_2P_4Si_8O_6C_{48}H_{106}$, space group $P2_1/n$, $a = 1256.3(2)$ pm, $b = 2000.0(3)$ pm, $c = 2986.9(2)$ pm, $\beta = 98.929(9)°$, $d_{calc} = 1.257$ g cm^{-3}, $Z = 4$, wR2 = 0.1334 at 11580 F^2 values). The Ba−P bond lengths vary between 318 and 338 pm.

Introduction

The solvent-free homoleptic bis(trimethylsilyl)amides of calcium, strontium, and barium form dimers of the type $R_2NM(\mu\text{-}NR_2)_2MNR_2$ in solution[1] as well as in the solid state.[2] The increasing pyramidalization of the coordination sphere of the three-coordinated metal center from magnesium to barium can be explained by d-orbital participation at the heavier alkaline earth metal atoms and by van der Waals ligand ligand attractions, especially since the scandium[3] and yttrium tris[bis(trimethylsilyl)amides][4] show a similar structural behavior. The homologue phosphanides precipitate as colorless and nearly insoluble polymeric solids, whereas the monomeric thf complexes[5] are soluble and can be easily characterized. The bis(trimethylsilyl)amides of the alkaline earth metals form bis(thf) adducts[2,6] regardless of the size of the metal center. Due to the longer metal phosphorus bonds the bis(trimethylsilyl)phosphanides strontium and barium crystallize as tetrakis(thf) complexes[5] the smaller magnesium derivative is a bis(thf) complex.[7] In the case of the strontium derivative we succeeded in solving the dependence between the thf content and its structure in the solid state, where a molecule of the type $R_2PSr(\mu\text{-}PR_2)_3Sr(thf)_3$ has been identified.[8] In toluene solution an equilibrium between the monomeric tetrakis(thf) complex and the bicyclic dimeric derivative has been found. The latter species is dominating at high temperatures. However, it was not possible to freeze all the dynamic intramolecular exchange processes between terminal and bridging substituents occurring in solution. Therefore only broad singlets are observed in the $^{31}P\{^1H\}$ NMR spectra.[8]

Similar structures have been calculated for the dimeric dihydrides of the heavier alkaline earth metals[9] and are stated for some alkoxides and siloxides[10] in the solid state. The temperature-dependent monomer−dimer equilibrium, however, seems to be characteristic for the phosphanides as can be proven for the first time for a barium derivative in solution as well as in the solid state, using the 1,2-dimethoxyethane adduct of barium bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide) as an example. In spite of predominately electrostatic anion−cation attraction within the dimeric alkaline earth metal dihydrides, Kaupp and Schleyer[9] hold the small d-orbital participation at the alkaline earth metals responsible for the bicyclic molecular structures.

Results and Discussion

Synthesis. The cyclic phosphane 2,2,5,5-tetramethyl-2,5-disilaphospholane yields from the reaction of (1,2-dimethoxy-

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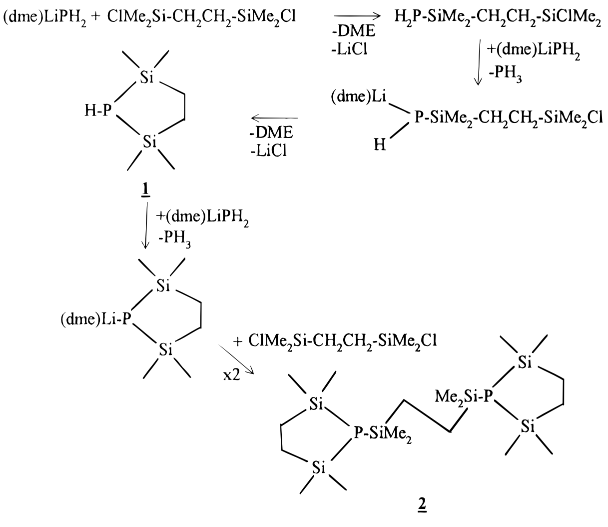
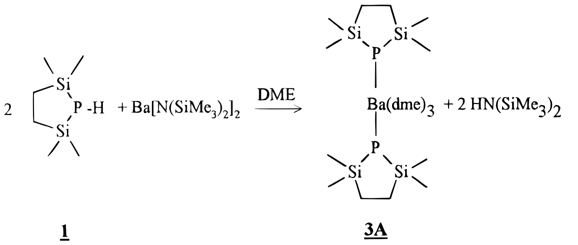
ethane-*O,O′*)lithium phosphanide, (dme)$LiPH_2$, or of dilithium phosphandiide, Li_2PH, with bis(chlorodimethylsilyl)ethane. The reaction sequence is summarized in eq 1. The first reaction step is the elimination of LiCl and the formation of a silyl-substituted phosphane. A similar reaction was successfully performed by Driess and co-workers[11] synthesizing the sterically shielded diphosphanylsilanes of the type $RR'Si(PH_2)_2$. Consequently the lithiation of the phosphane competes with the metathesis reaction. The intramolecular elimination of LiCl yields the cyclic 2,2,5,5-tetramethyl-2,5-disilaphospholane **1**, which once more can be lithiated by (dme)$LiPH_2$. The evolving phosphane is identified IR spectroscopically. The starting bis(chlorodimethylsilyl)ethane reacts with two of these lithium phosphanides to derivative **2**. The phosphanes **1** and **2** can be easily separated by distillation of **1** and a subsequent extraction of **2** from the residue by *n*-pentane. On cooling this solution, colorless single crystals of **2** suitable for X-ray crystallography are obtained. Since the second (dme)$LiPH_2$ molecule reacts as a lithiating reagent, these compounds can also be isolated starting from a Li_2PH suspension in 1,2-dimethoxyethane, prepared from (dme)$LiPH_2$ and lithium *n*-butanide. Performing the reaction this way reduces the loss of phosphane during the synthesis of **1** and **2**.



(1)

The metalation of phospholane **1** by barium bis[bis(trimethylsilyl)amide] in 1,2-dimethoxyethane yields the monomeric tris(dme)barium bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide), **3A**, according to eq 2. Derivative **3A** is a moisture sensitive colorless solid, which is soluble in etheral and aromatic solvents but almost insoluble in aliphatic hydrocarbons.



(2)

NMR Spectroscopy. The $\delta(^{31}P\{^1H\})$ values of the derivatives **1** and **2** are high field shifted to about 40 ppm compared to the trimethylsilyl substituted phosphanes.[7,12] Due to the ring strain the $^{29}Si\{^1H\}$ chemical shifts of the phospholane moities are shifted to lower field, and the doublets are observed between 22 and 25 ppm. Even the barium compound shows similar values in toluene solution at raised temperatures. Recrystallization of derivative **3A** from hot benzene or toluene solution leads to the loss of dme ligands and the precipitation of $(R_2P)(dme)Ba(\mu\text{-}PR_2)_3Ba(dme)_2$, **3B**.

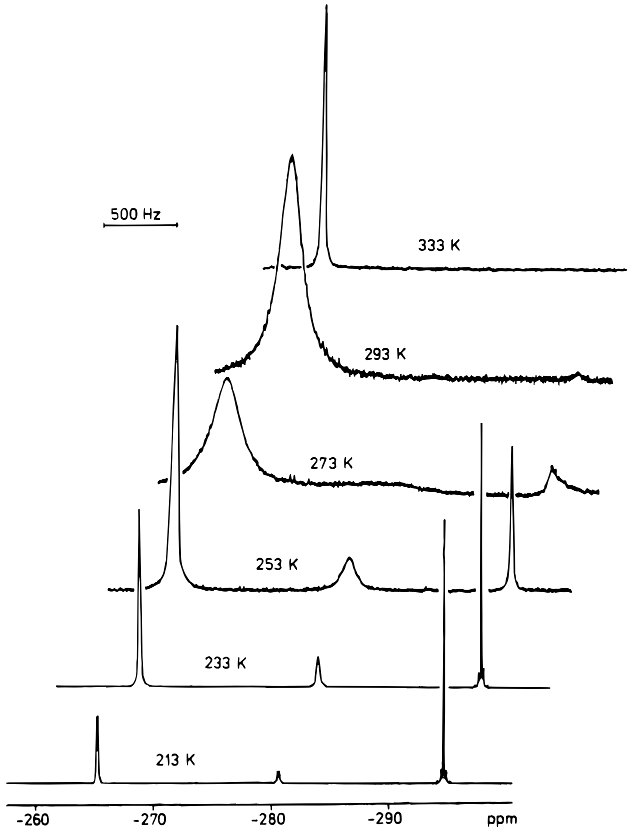


Figure 1. Dynamic $^{31}P\{^1H\}$ NMR spectra of tris(dimethoxyethane)barium bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide) **3** in toluene-d_8 solution (81.015 MHz, see text)

The phospholane **1** shows no inversion at the phosphorus center. As a result the two methyl groups at both the silicon atoms are chemically different. Although the $^{13}C\{^1H\}$ chemical shift variations are small, the coupling constants $^2J(PC)$ differ drastically. The $^2J(PC)$ value for the methyl substituent which is cis-arranged to the coordination gap amounts 25.6 Hz, whereas the CH_3 groups directing to the same side as the hydrogen atom display a value smaller than the resolution of the spectrometer. A similar situation is found in the phospholane **2**, but the difference is less than half the amount. The acyclic disilylethane fragment reflects comparable coupling constants; the methyl ligands show singlets in the $^{13}C\{^1H\}$-NMR spectrum and the methylene moities doublets of doublets with $^2J(PC)$ and $^3J(PC)$ values of 5.0 and 14.7 Hz, respectively.

The $^{31}P\{^1H\}$ NMR spectra of the barium derivative show a remarkable temperature dependency (Figure 1). At 213 K three signal groups can be assigned: a doublet at −259.76 ppm, a quartet at −275.21 ppm, and a singlet at −289.15 ppm, which can easily be explained by the presence of a monomeric molecule (**3A**) and a dimeric species of the type $RBa(\mu\text{-}R)_3Ba$ (**3B**). The $^2J(PP)$ coupling constant of 6.7 Hz of molecule **3B** shows a remarkably small value compared to $(thf)_4$barium bis[bis(trimethylsilyl)phosphanide] where the $^2J(PP)$ value of 23.5 Hz was calculated from the $^{29}Si\{^1H\}$ spectrum with an AA′X

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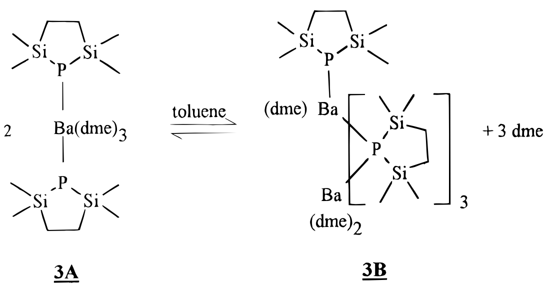
pattern.[5] The $^{31}P\{^1H\}$ low field shift of species **3A** resembles the highly anionic charge located at the phosphorus atom which can also be deduced from the comparison of the molecular structures of the compounds **2** and **3** as will be described later.

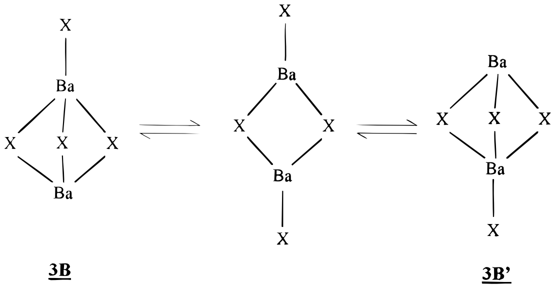
In the first instance, the temperature dependence of the ^1H NMR experiments seems to be unintelligible, however, with the knowledge of the results just described, an assignment is possible. At 60 °C a doublet for the methyl groups at the phosphorus atoms is observed, whereas the methylene protons show a singlet (Figure 2). Cooling of the sample to room temperature leads to a broad singlet for the methyl substituents and at even lower temperatures a further fine structure becomes evident. The two relatively sharp singlets at 0.54 and 1.36 ppm have to be assigned to the methyl and methylene protons of the phospholanide ligands of the monomeric derivative **3A**. The other resonances are associated with the dimeric bicyclic compound **3B**. This temperature dependent behavior also influences the resonances of the 1,2-dimethoxyethane molecules.

Figures 1 and 2 display the dynamic ^1H as well as $^{31}P\{^1H\}$ NMR experiments performed with a toluene-d_8 solution of derivative **3**. It is obvious that two major processes dominate the dynamic behavior: the monomer−dimer equilibrium as shown in eq 3 and the intramolecular exchange of phospholanide ligands between the terminal and bridging position within the dimeric molecule **3B**.



(3)

At low temperatures the monomeric species **3A** is the major compound. Upon raising the temperature this derivative diminishes and the formation of the dimeric compound is favored due to the entropy effect. At the same time an exchange reaction occurs such as presented in eq 4. A similar behavior



(4)

was found for the homoleptic bis(trimethylsilyl)amides of calcium and strontium.[1] The intermediate of the type $XBa(\mu-X)_2BaX$, however, was not detectable by NMR spectroscopy. At raised temperatures no monomeric molecules **3A** are observed and the dimeric species **3B** appears as a broad singlet in the $^{31}P\{^1H\}$ NMR spectrum.

As mentioned earlier the existence of these two molecules could be shown by crystallization of the bicyclic dimeric molecule **3B** at raised temperatures. Slow cooling of a hot benzene solution of **3** saturated at 70 °C down to 30 °C leads to the growth of colorless single crystals of compound **3B**·$2C_6H_6$, which is thermally far less sensitive toward moisture than derivative **3A**.

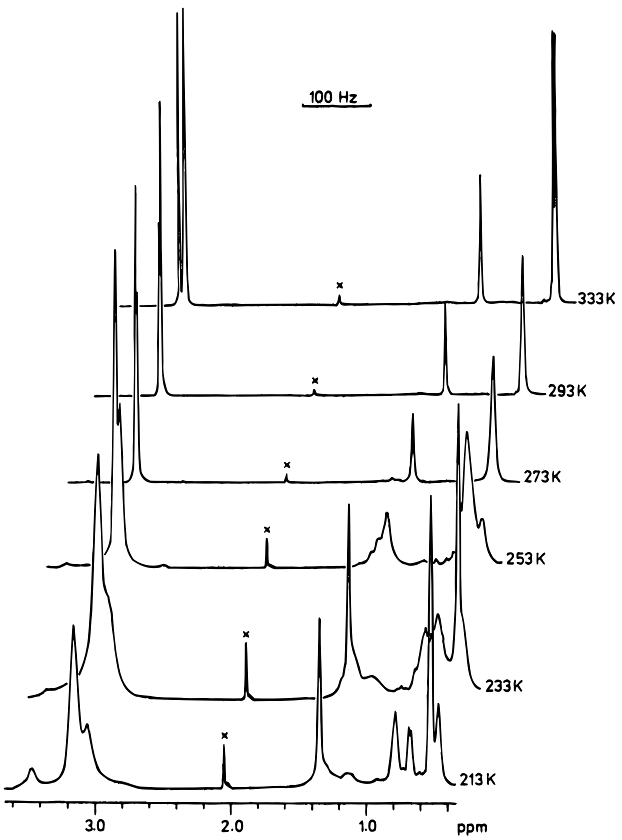


Figure 2. Dynamic ^1H NMR spectra of tris(dimethoxyethane)barium bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide) **3** in toluene-d_8 solution (200.133 MHz, methyl group of toluene is marked with an asterisk; see text)

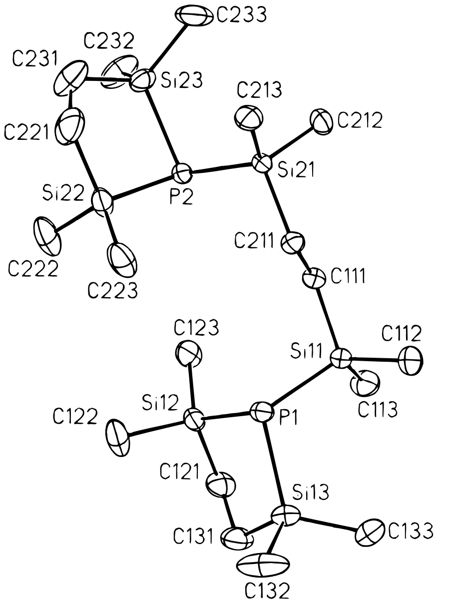


Figure 3. Molecular structure of 1,1,4,4-tetramethyl-1,4-bis(2,2,5,5-tetramethyl-2,5-disilaphospholanyl)-1,4-disilabutane, **2**. The ellipsoids represent a 50% probability, all hydrogen atoms are omitted for clarity.

Molecular Structures. Figure 3 shows the molecular structure of derivative **2** as well as the numbering scheme. Table 1 shows selected bond lengths and angles. The phosphorus atoms P(1) and P(2) are surrounded pyramidically with Si−P distances of 226 pm. This Si−P value corresponds well to the bond length determined in the gaseous phase at tris(trimethylsilyl)phosphane[13] or to the values in diphosphanylbis[2,4,6-triisopropylphenyl]silane.[11] The endocyclic Si−P−Si angles lie

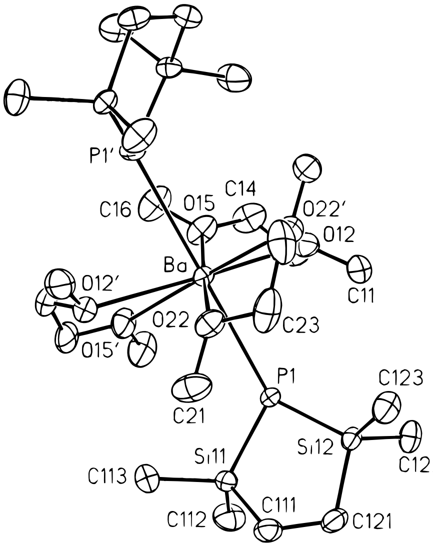


Figure 4. Molecular structure of tris(dimethoxyethane)barium bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide), **3A**. The atoms generated by the crystallographic C_2-symmetry are marked with primes. The ellipsoids represent a 40% probability, the carbon atoms of the phospholanide ligand and all the hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (pm) and Angles (deg) of **2**

(a) Bond Lengths

	$n = 1$		$n = 2$	$n = 3$
P(1)−Si(1n)	225.6(1)		225.4(1)	226.6(1)
P(2)−Si(2n)	225.2(1)		225.3(1)	226.4(1)
Si(11)−C(11n)	188.1(3)		187.4(3)	187.4(3)
Si(12)−C(12n)	187.5(3)		188.2(4)	186.0(3)
Si(13)−C(13n)	188.9(3)		185.7(4)	186.8(4)
Si(21)−C(21n)	188.0(3)		186.5(3)	187.3(3)
Si(22)−C(22n)	188.2(4)		187.6(4)	187.2(4)
Si(23)−C(23n)	190.6(4)		185.9(4)	186.5(4)
C(111)−C(211)	153.7(4)	C(121)−C(131)		153.3(5)
C(221)−C(231)	149.7(6)			

(b) Bond Angles

	$n = 1$	$n = 2$
Si(n1)−P(n)−Si(n2)	104.97(5)	103.60(4)
Si(n1)−P(n)−Si(n3)	107.04(5)	104.56(5)
Si(n2)−P(n)−Si(n3)	89.82(5)	89.97(5)

at 90°, whereas the exocyclic angles display values around 106°. The ring strain influences neither the Si−P nor the Si−C bond lengths. The endocyclic C−C distances, however, are about 3 pm longer than the C−C bond within the disilylethane group bridging both the phosphorus atoms.

Tris(dimethoxyethane)barium bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide), **3A**, has a metal center with the coordination number of eight. This can be described best as a distorted hexagonal bipyramide with the phospholanide ligands in axial positions. The molecule as well as the numbering scheme is presented in Figure 4. The atoms related by crystallographic C_2-symmetry are marked with primes. Table 2 contains selected bond lengths and angles.

Due to the high coordination number of the barium atom, the Ba−P bond lengths with 333 pm are about 15 pm longer than in tetrakis(tetrahydrofuran)barium bis[bis(trimethylsilyl)-phosphanide].[5] In both these complexes the ether molecules are located in the equatorial plane. In **3A** the dme ligands are oriented propeller-like and display twist conformations. The Ba−O distances are also elongated up to 290 pm.

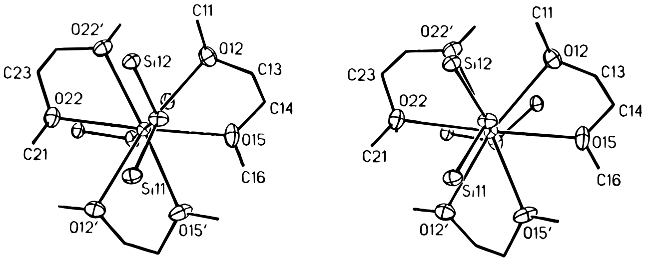


Figure 5. Stereoscopic view along the P(1)−Ba−P(1)′ moiety to show the arrangement of the dme ligands in regard to the P-Si bonds. The atoms generated by the crystallographic C_2-symmetry are marked with primes.

Table 2. Selected Bond Lengths (pm) and Angles (deg) of **3A**

(a) Bond Lengths

Ba−P(1)	333.28(7)	Ba−O(12)	290.3(2)
Ba−O(15)	277.5(2)	Ba−O(22)	281.1(2)
P(1)−Si(11)	220.41(11)	P(1)−Si(12)	221.09(10)
Si(11)−C(111)	188.9(3)	Si(12)−C(121)	190.3(4)
Si(11)−C(112)	189.2(4)	Si(12)−C(122)	188.3(4)
Si(11)−C(113)	187.9(4)	Si(12)−C(123)	188.4(3)
C(111)−C(121)	153.2(5)		

(b) Bond Angles

P(1)−Ba−O(12)	73.66(5)	P(1)−Ba−O(15)	98.45(5)
P(1)−Ba−O(22)	82.95(5)	P(1)−Ba−P(1)′	178.89(3)
P(1)−Ba−O(12)′	106.24(5)	P(1)−Ba−O(15)′	80.62(5)
P(1)−Ba−O(22)′	98.02(5)	Ba−P(1)−Si(11)	120.96(4)
Ba−P(1)−Si(12)	129.64(4)	Si(11)−P(1)−Si(12)	89.66(4)

The anionic charge on the phospholanide ligand of **3A** leads to a shortening of the Si−P bond lengths comparable to $(thf)_4Ba[P(SiMe_3)_2]_2$ mentioned above. The C(111)−C(121) bond as well as the Si−P−Si angle have similar values as in derivative **2**. The angle sum at the phosphorus atom is increased to 340° as a consequence to the steric hindrance between the phospholanide and the dme molecules. The projection along the P(1)−Ba−P(1)′ moiety (Figure 5) shows the eclipsed conformation of the bonds Ba−O(12)′ and P(1)−Si(11) as well as Ba−O(22)′ and P(1)−Si(12). This conformation enforces the deviation of the ether oxygen atoms from the equatorial hexagonal plane.

Ether-saturated lithium bis(trimethylsilyl)phosphanides crystallize as dimeric molecules with a central Li_2P_2-moiety.[14,15] The solvent-poorer derivatives form ladder structures, understandable as annelated four-membered cycles.[14,16] The heavy alkaline earth metal diphosphanides **3B** as well as $(thf)_3Sr[\mu\text{-}P(SiMe_3)_2]_3Sr\text{-}P(SiMe_3)_2$ display another structural motive.

The molecular structure of tris(1,2-dimethoxyethane-O,O′)-dibarium tetrakis(2,2,5,5-tetramethyl-2,5-disilaphospholanide), **3B**, is represented in Figure 6. Three phospholanide ligands bridge the barium atoms, whereas the fourth one is coordinated terminally at the metal center Ba(1). The coordination number of six is completed by a 1,2-dimethoxyethane molecule. Two additional bidentate ligands are bonded to the barium atom Ba(2), thus leading to a 7-fold coordination. In contrast to the Ba−O distances, which lie all in a narrow range of about 280 pm, the Ba−P bond lengths differ from 318 pm for the terminal Ba(1)−P(4) bond up to 338 pm for Ba(1)−P(3). Per dimeric barium diphospholanide unit the crystal also contains two benzene molecules in the gaps. These are refined anisotropically and show neither coordination to one of the metal centers nor

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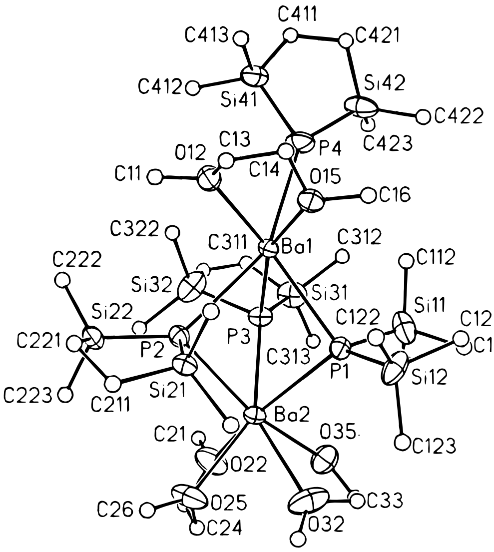

Figure 6. Molecular structure of **3B**. The carbon atoms are drawn with an arbitrary radius to show clearly the central Ba_2P_3 core. The ellipsoids of the non-carbon atoms represent a 40% probability; the hydrogen atoms are omitted for clarity.

Table 3. Pertinent Bond Lengths (pm) and Angles (deg) of **3B**

(a) Bond Lengths

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
Ba(1)−P(*n*)	327.2(2)	332.7(2)	338.1(2)	317.8(2)
Ba(2)−P(n)	326.8(2)	328.7(2)	325.4(2)	
P(n)−Si(n1)	221.1(3)	221.2(2)	220.7(3)	219.2(3)
P(n)−Si(n2)	220.8(3)	222.3(3)	221.0(3)	217.5(3)

Ba(1)−O(12)	277.5(5)	Ba(1)−O(15)	281.6(4)
Ba(2)−O(22)	281.4(5)	Ba(2)−O(25)	279.5(5)
Ba(2)−O(32)	279.7(6)	Ba(2)−O(35)	281.3(6)

(b) Bond Angles

Ba(1)−P(1)−Ba(2)	88.12(4)	Ba(1)−P(2)−Ba(2)	86.88(4)
Ba(1)−P(3)−Ba(2)	86.51(4)	P(1)−Ba(1)−P(2)	78.78(4)
P(1)−Ba(1)−P(3)	76.57(4)	P(1)−Ba(1)−P(4)	129.53(6)
P(2)−Ba(1)−P(3)	75.30(4)	P(2)−Ba(1)−P(4)	151.35(6)
P(3)−Ba(1)−P(4)	104.40(5)	P(1)−Ba(2)−P(2)	79.41(4)
P(1)−Ba(2)−P(3)	78.40(5)	P(2)−Ba(2)−P(3)	77.58(4)
Ba(1)−P(4)−Si(41)	127.65(11)	Ba(1)−P(4)−Si(42)	141.00(12)
Si(41)−P(4)−Si(42)	91.30(12)		

other remarkable features. The discussion is therefore limited to the molecular structure of **3B**. Selected bond lengths and angles are summarized in Table 3.

The Ba(1)−P(4) distance of 318 pm to the terminal coordinated phospholanide is remarkably short compared to the value found in tris(dimethoxyethane)barium bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide), **3A** (333 pm, Table 2). The P(4)−Si(41) and P(4)−Si(42) bond lengths with values of 218 pm are clearly shorter than the corresponding bonds in the ligand of **3A** or as the ones in the bridging phospholanides of **3B**. In spite of the angle sum of the phosphorus atom P4 of 360° and the short Ba(1)−P(4) distance a $(p_P-d_{Ba})_\pi$ back-bonding from the phospholanide ligand to the metal center cannot be assumed. However, a similar bond shortening of about 10 pm is found in the hafnium complex $Cp_2Hf[P(SiMe_3)_2]_2$ where one of the bis(trimethylsilyl)phosphanide substituents with a short Hf−P bond of 255 pm displays a planar coordinated phosphorus atom and the other one an angle sum of 336° at the phosphorus center.[17] On the other hand tetrakis(tetrahydrofuran)barium bis[bis(trimethylsilyl)phosphanide] shows similar Ba−P bond lengths at an also 6-fold coordinated metal center with angle sums at the phosphorus atoms of about 345°.[5]

The bridging phospholanide substituents of **3B** display bonding parameters comparable to the corresponding values of derivative **3A** where a back-bonding from the distorted tetrahedrally coordinated phosphorus atom to the metal center is impossible. As a consequence the range for Ba−P distances is rather wide, mainly dependent on the coordination number of the phosphorus and the barium atoms as could be shown earlier.[18] This solid state structure clearly confirms the molecule derived from the chemical shifts and the fine structure of the NMR spectra.

Concluding Remarks

The existence of the bicyclic dimer with a central moiety of the type $RBa(\mu\text{-}R)_3Ba$ has been shown in benzene or toluene solution as well as for the crystalline state for a barium diphospholanide. A similar behavior was already observed for $(thf)_3Sr[\mu\text{-}P(SiMe_3)_2]_3SrP(SiMe_3)_2$.[8] However, there exist also examples for derivatives with a monocyclic central four-membered M_2E_2-cycle.[19] Westerhausen et al.[2a−c] as well as Caulton and co-workers[2d] synthesized the homoleptic monocyclic bis(trimethylsilyl)amides of magnesium, calcium, strontium, and barium. Grützmacher[19] isolated dimeric bis(1,2-dimethoxyethane-*O*,*O*′)barium 2,4,6-tri(isopropyl)thiophenolate with a central $SBa(\mu\text{-}S)_2BaS$ fragment. Hanusa and co-workers[20] prepared a monocyclic calcium dialkoxide although most of the alkoxides and siloxides of the heavier alkaline earth metals contain polycyclic metal oxygen cores.[10] Heteroleptic dimeric $(Me_4EtC_5)CaN(SiMe_2CH_2)_2$[21] also crystallizes with a monocyclic Ca_2N_2 moiety, mainly due to the steric demand and the low basicity of the peralkyl-substituted cyclopentadienide ligand. Further preparative and theoretical research is intended to investigate the factors that enforce the mono or bicyclic structure in solution and the crystalline state.

Experimental Section

All experiments and manipulations were carried out under an atmosphere of argon purified by passage through BTS catalyst[22] and P_4O_{10}. Reactions were performed using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting materials $(dme)LiPH_2$[23] and $Ba[N(SiMe_3)_2]_2$[1] were prepared by literature procedures. NMR spectra were recorded on the Bruker spectrometers AM200 and AC250. All $^{31}P\{^1H\}$ NMR are referenced to an external standard of 85% phosphoric acid. A Perkin-Elmer 883 spectrophotometer was used to record the IR spectra.

Reaction of (dme)LiPH$_2$ with ClMe$_2$SiCH$_2$CH$_2$SiMe$_2$Cl. A 50 mL aliquot of a 2.5 M hexane solution of lithium *n*-butanide (125 mmol) was added dropwise at room temperature to 16.0 g of $(dme)LiPH_2$ (123 mmol) in 250 mL of thf. Into this Li_2PH suspension was dropped rapidly a solution of 25 g of bis(chloro-dimethylsilyl)ethane (116 mmol) in 60 mL of thf. After the precipitated lithium chloride was removed, the solvent was distilled off at room temperature and reduced pressure. Thereafter a vacuum distillation yielded 2.0 g of **1** (11 mmol, 10%). The residue of the distillation was extracted with *n*-pentane to yield a further 12 g of **2** (24.2 mmol; 39.3%). A yellow insoluble residue of oligomeric/polymeric phosphanes, however, remained.

Physical Data. 2,2,5,5-Tetramethyl-2,5-disilaphospholane, 1. Bp: 56 °C/6 mbar. NMR (benzene-d_6, 30 °C): ^1H: δ 0.78 (s, CH_2),

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0.23 (d, Me, $^{3}J_{(PH)} = 1.5$ Hz), 0.18 (d, Me, $^{3}J_{(PH)} = 7.3$ Hz), −0.06 (d, PH, $^{1}J_{(PH)} = 174.1$ Hz). ^{13}C: δ 14.43 (CH$_2$, $^{2}J_{(PC)} = 3.0$ Hz, $^{1}J_{(CH)} = 122.1$ Hz), 1.60 (Me, $^{1}J_{(CH)} = 120.5$ Hz), 0.60 ($^{2}J_{(PC)} = 25.6$ Hz, $^{1}J_{(CH)} = 120.7$ Hz). ^{29}Si{^{1}H}: δ 24.31 (d, $^{1}J_{(PSi)} = 28.4$ Hz). ^{31}P{^{1}H}: δ −275.30 ppm. IR (capillary, CsBr): 2953 s, 2877 s, 2860 sh, 2794 w, 2366 m, 1416 m, 1253 vs, 1228 w, 1036 m, 926 w, 837 vs, 810 s, 780 vs, 684 s, 612 m, 577 w, 434 w, 419 s cm^{-1}. MS (source 470 K, sample 295 K, 70 eV): 176 (100%, M^{+}), 161 (68.58%, M − Me), 148 (51.78%, M − C_2H_4), 147 (13.32%, M − C_2H_5), 145 (23.05%, M − 2Me − H), 133 (51.96%, M − C_2H_4 − Me), 117 (26.30%, M − C_2H_5 − 2Me), 115 (22.27%, M − 4Me − H), 85 (10.96%), 73 (78.18%), 59 (34.10%). Anal. Found (calcd for $PSi_2C_6H_{17}$, 176.35 g mol^{-1}): C, 40.87 (40.87); H, 9.63 (9.72).

1,1,4,4-Tetramethyl-1,4-bis(2,2,5,5-tetramethyl-2,5-disilaphospholanyl)-1,4-disilabutane, **2.** Mp: 71−72 °C. NMR (benzene-d_6, 30 °C): ^{1}H: δ 0.85 (s, CH$_2$ cycl.), 0.84 (s, CH$_2$ chain), 0.34 (s, Me), 0.32 (s, Me), 0.29 (d, Me, $^{3}J_{(PH)} = 4.3$ Hz). ^{13}C: δ 14.45 (CH$_2$, $^{1}J_{(CH)} = 122.8$ Hz), 13.63 (CH$_2$, $^{2}J_{(PC)} = 14.7$ Hz, $^{1}J_{(CH)} = 118$ Hz), 2.80 (Me, $^{1}J_{(CH)} = 120.0$ Hz), 2.51 (Me, $^{1}J_{(CH)} = 120.6$ Hz), 1.91 (Me, $^{2}J_{(PC)} = 10.3$ Hz, $^{1}J_{(CH)} = 119.8$ Hz). ^{29}Si{^{1}H}: δ 22.55 (d, cycl., $^{1}J_{(PSi)} = 31.7$ Hz), 8.56 (d, chain, $^{1}J_{(PSi)} = 35.1$ Hz). ^{31}P{^{1}H}: δ −287.72 ppm. IR (Nujol, CsBr): 1253 vs, 1227 w, 1135 m, 1054 m, 1040 m, 974 w, 836 vs, 805 vs, 771 s, 682 vs, 644 m, 630 w, 609 s, 468 s, 429 s, 402 w, 390 w cm^{-1}. RE (single crystal): 749 w, 685 m, 645 m, 610 m, 469 w, 461 w, 400 vs, 391 sh, 232 m, 194 s, 174 s cm^{-1}. MS (source 490 K, sample 340 K, 20 eV): 480 (0.47%, M − Me), 319 (100%), 233 (5.83%), 231 (6.52%), 225 (4.80%), 223 (4.48%), 176 (4.72%), 161 (4.60%), 145 (10.99%), 117 (4.58%), 85 (7.20%), 73 (56.22%), 59 (8.95%). Anal. Found (calcd for $P_2Si_6C_{18}H_{48}$, 495.04 g mol^{-1}): C, 43.23 (43.67); H, 9.57 (9.77).

Tris(dimethoxyethane)barium Bis(2,2,5,5-tetramethyl-2,5-disilaphospholanide), **3.** A solution of 1.04 g of phospholane **1** (5.9 mmol) in 5 mL of thf was added dropwise at room temperature to 1.7 g of bis(tetrahydrofuran)barium bis[bis(trimethylsilyl)amide] (2.8 mmol) dissolved in 10 mL of 1,2-dimethoxyethane. After this solution was stirred for an additional hour the major part of the solvent was distilled off at reduced pressure at room temperature. When this solution was cooled, colorless crystals of **3A** are precipitated. The usual workup of the mother liquor yielded another crop of crystals of **3A**. Yield: 1.8 g (2.4 mmol), 84%. Mp: 86−92 °C dec. NMR (toluene-d_8, −60 °C): ^{1}H: δ 0.54 (s, Me), 1.36 (s, CH$_2$); ^{31}P{^{1}H}, δ −289.15 ($^{1}J_{(PSi)} = 14.9$ Hz). IR (Nujol, CsBr): 1286 m, 1235 s, 1220 sh, 1200 m, 1165 m, 1105 sh, 1074 vs, 1031 m, 1020 sh, 860 s, 826 vs, 798 s, 751 s, 698 w, 666 s, 612 s, 594 m, 571 m, 446 vs, 393 w, 370 w cm^{-1}. Anal. Found (calcd for $BaP_2Si_4O_6C_{24}H_{62}$, 758.38 g mol^{-1}): C, 37.89 (38.01); H, 8.20 (8.24); Ba, 18.20 (18.11).

Drying of compound **3A** in vacuum, dissolving in a few milliliters of hot toluene or benzene and finally cooling to room temperature leads to the crystallization of the colorless derivative **3B**. Mp: 99−100 °C dec. NMR (toluene-d_8, −60 °C): ^{1}H, δ 0.80 and 0.48 (s, Me, bridge), 0.70 and 0.68 (s, Me, term.), 1.1 and 1.3 (s, broad, assignment to bridging and terminal substituent not possible); ^{31}P{^{1}H} δ −275.21 (q, term.), −259.76 (d, bridge, $^{2}J_{(PP)} = 6.7$ Hz). NMR (benzene-d_6, 70 °C): ^{1}H, δ 0.57 (d, Me, $^{3}J_{(PH)} = 3.6$ Hz), 1.14 (s, CH$_2$) 3.19 (s, Me, dme), 3.30 and 3.33 (s, CH$_2$, dme); ^{13}C, δ 6.62 (d, Me, $^{2}J_{(PC)} = 11.9$ Hz, $^{1}J_{(SiC)} = 44.8$ Hz, $^{1}J_{(CH)} = 119.0$ Hz), 17.04 (d, CH$_2$, $^{2}J_{(PC)} = 3.3$ Hz, $^{1}J_{(CH)} = 122.3$ Hz), 59.07 and 72.08 (broad); ^{29}Si{^{1}H}, δ +22.72 (d, $^{1}J_{(PSi)} = 45.0$ Hz); ^{31}P{^{1}H}, δ −258.55 (s). IR (Nujol, CsBr): 1330 m, 1298 w, 1289 sh, 1232 vs, 1193 m, 1157 w, 1108 s, 1071 vs, 1022 s, 985 s, 829 vs, 798 s, 691 sh, 670 vs, 612 s, 594 m, 551 w, 502 s, 465 sh, 451 s, 442 m cm^{-1}. Anal. Found (calcd for $Ba_2P_4Si_8O_6C_{48}H_{106}$, 1402.61 g mol^{-1}): C, 40.96 (41.10); H, 7.59 (7.62).

X-ray Crystal Structure Determinations. Colorless crystals of **2** were obtained by cooling a pentane solution saturated at room temperature down to −60 °C. Derivative **3** crystallizes from a 1,2-dimethoxyethane solution on cooling to −10 °C. The single crystals were sealed in thin-walled capillaries and mounted on a four-circle diffractometer Siemens P4 with graphite monochromated Mo Kα radiation. Crystallographic parameters and details of data collection performed at −80 °C are summarized in Table 4.

Table 4. Summary of Crystallographic Data for **2**, **3A**, and **3B** as Well as Details of the Structure Solution and Refinement Procedures

	2	**3A**	**3B**
empirical formula	$P_2Si_6C_{18}H_{48}$	$BaP_2Si_4O_6$-$C_{24}H_{62}$	$Ba_2P_4Si_8O_6$-$C_{48}H_{106}$
fw (g mol^{-1})	495.04	758.38	1402.61
T (°C)	−80	−80	−80
space group[24]	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
unit cell dimens			
a (pm)	943.3(2)	2152.3(1)	1256.3(2)
b (pm)	1278.3(3)	1381.5(1)	2000.0(3)
c (pm)	1413.5(3)	1459.7(1)	2986.9(2)
α (deg)	72.45(1)	90	90
β (deg)	78.13(1)	113.73(1)	98.929(9)
γ (deg)	70.83(1)	90	90
V (nm^3)	1.5208(6)	3.9733(4)	7.414(2)
Z	2	4	4
ρ_{calcd} (g cm^{-3})	1.081	1.268	1.257
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.384	1.230	1.307
no. of data	6548	5220	11580
no. of params	427	293	613
goodness-of-fit s on F^2 [a]	1.605	1.031	1.214
R indices [all data] R1[b]	0.0623	0.0488	0.0828
wR2[b]	0.1553	0.0989	0.1334
R indices [$I > 2\sigma(I)$, data]	5510	4485	8431
R1[b]	0.0495	0.0380	0.0517
wR2[b]	0.1474	0.0930	0.1195

[a] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$. [b] Definition of the R indices: $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.[26]

Both the structures were solved by direct methods with the software package SHELXTL Plus[25] and refined with the program SHELXL-93.[26] Neutral atom scattering factors were taken from Cromer and Mann[27] and for the hydrogen atoms from Stewart et al.[28] The non-hydrogen atoms were refined anisotropically.

The hydrogen atoms of **2** and **3A** were refined isotropically, whereas the H atoms of derivative **3B** were kept in a riding position with C−H distances of 97 pm by enforcing ideal tetrahedral geometry at the corresponding carbon atoms.

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Supporting Information Available: A full list of Crystallographic data (Table S-1) and for the compounds **2**, **3A**, and **3B** positional coordinates (Tables S-2, S-7, and S-12) bond distances (Tables S-3, S-8, and S-13, respectively), bond angles (Tables S-4, S-9, and S-14, respectively), fractional parameters of all H atoms (Tables S-5, S-10, and S-15, respectively), and thermal parameters of all non-H atoms (Tables S-6, S-11, and S-16, respectively) and stereoscopic views of the structures and unit cells of **2**, **3A**, and **3B** (24 pages). Ordering information is given on any current masthead page.

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