# Synthesis and Homomolecular Metalation of Trialkylsilylphosphanides of Calcium and Barium

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Metalation of triisopropylsilylphosphane with bis(tetrahydrofuran-*O*)calcium bis[bis(trimethylsilyl)amide] in tetrahydropyran (thp) in a molar ratio of 3:2 yields $(Me_3Si)_2NCa[\mu\text{-}P(H)Si\textit{i}Pr_3]_3Ca(thp)_3$ (**1**) containing a trigonal-bipyramidal $Ca_2P_3$ core, the metal atoms occupying apical positions. Reaction of two equivalents of triisopropylsilylphosphane or -arsane with bis(tetrahydrofuran-*O*)barium bis[bis(trimethylsilyl)amide] in tetrahydrofuran gives the corresponding bis(phosphanide) **2** and bis(arsanide) **3**, compounds of the type $(thf)_3Ba[\mu\text{-}E(H)Si\textit{i}Pr_3]Ba(thf)_2E(H)Si\textit{i}Pr_3$ with E = P, As. The equimolar reaction of (tri-*tert*-butylsilyl)phosphane with $(thf)_2Ba[N(SiMe_3)_2]_2$ in toluene yields heteroleptic dimeric $(thf)_2Ba[N(SiMe_3)_2][P(H)Si\textit{t}Bu_3]$ (**4**). Addition of a further equivalent of $H_2PSi\textit{t}Bu_3$ leads to the formation of homoleptic $(thf)_nBa[P(H)Si\textit{t}Bu_3]_2$ (**5**). Dissolution of the latter in aromatic hydrocarbons leads to the elimination of $H_2PSi\textit{t}Bu_3$, yielding dimeric $(thf)Ba_3(PSi\textit{t}Bu_3)_2[P(H)Si\textit{t}Bu_3]_2$ (**6**). The inner core of **6** consists of the tetramer $(BaPSi\textit{t}Bu_3)_4$ based on a $Ba_4P_4$ heterocubane unit, two opposite faces being capped with $(thf)Ba[P(H)Si\textit{t}Bu_3]_2$ molecules.

## Introduction

The bis(trialkylsilyl)amides and -phosphanides of the heavier alkaline earth metals calcium, strontium, and barium are gaining interest not only due to their unexpected solid-state and solution structures, but also due to their high reactivity.[1] Addition reactions of alkaline earth metal bis[bis(trimethylsilyl)amides] and the corresponding phosphanides with benzonitrile are followed by 1,3-trimethylsilyl group shifts, as is seen in the syntheses of the alkaline earth metal bis[*N*,*N'*-bis(trimethylsilyl)benzamidinates][2] and bis-[1,3-bis(trimethylsilyl)-2-phenyl-1-aza-3-phosphapropenides].[3] Addition reactions of $M[P(SiMe_3)_2]_2$ (M = Ca, Sr, Ba) with diphenylbutadiyne yield the alkaline earth metal phospholides by a 1,3-trimethylsilyl group migration from the phosphorus to a carbon atom.[4]

Another type of reactivity stems from the $pK_s$ values of compounds $HE(SiMe_3)_2$ (E = N, P). Metallations of substrates with more acidic hydrogen atoms such as alcohols,[1] thiols,[5] selenols,[1,6,7] and tellurols[7,8] are well known. The IR spectra of mono(trialkylsilyl)-substituted phosphanides such as tetrakis(tetrahydrofuran-*O*)calcium bis(triisopropylsilylphosphanide)[9] reveal a reduced force constant of the P−H bond compared with the corresponding bonds in the phosphanes $H_2PSi\textit{i}Pr_3$ and $HP(Si\textit{i}Pr_3)_2$.[9,10] This enhanced reactivity leads to slow decomposition of these compounds when they are dissolved in hydrocarbons such as toluene or benzene, but as yet we have been unable to determine the structures of the products thus formed. Because phosphanediides tend to be polymeric, insoluble, and poorly characterized materials, the synthesis of such compounds has remained a challenge and hence there are relatively few examples. Driess and co-workers prepared oxygen-centered $Li_2O$-containing oligomers[11] and $R_3SiF$ adducts of a dimer[12] of dilithium triorganylsilylphosphanediide and -arsanediide. Monomeric bis[tris(trimethylsilyl)methylzinc] triisopropylsilylphosphanediide[13] displays a pyramidal coordination sphere at the phosphorus atom. Hexameric tin(II) triisopropylsilylphosphanediide crystallizes as a hexagonal $Sn_6P_6$ prism.[14]

The structures of dimeric alkaline earth metal bis(phosphanides) show an energetic minimum for the bicyclic derivatives $M(\mu\text{-}PH_2)_3MPH_2$ with M = Ca, Sr, and even for the tricyclic isomer $Ba(\mu\text{-}PH_2)_4Ba$, as shown by ab initio calculations.[1,9] The steric demand of the substituents at the phosphorus atom forces the adoption of a monocyclic dimeric structure, with two bridging and two terminally bonded phosphanide substituents.[15] The bicyclic nature of $(Me_3Si)_2NCa[\mu\text{-}P(H)Si\textit{i}Pr_3]_3Ca(thf)_3$ has been deduced by NMR spectroscopy,[9] although we were unable to obtain single crystals to allow corroboration of this by an X-ray structure determination.

## Results and Discussion

### Synthesis

Metalation of triisopropylsilylphosphane with calcium bis[bis(trimethylsilyl)amide][16,17] in a 3:2 stoichiometric ratio in tetrahydropyran (thp) yields almost quantitatively bicyclic $(Me_3Si)_2NCa[\mu\text{-}P(H)Si\textit{i}Pr_3]_3Ca(thp)_3$ (**1**). This compound exhibits somewhat surprising NMR data (vide infra).

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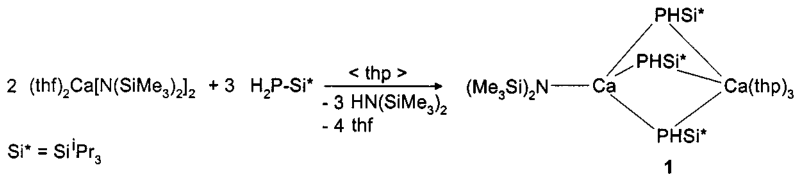
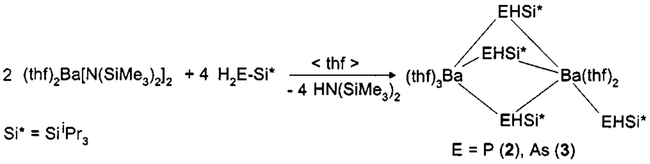
[+] X-ray structure determinations.

1434−1948/99/0505−0743 $ 17.50+.50/0



Scheme 1. Synthesis of **1**



Scheme 2. Synthesis of **2** and **3**

Barium bis[bis(trimethylsilyl)amide][16,18] metalates triisopropylsilylphosphane in thf to give the dimeric barium bis(triisopropylsilylphosphanide) **2** in a good yield. In contrast to the alkaline earth metal phosphanides characterized to date, **2** shows a monomer−dimer equilibrium in thf. Analogous investigations of a toluene solution were not possible since **2** undergoes immediate decomposition upon removal of the neutral coligand in vacuo or after dissolution in toluene. The corresponding arsanide $H_2AsSi\textit{i}Pr_3$[19] displays a similar reactivity towards $(thf)_2Ba[N(SiMe_3)_2]_2$, the metalation resulting in the formation of barium bis(triisopropylsilylarsanide) **3**, although we were unable to obtain single crystals of this material. All these colorless compounds were found to be extremely air- and moisture-sensitive.

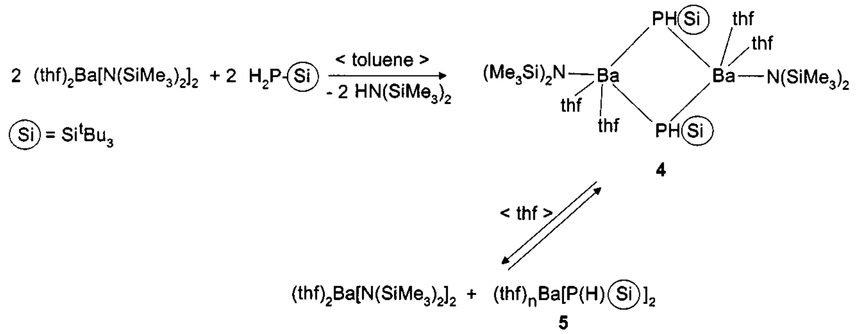
Compounds **1** and **2** decompose in toluene solution within a few days. The decomposition products show a 1:1 ratio of triisopropylsilylphosphanide and triisopropylsilylphosphanediide substituents, but all efforts to obtain a pure crystalline product were unsuccessful. Therefore, we metalated tri-*tert*-butylsilylphosphane[20] with barium bis[bis(trimethylsilyl)amide]. Reaction of equimolar amounts of $(thf)_2Ba[N(SiMe_3)_2]_2$ and $H_2PSi\textit{t}Bu_3$ in toluene quantitatively affords heteroleptic dimeric bis(tetrahydrofuran-*O*)barium bis(trimethylsilyl)amide tri-*tert*-butylsilylphosphanide (**4**), featuring a central $Ba_2P_2$ ring. Only the centrosymmetric isomer crystallizes from toluene, although numerous isomers were observed in solution. Assignment of the NMR data to specific isomers was not possible. Dissolution of **4** in thf leads to dismutation reactions and the formation of homoleptic derivatives, namely barium bis[bis(trimethylsilyl)amide] and barium bis(tri-*tert*-butylsilylphosphanide) **5**. Reaction of **4** with a further equivalent of $H_2PSi\textit{t}Bu_3$ also quantitatively yields compound **5**, which decomposes with elimination of $H_2PSi\textit{t}Bu_3$. Therefore, no monomer−dimer equilibrium could be investigated.

Decomposition of **5** yields colorless $\{(thf)Ba_3(\mu_4\text{-}PSi\textit{t}Bu_3)_2[\mu_2\text{-}P(H)Si\textit{t}Bu_3]_2\}_2$ (**6**) with a 1:1 molar ratio of $\textit{t}Bu_3SiP(H)^-$ and $\textit{t}Bu_3SiP^{2-}$ anions. This complex can be regarded as a $Ba_4P_4$ heterocubane with two opposite sides capped by $(thf)Ba[P(H)Si\textit{t}Bu_3]_2$ molecules, although the mechanism of its formation might well proceed via a polyhedron best described as a dimer of two pentagonal bipyramids with a common $MP_2$ face. Although heterocubane structures with heavier alkaline earth metals are only known for heterobimetallic tin(II)-containing molecules such as $[(thf)_3Ca]_2Sn_2(PSiMe_3)_4$[21] and $(toluene)BaSn_3(PSi\textit{t}Bu_3)_4$,[22] the trigonal-bipyramidal $M_2P_3$ core seems to be more common.[1,21,23] Similar findings were published by Rabe et al.[24] in relation to the arylphosphanides of Rb (tetrameric, $Rb_4P_4$ heterocubane core) and Cs {dimeric, $Cs^+[Cs(\mu\text{-}PHR)_3Cs]^-$ with a trigonal $Cs_2P_3$ bipyramid}, whereas $NaP(H)Si\textit{t}Bu_3$ crystallizes as a dimer with a central $Na_2P_2$ ring.[20c] The constitution of complex **6** was further proven by an X-ray structure determination (vide infra). Although the central $Ba_6P_8$ moiety is shielded by eight tri-*tert*-butylsilyl substituents, derivative **6** proved to be air- and moisture-sensitive.

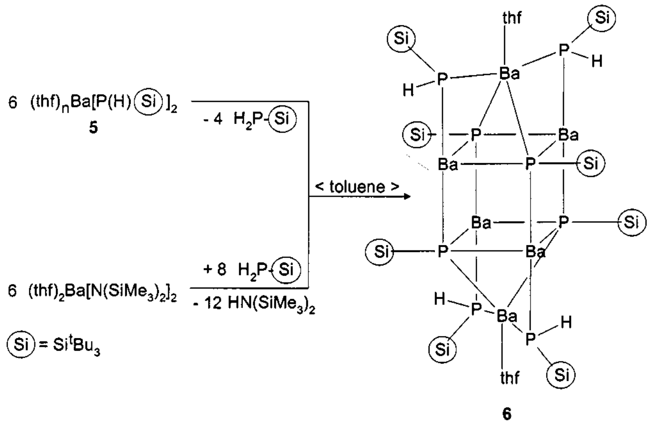
Metalations of $H_2PSi\textit{i}Pr_3$, $H_2AsSi\textit{i}Pr_3$, and $H_2PSi\textit{t}Bu_3$ lead to shifts of the P−H stretching vibrations of approximately 70 $cm^{-1}$ towards lower wavenumbers. The large reduction of the P−H force constant explains the increased reactivity with regard to the metalation reaction and accounts for the fact that compounds of the type $M[P(H)SiR_3]_2$ decompose so readily. In complex **6**, the remaining P−H fragments are shielded by the sterically demanding tri-*tert*-butylsilyl groups, which prevent further metalation, even in refluxing toluene.

## NMR Spectroscopy

The $^{31}$P-NMR spectrum of compound **1** (Figure 1) displays a coupling pattern of the AA′A′′XX′X′′ type with remarkably large $^2J$(P,P) and $^3J$(P,H) coupling constants of 92.3 and 11.7/2.1 Hz, respectively, which were verified by simulation. The $^1J$(P,H) coupling constant of 186.1 Hz lies within the characteristic range. An explanation for these observations could be the close contact of the phosphanide anions due to the formation of the bicyclic $Ca_2P_3$ bipyramid. The barium complex **2** with a similar $Ba_2P_3$ core is dynamic in thf solution, with even the terminal and bridging substituents being indistinguishable by NMR. Only very broad signals with half-height widths between 15 (at



Scheme 3. Synthesis of **4** and dismutation reaction in thf



Scheme 4. Synthesis of **6**

−30°C, δ = −291.7) and 1060 Hz (at +50°C, δ = −280.2) are observed. Corresponding investigations of a toluene solution were not possible due to the decomposition of **2**. Similar results were obtained for **5**, which do not merit special comment.

In contrast to the NMR data of **1**, the $^{2}J$(P,P) coupling constants of **6** are smaller than 3 Hz and are not resolved. With a $^{1}J$(P,H) coupling constant of 149 Hz, however, the signal at δ = −222.9 can clearly be assigned to the phosphanide ligands. The tri-*tert*-butylsilylphosphanediide substituents show a remarkable low-field shift of δ = −25.0. This chemical shift may be explained by the rather high coordination number of five at the phosphorus atoms and might be taken as an indication that these molecules do not dissociate in solution.

## Molecular Structures

The molecular structure of **1**, showing the numbering scheme, is depicted in Figure 2. Ca1 is surrounded by three phosphorus atoms and an amide ligand in a distorted tetrahedral arrangement, whereas Ca2 has a coordination number of six and a distorted octahedral coordination sphere with a facial arrangement of the phosphorus and oxygen atoms. The thp coligands adopt chair conformations. The Ca2−O(*n*) distances are between 235 and 241 pm and thus lie within the characteristic range.[1]

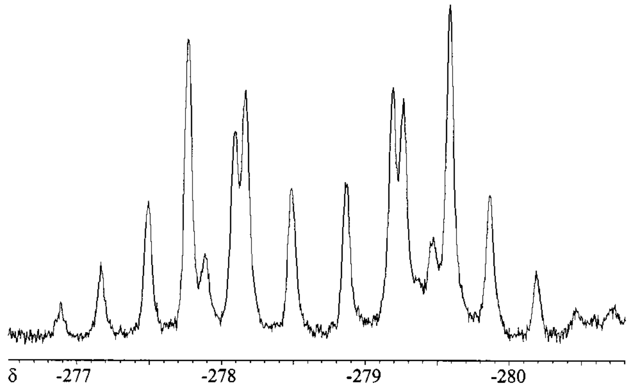


Figure 1. $^{31}$P-NMR spectrum of (Me$_3$Si)$_2$NCa[μ-P(H)Si*i*Pr$_3$]$_3$Ca(thp)$_3$ (**1**) at δ = −278.68 ([D$_8$]toluene, 25°C, 109.365 MHz; coupling constants see text)

The terminally bonded bis(trimethylsilyl)amide substituent exhibits a trigonal-planar coordination sphere at the nitrogen atom, the Ca1−N1 bond length of 228 pm matching the corresponding bond lengths in the calcium bis[bis(trimethylsilyl)amides].[1][25]

The triisopropylsilylphosphanide substituents occupy bridging positions. Due to the higher coordination number of Ca2, the Ca2−P(*n*) bonds (mean value 297.7 pm) are approximately 6 pm longer than the Ca1−P(*n*) bonds (mean distance 291.3 pm). These bond lengths are consistent with the Ca−P distances observed in other calcium bis-

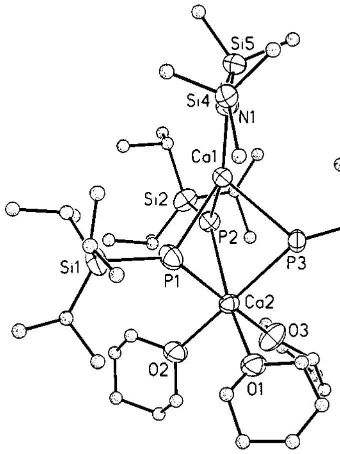


Figure 2. Molecular structure of **1**; C atoms are drawn with arbitrary radii and H atoms are omitted for clarity; the ellipsoids of the heavier atoms are drawn at a 40% probability level; selected bond lengths [pm] and angles [°]: Ca1−N1 228.1(9), Ca1−P1 290.9(4), Ca1−P2 294.7(4), Ca1−P3 288.2(3), Ca2−P1 297.8(4), Ca2−P2 298.3(3), Ca2−P3 297.1(4), Ca2−O1 240.7(8), Ca2−O2 240.1(7), Ca2−O3 235.0(9), P1−Si1 223.3(4), P2−Si2 221.8(4), P3−Si3 221.8(4), Ca1···Ca2 389.9(3); Ca1−P1−Ca2 83.0(1), Ca1−P1−Si1 128.8(2), Ca2−P1−Si1 139.3(2), Ca1−P2−Ca2 82.20(9), Ca1−P2−Si2 133.9(2), Ca2−P2−Si2 142.6(2), Ca1−P3−Ca2 83.51(9), Ca1−P3−Si3 123.0(2), Ca2−P3−Si3 138.8(2), P1−Ca1−P2 82.7(1), P1−Ca1−P3 81.8(1), P2−Ca1−P3 81.6(1), P1−Ca2−P2 80.9(1), P1−Ca2−P3 79.1(1), P2−Ca2−P3 79.57(9)

(phosphanides).[1] The distortion of the tetrahedral environments of the phosphorus atoms is best illustrated by the angle sums at these centers, neglecting the hydrogen atoms [M, M′ = Ca1, Ca2, Si(*n*); ΣMP1M′ = 351.1°; ΣMP2M′ = 358.7°; ΣMP3M′ = 345.2°]. Compared to those in HP(Si*i*Pr$_3$)$_2$ (P−Si 226.5 pm[9]), the P(*n*)−Si(*n*) bonds are approximately 4 pm shorter due to the negative charge on the phosphorus atoms. Furthermore, the higher coordination number of four at the phosphorus atoms leads to elongated P−Si bonds compared with those in tetrakis(tetrahydrofuran-*O*)calcium bis[bis(trimethylsilyl)phosphanide] (P−Si 219 pm[21]) and tetrakis(tetrahydrofuran-*O*)bis(triisopropylsilylphosphanide) (P−Si 219.6 pm[9]). Moreover, the elongation of bond lengths within the ESi*i*Pr$_3$ fragment is a well-known consequence of the steric strain.[26]

Figure 3 shows the molecular structure and the numbering scheme of (thf)$_5$Ba$_2$[P(H)Si*i*Pr$_3$]$_4$ (**2**). The central moiety is a trigonal-bipyramidal Ba$_2$P$_3$ core with the barium atoms in apical positions. Both alkaline earth metal centers have a distorted octahedral coordination sphere. The asymmetric unit contains two virtually identical molecules with the barium atoms labelled Ba(*mn*), where *m* = 1 or 2 denotes the molecule number and *n* is a digit to distinguish between different atoms. Here, the discussion is limited to the molecule with *m* = 1.

Ba11 is bonded to four phosphanide anions and two thf molecules, whereas Ba12 is surrounded by three phosphanide substituents and three thf molecules. The Ba11−P(*n*) bond lengths vary over the narrow range of 331 ± 3 pm regardless of whether the phosphanide ligand is in a bridging or terminal position. The Ba12−P(*n*) distances have a mean value of 323.4 pm and are clearly smaller. These findings are consistent with an electrostatic viewpoint, where the size of the ions largely determines the intramolecular distances between the cations and anions, but not the coordination number at the phosphorus atoms. All the aforementioned Ba−P distances lie within the broad range of Ba−P values found in barium bis(phosphanides).[1]

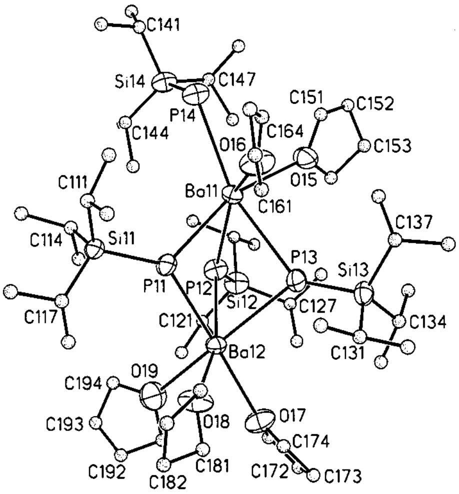


Figure 3. Molecular structure and numbering scheme of **2**; only one molecule is displayed; thermal ellipsoids represent a 40% probability level; C atoms are drawn with arbitrary radii and H atoms are omitted for clarity; selected bond lengths [pm] and angles [°]: Ba11−P11 330.6(2), Ba11−P12 330.1(2), Ba11−P13 333.5(2), Ba11−P14 328.5(3), Ba11−O15 273.8(6), Ba11−O16 272.9(6), Ba12−P11 324.7(2), Ba12−P12 323.9(2), Ba12−P13 321.5(2), Ba12−O17 274.7(6), Ba12−O18 273.9(6), Ba12−O19 274.0(7), P11−Si11 221.4(3), P12−Si12 221.0(3), P13−Si13 220.2(3), P14−Si14 219.3(3), Ba11···Ba12 461.03(9); Ba11−P11−Ba12 89.41(5), Ba11−P11−Si11 123.2(1), Ba12−P11−Si11 135.2(1), Ba11−P12−Ba12 89.64(5), Ba11−P12−Si12 137.9(1), Ba12−P12−Si12 121.0(1), Ba11−P13−Ba12 89.46(5), Ba11−P13−Si13 138.0(1), Ba12−P13−Si13 131.6(1), Ba11−P14−Si14 115.5(1), P11−Ba11−P12 77.60(6), P11−Ba11−P13 74.28(6), P12−Ba11−P13 72.41(6), P11−Ba12−P12 79.33(6), P11−Ba12−P13 76.69(6), P12−Ba12−P13 74.79(6)

As described for **1**, a flattening of the coordination spheres about the bridging phosphorus atoms is observed [M, M′ = Ba11, Ba12, Si(1*n*); ΣMP11M′ = 347.8°; ΣMP12M′ = 348.5°; ΣMP13M′ = 359.1°]. The smallest Ba−P(1*n*)−Si(1*n*) angle is realized within the terminal phosphanide substituent (*n* = 4), with a value of 115.5°. Due to the intramolecular strain, the Si*i*Pr$_3$ groups are pushed to the periphery of the molecule, thereby widening the Ba−P−Si angles and flattening the coordination spheres of the P atoms.

Figure 4 shows the molecular structure as well as the numbering scheme of dimeric heteroleptic **4**. The apostrophes indicate symmetry-related atoms. The bis(trimethylsilyl)amide ligand is in a terminal position, while the tri-*tert*-butylsilylphosphanide substituent adopts a bridging position. A coordination number of five at the alkaline earth metal center is achieved by the coordination of two thf coligands. In this case, we were able to locate the phosphorus-bonded hydrogen atoms. The Ba−N (260.1 pm) and Ba−P bond lengths (330 pm) have values in the expected

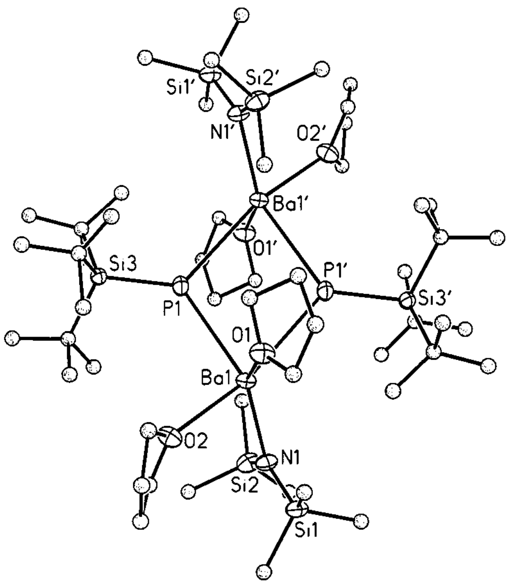


Figure 4. Molecular structure of **4**; thermal ellipsoids are drawn at a 40% probability level; C atoms are shown with arbitrary radii and H atoms are omitted for clarity; symmetry-related atoms ($-x+1$, $-y$, $-z$) are marked with an apostrophe; selected bond lengths [pm] and angles [°]: Ba1−N1 260.1(2), Ba1−P1 330.27(7), Ba1−P1′ 329.25(7), Ba1−O1 275.4(2), Ba1−O2 278.9(2), N1−Si1 168.5(2), N1−Si2 167.5(2), P1−Si3 222.96(9); P1−Ba1−P1′ 73.25(2), Ba1−P1−Ba1′ 106.75(2), Ba1−P1−Si3 127.92(3), Ba1′−P1−Si3 124.45(3), Ba1−N1−Si1 117.6(1), Ba1−N1−Si2 115.3(1), Si1−N1−Si2 127.1(2)

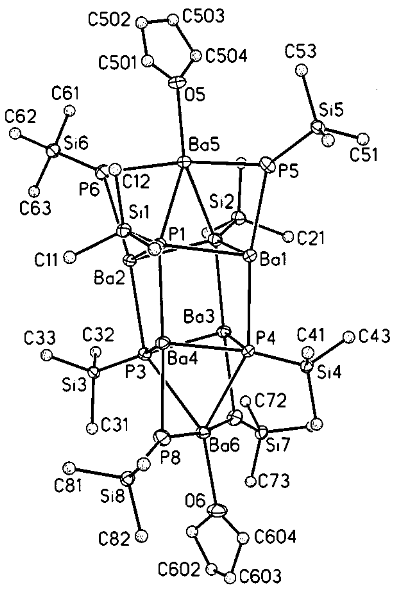


Figure 5. Molecular structure of **6**; the methyl groups of the Si*t*Bu$_3$ substituents and the H atoms are omitted for clarity; the remaining C atoms are shown with arbitrary radii; ellipsoids are drawn at a 40% probability level; selected bond lengths [pm] and angles [°]: see Table 1

ranges[1] and are essentially similar to those found in $\{(Me_3Si)_2NBa[\mu\text{-}P(SiMe_3)_2]\}_2$.[23] Neglecting H1, the coordination sphere about P1 is almost planar, having an angle sum of 359.1°.

Figure 5 displays the molecular structure and the numbering scheme of **6**. This molecule is built-up of four inner tri-*tert*-butylsilylphosphanediide ligands (P1 to P4) and four outer tri-*tert*-butylsilylphosphanide ligands (P5 to P8), held together by six barium atoms. The central $Ba_6P_8$ core is depicted in Figure 6 in a stereoscopic view. Whereas the phosphanide ligands contain quadruply coordinated phosphorus atoms, the inner P atoms are surrounded by four barium centers and one silicon atom. The Ba−P bond lengths are spread over a wide range from 311 to 347 pm (Table 1). The shortest Ba−P bond lengths are found within the four-membered rings Ba1−P1−Ba2−P2 and Ba3−P3−Ba4−P4. The Ba−P distances between these $Ba_2P_2$ cycles as well as the Ba−P values to the P(H)Si*t*Bu$_3$ substituents are significantly longer. All the barium atoms are bonded to four phosphorus atoms. Their coordination spheres are completed by the coordination of a thf molecule (Ba5 and Ba6) or by agostic interactions with *tert*-butyl groups (Ba1 to Ba4). The Ba−O bond lengths of 273 pm lie within the characteristic range.[1,18b] The close contacts between Ba5 and Ba6, respectively, and the neighboring metal centers are a consequence of the rather low coordination numbers of these barium atoms and the strong electrostatic attraction between the dianions and dications. The coordination polyhedra of Ba5 and Ba6 are trigonal-bipyramids with the phosphanide ligands in apical positions [P5−Ba5−P6 170.30(7)°, P7−Ba6−P8 172.73(7)°].

The angle sums ΣMPM′ at P5 (359.7°), P6 (359.7°), P7 (358.7°), and P8 (356.9°) indicate an almost planar environment at the phosphorus atoms. The hydrogen atoms at these P atoms were not located and due to the planar $Ba_2PSi$ fragments the H atoms could be bonded on either side and several isomers are possible. However, the $^{31}$P-NMR data show only one resonance for the PH groups. The P−Si bond lengths have values of approximately 222 pm, irrespective of whether mono- or dianions are considered. Due to shielding by the *tert*-butyl groups, the P−H moieties are not metalated by the still present barium bis[bis(trimethylsilyl)amide], not even at elevated temperatures such as in boiling toluene.

## Conclusion

Metalations of $H_2PSiR_3$ (R = *i*Pr, *t*Bu) with bis(tetrahydrofuran-*O*)calcium and bis(tetrahydrofuran-*O*)barium bis[bis(trimethylsilyl)amide] yield the corresponding alkaline earth metal bis(trialkylsilylphosphanides) of the type $(L)_nM[P(H)SiR_3]_2$. These phosphanides show a weakening of the P−H bond compared to the phosphane and hence an increased reactivity. Consequently, these compounds react as metalating reagents and as metalation substrates. The elimination of $H_2PSiR_3$ yields a product of the type $(L)_nM[P(H)SiR_3]_2(PSiR_3)_2$. With R = *t*Bu, an X-ray structure determination has revealed a dimer of this formula unit. The central $M_6P_8$ core can be considered as two trigonal bipyramids with a common $MP_2$ face; this polyhedron dimerizes via the square-planar $M_2P_2$ plane.

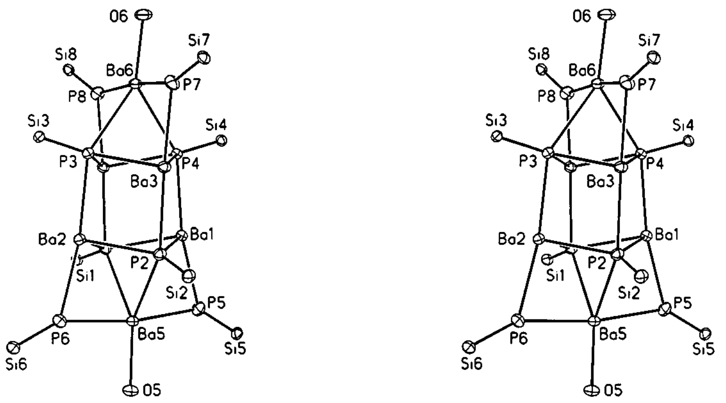
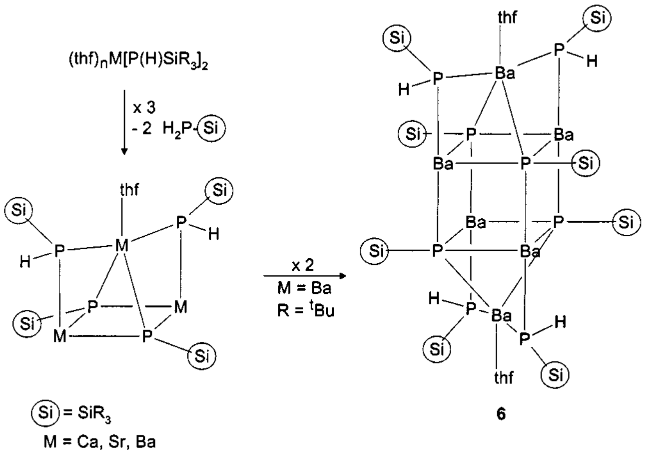


Figure 6. Stereoscopic view of the $Ba_6P_8$ polyhedron of **6**; the atoms are drawn at a 40% probability level

Table 1. Selected bond lengths [pm] and angles [°] of **6**

| *n* | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Ba1−P(*n*) | 314.3(2) | 311.1(2) |  | 325.6(2) | 313.8(2) |  |  |  |
| Ba2−P(*n*) | 313.6(2) | 314.7(3) | 331.6(2) |  |  | 322.7(2) |  |  |
| Ba3−P(*n*) |  | 333.3(2) | 314.2(2) | 315.5(2) |  |  | 324.6(2) |  |
| Ba4−P(*n*) | 328.7(2) |  | 313.4(2) | 316.2(2) |  |  |  | 318.3(2) |
| Ba5−P(*n*) | 337.7(2) | 339.5(2) |  |  | 327.1(3) | 322.2(3) |  |  |
| Ba6−P(*n*) |  |  | 347.4(2) | 331.5(2) |  |  | 320.7(3) | 323.9(3) |
| Ba(*n*)−O(*n*) |  |  |  |  | 272.7(6) | 272.7(6) |  |  |
| P(*n*)−Si(*n*) | 222.3(3) | 221.9(3) | 222.0(3) | 222.4(3) | 221.8(3) | 222.2(4) | 222.3(3) | 222.1(3) |
| Ba1···Ba(*n*) |  | 469.89(7) | 436.82(7) | 422.10(8) | 402.58(5) |  |  |  |
| Ba2···Ba(*n*) |  |  | 432.71(8) | 435.14(7) | 405.77(5) |  |  |  |
| Ba3···Ba(*n*) |  |  |  | 475.78(7) |  | 409.53(5) |  |  |
| Ba4···Ba(*n*) |  |  |  |  |  | 401.42(5) |  |  |
| Ba1−P(*n*)−Si(*n*) | 133.3(1) | 134.0(1) |  | 98.36(9) | 137.6(1) |  |  |  |
| Ba2−P(*n*)−Si(*n*) | 129.8(1) | 128.5(1) | 99.55(9) |  |  | 128.5(1) |  |  |
| Ba3−P(*n*)−Si(*n*) |  | 101.1(1) | 129.2(1) | 133.2(1) |  |  | 124.4(1) |  |
| Ba4−P(*n*)−Si(*n*) | 98.46(9) |  | 132.2(1) | 129.1(1) |  |  |  | 134.0(1) |
| Ba5−P(*n*)−Si(*n*) | 111.71(9) | 107.9(1) |  |  | 144.3(1) | 153.2(1) |  |  |
| Ba6−P(*n*)−Si(*n*) |  |  | 111.62(9) | 109.72(9) |  |  | 155.6(1) | 145.5(1) |



Scheme 5. Metalation of $H_2P-SiiPr_3$ and formation of **6**

## Experimental Section

**General Remarks:** All experiments and manipulations were carried out under argon or nitrogen that had been purified by passage through BTS catalyst and $P_4O_{10}$. Reactions were performed using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting materials $(thf)_2Ca[N(SiMe_3)_2]_2$,[16][17] $(thf)_2Ba[N(SiMe_3)_2]_2$,[16][18] $H_2PSi\mathit{i}Pr_3$,[9] and $H_2PSi\mathit{t}Bu_3$[20] were prepared according to literature procedures. − NMR spectra were recorded with Jeol GSX270 and EX400 spectrometers. − A Perkin-Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra; solid substances were examined as Nujol mulls between CsBr plates (vs very strong, s strong, m medium strong, w weak, vw very weak, sh shoulder). The frequencies in the region of the Nujol vibrations are not listed. − The low carbon values obtained in the elemental analyses can be attributed to carbide and carbonate formation, as well as to the loss of neutral coligands during handling and combustion of the compounds.

**$(Me_3Si)_2NCa[\mu\text{-}P(H)Si\mathit{i}Pr_3]_3Ca(thp)_3$ (1):** To 2.78 g of $(thf)_2Ca[N(SiMe_3)_2]_2$ (5.50 mmol), dissolved in 12 mL of thp, 1.33 mL of triisopropylsilylphosphane (8.25 mmol) was added at −60°C. After warming to room temp., this solution was stirred for a further 12 h. All volatiles were then removed at room temp. in vacuo. Addition of toluene and storage at −30°C led to the deposition of 0.93 g of crystalline **1** (0.87 mmol; 32%); dec. above 110°C. − NMR ($[D_8]$toluene, 30°C); $^1H$: $\delta = -0.49$ (m, PH), 0.50 (s, $SiMe_3$), 1.25 (m, CH), 1.31 (s, Me), 1.31, 1.39 and 3.77 (thp); $^{31}P\{^1H\}$: $\delta = -278.68$; $^{31}P$: $\delta = -278.63$ [AA′A′′XX′X′′, simulation: $^1J(P,H) = 186.1(1)$ Hz, $^2J(P,P) = 92.3(1)$ Hz, $^3J(P,H') = 11.7(6)$ Hz, $^3J(P,H'') = 2.1(6)$ Hz]. − IR: $\tilde{\nu}$ = 2274 m, 1462 s, 1442 m, 1384 w, 1379 w, 1362 w, 1357 w, 1328 vw, 1310 m, 1277 w, 1248 s, 1240 s, 1194 s, 1181 sh, 1125 sh, 1098 m, 1077 s, 1048 vs, 1033 vs, 1015 s, 992 s, 966 m, 931 m, 918 m, 881 vs, 865 s, 833 s, 820 s, 812 s, 767 m, 747 w, 708 sh, 683 sh, 664 sh, 652 s, 639 s, 626 m, 609 m, 584 s, 572 s, 563 s, 511 s, 474 m, 446 m, 429 w, 412 w, 381 w, 363 m. − $C_{33}H_{84}Ca_2NP_3Si_5$ (808.53, coligand-free complex): calcd. C 49.02, H 10.47, N 1.73; found C 47.60, H 9.85, N 1.63.

**[*i*Pr$_3$Si(H)P](thf)$_2$Ba[μ-P(H)Si*i*Pr$_3$]$_3$Ba(thf)$_3$ (2):** At −60°C, 1.36 mL of triisopropylsilylphosphane (6.08 mmol) was slowly added dropwise to a solution of 1.83 g of (thf)$_2$Ba[N(SiMe$_3$)$_2$]$_2$ (3.04 mmol) in 10 mL of thf. After completion of the addition, the solution was stirred for a further 48 h at room temp. and then concentrated to an oily residue. At −30°C, 1.24 g of colorless crystals of **2** (0.89 mmol; 59%) precipitated; m.p. 47°C. − NMR ([D$_8$]THF, 30°C); $^1$H: $\delta = -1.97$ [d, PH, $^1J$(P,H) = 152.7 Hz], 0.91 (sept, CH), 1.02 [d, Me, $^3J$(H,H) = 7.2 Hz], 1.76 and 3.62 (thf); $^{13}$C{$^1$H}: $\delta = 15.03$ [d, CH, $^2J$(P,C) = 6.1 Hz], 19.62 (s, Me), 25.45 and 67.35 (thf); $^{29}$Si{$^1$H}: $\delta = 27.19$ [d, $|^1J(P,Si) + {}^3J(P,Si)| = 52.6$ Hz]; $^{31}$P{$^1$H}: $\delta = -287.76$. − IR: ṽ = 2241 m, 1359 w, 1306 sh, 1293 vw, 1242 m, 1181 w, 1156 w, 1130 w, 1072 s, 1042 vs, 1012 m, 1005 sh, 989 s, 916 m, 882 vs, 843 sh, 747 vw, 698 w, 640 vs, 622 s, 586 s, 565 s, 512 s, 474 m, 445 w, 431 w, 416 w. − $C_{36}H_{88}Ba_2P_4Si_4$ (1031.90, coligand-free complex): calcd. C 41.90, H 8.60; found: C 39.21, H 8.03.

**[*i*Pr$_3$Si(H)As](thf)$_2$Ba[μ-As(H)Si*i*Pr$_3$]$_3$Ba(thf)$_3$ (3):** To a solution of 1.83 g of (thf)$_2$Ba[N(SiMe)$_3$]$_2$ (3.04 mmol) in 10 mL thf at −70°C, was slowly added 1.26 mL of triisopropylsilylarsane (6.08 mmol). Following the addition, the mixture was stirred for a further 48 h at room temp. Reduction to a volume of approximately 5 mL and storage at −30°C led to the deposition of waxy crystals of **3** (0.93 g, 0.69 mmol; 45%); m.p. 40°C. − NMR ([D$_8$]THF, 30°C); $^1$H: $\delta =$ 0.27 (s, AsH), 0.95 (br., CH), 1.04 [Me, $^3J$(H,H) = 6.8 Hz], 1.76 and 3.61 (thf); $^{13}$C{$^1$H}: $\delta = 15.22$ (CH), 19.87 (Me), 25.47 and 67.44 (thf); $^{29}$Si{$^1$H}: $\delta = 32.25$. − IR: ṽ = 2019 m, 1462 vs, 1382 sh, 1378 m, 1361 w, 1294 vw, 1250 m, 1226 sh, 1180 m, 1070 m, 1042 s, 1014 m, 1005 m, 989 s, 929 sh, 917 s, 882 vs, 842 m, 771 vw, 754 vw, 663 s, 648 s, 635 s, 603 sh, 586 sh, 573 s, 558 s, 503 s, 464 m, 444 sh, 425 vw, 385 w, 354 vw. − $C_{44}H_{104}As_4Ba_2O_2Si_4$ [1352.00, bis(thf) complex]: calcd. C 39.09, H 7.75; found C 39.09, H 7.32.

**[(Me$_3$Si)$_2$N](thf)$_2$Ba[μ-P(H)Si*t*Bu$_3$]$_2$Ba(thf$_2$)[N(SiMe$_3$)$_2$] (4):** A solution of 256 mg of tri-*tert*-butylsilylphosphane (1.1 mmol) in 5 mL of toluene was added dropwise to 663 mg of (thf)$_2$Ba[N(SiMe$_3$)$_2$]$_2$ (1.1 mmol), dissolved in 35 mL of toluene. After completion of the addition, the solution was reduced to a volume of a few mL. At 4°C, 607 mg of colorless cuboids of **4** (0.45 mmol; 82%) precipitated; m.p. 359°C (dec.). − NMR (30°C); $^1$H ([D$_6$]benzene): $\delta =$ 0.32 (SiMe$_3$), 1.33 (*t*Bu), 1.36 and 3.58 (thf), PH signal not observed; $^{13}$C{$^1$H} ([D$_6$]benzene): $\delta = 5.42$ (SiMe$_3$), 24.05 (PSiC$_3$), 31.87 (Me$_{Bu}$), 24.98 and 68.61 (thf); $^{31}$P ([D$_8$]toluene, three major isomers): $\delta = -220.1$ [$^1J$(P,H) = 153 Hz], −229.1 [$^1J$(P,H) = 150 Hz], −233.5 [$^1J$(P,H) = 152 Hz]. − IR: ṽ = 2225 w, 1251 m, 1180 m, 1064 m, 1037 m, 1013 s, 932 s, 882 m, 842 s, 816 vs, 803 s, 757 vw, 729 vw, 694 vw, 664 vw, 594 m, 569 s, 511 s, 478 w, 456 m, 389 vw, 360 vw, 331 w. − $C_{44}H_{108}Ba_2N_2O_2P_2Si_6$ (1202.47): calcd. C 43.95, H 9.05, N 2.33; found C 43.93, H 7.97, N 2.12.

**(thf)*n*Ba[P(H)Si*t*Bu$_3$]$_2$ (5):** A solution of 558 mg of tri-*tert*-butylsilylphosphane (2.4 mmol) in 15 mL of toluene was slowly added dropwise to a solution of 723 mg of (thf)$_2$Ba[N(SiMe$_3$)$_2$]$_2$ (1.2 mmol) in 20 mL of toluene. After reduction to a volume of a few mL, the precipitate was dissolved by adding thf and characterized NMR-spectroscopically. − NMR ([D$_6$]benzene, 30°C); $^1$H: $\delta =$ 1.24 (*t*Bu), 1.35 and 3.54 (thf), PH signal was not observed; $^{13}$C{$^1$H}: $\delta = 24.00$ (PSiC), 31.97 (Me), 25.49 and 67.46 (thf); $^{31}$P: $\delta = -242.5$ [$^1J$(P,H) = 147 Hz].

**{(thf)Ba$_3$(μ$_4$-PSi*t*Bu3)$_2$[μ$_2$-P(H)Si*t*Bu$_3$]$_2$}$_2$ (6):** 906 mg of (thf)$_2$Ba[N(SiMe$_3$)$_2$]$_2$ (1.5 mmol) and 466 mg of tri-*tert*-butylsilylphosphane (2.0 mmol) were dissolved in 23 mL of toluene and heated to 100°C for approximately 6 h. The solution turned dark brown. After cooling to room temp., the solid materials were removed and the solu-

Table 2. Crystallographic data of **1**, **2**, **4**, and **6**, as well as details of the structure solution and refinement procedures

| Compound | **1** | **2** | **4** | **6** |
|---|---|---|---|---|
| Empirical formula | $C_{48}H_{111}Ca_2NO_3P_3Si_5$ | $C_{56}H_{128}Ba_2O_5P_4Si_4$ | $C_{52}H_{122}Ba_2N_2O_4P_2Si_6$ | $C_{119}H_{250}Ba_6O_{2.25}P_8Si_8$ |
| Molecular mass [g·mol$^{-1}$] | 1063.90 | 1392.51 | 1344.68 | 3013.71 |
| $T$ [K] | 183 | 183 | 173 | 173 |
| Space group[28] | $Cc$ (no. 9) | $P-1$ (no. 2) | $P2_1/c$ (no. 14) | $P2/c$ (no. 13) |
| $a$ [pm] | 1406.0(3) | 1387.5(2) | 1389.57(3) | 3136.17(3) |
| $b$ [pm] | 2160.0(5) | 2240.1(4) | 1440.01(3) | 1454.17(3) |
| $c$ [pm] | 2199.8(6) | 2426.7(4) | 1931.21(4) | 3616.84(1) |
| α [°] | 90 | 90.884(6) | 90 | 90 |
| β [°] | 101.813(9) | 90.865(7) | 107.814(1) | 103.275(1) |
| γ [°] | 90 | 90.704(6) | 90 | 90 |
| $V$ [nm$^3$] | 6.539(3) | 7.540(2) | 3.6791(1) | 16.0539(4) |
| $Z$ | 4 | 4 | 2 | 4 |
| $d_{calcd.}$ [g·cm$^3$] | 1.081 | 1.227 | 1.214 | 1.247 |
| μ [mm$^{-1}$] | 0.373 | 1.224 | 1.241 | 1.626 |
| $F$(000) | 2340 | 2928 | 1412 | 6200 |
| Scan range [°] | $1.75 < \theta < 27.76$ | $0.84 < \theta < 29.52$ | $1.54 < \theta < 29.30$ | $0.67 < \theta < 29.41$ |
| Measured data | 11050 | 44857 | 20540 | 90128 |
| Unique data ($R_{int}$) | 8693 (0.0747) | 24072 (0.0351) | 6641 (0.0209) | 30674 (0.0765) |
| Parameters | 539 | 1142 | 386 | 1239 |
| Restraints | 15 | 94 | 0 | 0 |
| $wR_2$[a] (all data, on $F^2$) | 0.2254 | 0.1711 | 0.0704 | 0.1767 |
| $R_1$[a] (all data) | 0.1380 | 0.1008 | 0.0347 | 0.1370 |
| Data with $I > 2\sigma(I)$ | 5560 | 14458 | 5876 | 14762 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0865 | 0.0565 | 0.0283 | 0.0551 |
| Goof $s$[b] on $F^2$ | 1.194 | 1.083 | 1.085 | 1.099 |
| Residual density [e·nm$^{-3}$] | 744, −438 | 816, −756 | 452, −661 | 1625, −687 |

[a] Definition of the $R$ values: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. − [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

tion was reduced to a volume of a few mL. At 4°C, 508 mg of light-brown crystals of **6** (0.19 mmol; 76%) precipitated; m.p. 378°C (dec.). − NMR (30°C); $^{1}$H ([D$_6$]benzene): $\delta$ = 1.31 (PHSi*t*Bu$_3$), 1.53 (PSi*t*Bu$_3$), 1.36 and 3.56 (thf), PH signal was not observed; $^{13}$C{$^{1}$H}: $\delta$ = 24.06 (PHSiC), 26.82 (PSiC), 31.83 (PHSiC*Me*$_3$), 33.90 (PSiC*Me*$_3$), 25.09 and 68.48 (thf); $^{31}$P ([D$_8$]toluene): $\delta$ = −25.0 (s, PSi*t*Bu$_3$), −222.9 [d, PHSi*t*Bu$_3$, $^{1}J$(P,H) = 149 Hz]. − IR: $\tilde{\nu}$ = 2234 w, 1251 m, 1180 m, 1064 m, 1037 m, 1013, 932 s, 881 m, 842 s, 816 vs, 803 s, 757 w, 729 vw, 694 vw, 685 vw, 664 vw, 594 m, 569 s, 511 vs, 478, 456 m, 389 vw, 360 vw, 331 vw. − $C_{96}H_{220}Ba_6P_8Si_8$ (2671.24): calcd. C 43.17, H 8.30; found C 43.15, H 7.31.

**Structure Determinations:**[27] Single crystals were covered with Nujol, sealed in thin-walled capillaries, mounted on a Siemens P4 diffractometer, and examined with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 71.073 pm). A Siemens SMART-CCD area detector was used to monitor the reflections of **1**, **2**, **4**, and **6**. Crystallographic parameters and details of the data collection are summarized in Table 2.

All structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97.[29] Neutral atom scattering factors were taken from Cromer and Mann,[30] and for the hydrogen atoms from Stewart et al.[31] The non-hydrogen atoms were refined anisotropically. The H atoms were considered as a riding model under restriction of ideal symmetry at the atoms to which they were attached. The disordering of *i*Pr groups in **1** and **2** is not shown in Figures 2 and 3. The methyl groups of the *t*Bu$_3$Si substituent of **4** show a two-site disorder. The structure of **6** contains two toluene molecules and a thf molecule between the barium phosphanide complexes. The carbon and oxygen atoms of these solvent molecules were refined isotropically.

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[27] Crystallographic data (excluding structure factors) for the structures of **1**, **2**, **4**, and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-111475 for **1**, -111476 for **2**, -111477 for **4**, and -111478 for **6**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [E-mail: deposit@ccdc.cam.ac.uk].

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