Magnesiation of Triisopropylsilylphosphane: Synthesis and Structures of New $Mg_{2n}P_{2m}$ Polyhedra

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Dedicated to Prof. Alfred Schmidpeter on the occasion of his 70th birthday

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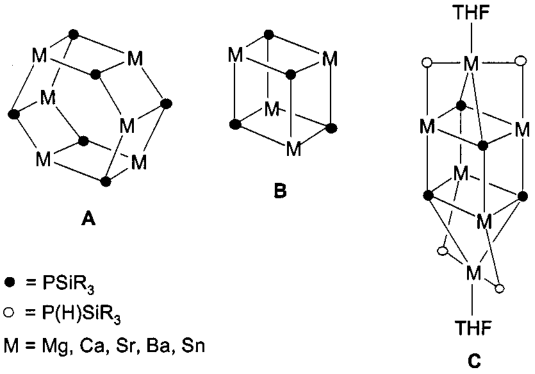
The magnesiation of triisopropylsilylphosphane with dibutylmagnesium in toluene yields the octanuclear complex $[Mg_8(PSi^iPr_3)_6\{P(H)Si^iPr_3\}_4]$ **(1)** which consists of $MgPSi^iPr_3$ units forming a hexagonal Mg_6P_6 prism, with two opposite Mg_2P_2 moieties capped by additional $Mg[P(H)Si^iPr_3]_2$ groups. If a small amount of THF is present during the metalation reaction $[(THF)_4Mg_6(PSi^iPr_3)_6]$ **(2)** also containing a hexagonal Mg_6P_6 prism can be isolated. The magnesiation of $H_2P–Si^iPr_3$ in tetrahydrofuran leads to the formation of the tetrameric complex $[(THF)MgPSi^iPr_3]_4$ **(3)** with a slightly distorted Mg_4P_4 cubane-like structure.The structures depend strongly on the steric strain caused by the trialkylsilyl substituents and the neutral coligands at the magnesium center. The highest steric strain, which is induced by coordination to every magnesium atom, leads to the smallest Mg_nP_n polyhedron – the central Mg_4P_4 heterocubane moiety. In compounds **1** and **2** the hexagonal Mg_6P_6 prism is formed, however, with reduced steric strain as observed for **2** where the Mg–P bond lengths become more similar.

Introduction

The synthesis of phosphandiides of the main group metals has been attracting increasing interest over the last few years due to their expected synthetic potential. Bulky substituents at the phosphorus atoms are necessary to avoid polymerization and to obtain oligomers soluble in common organic solvents. One of the most favored groups is the tri(*tert*-butyl)silyl[1] moiety, which is able to stabilize the negative charge and to shield the reactive center effectively. Therefore, solvent-free hexameric $[MgPSi^tBu_3]_6$ **(A)**[2] and tetrameric $[SnPSi^tBu_3]_4$ **(B)**[3] are well-known (Scheme 1). With regard to the heavier alkaline earth metals, the complete deprotonation of $H_2P-Si^tBu_3$ to a phosphandiide has not yet been achieved. Even in the presence of an excess of metalating reagent, bis(tetrahydrofuran-*O*)hexakisbarium tetrakis[tri(*tert*-butyl)silylphosphanide] tetrakis[tri(*tert*-butyl)silylphosphandiide] **(C)** with an $RP(H)^-/RP^{2-}$ ratio of 1:1 was isolated.[4] Smaller substituents such as triisopropylsilyl groups yield higher oligomers as shown for the solvent-free hexameric $[SnPSi^iPr_3]_6$ with a hexagonal Sn_6P_6 prism[5] similar to **A**. Herein we report on the magnesiation of triisopropylsilylphosphane with dibutylmagnesium and the influence of the THF content on the structures of the magnesiated phosphanes.

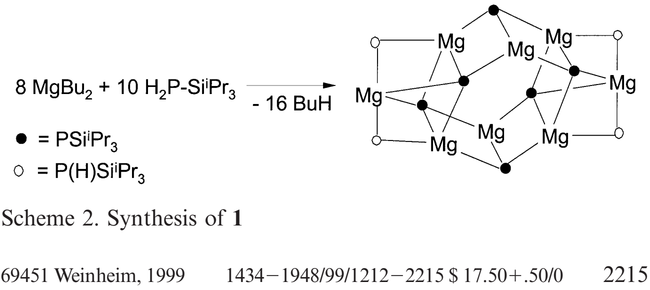


Scheme 1. Known phosphandiides of selected divalent main group metals (see text)

Results and Discussion

Synthesis

The metalation of triisopropylsilylphosphane[6] in toluene with dibutylmagnesium in the absence of Lewis bases such as THF yields compound **1** as shown in Scheme 2. Heating of the reaction solution to approximately 100 °C and subsequent cooling to 6 °C lead to the precipitation of colorless crystals of **1** with a melting point of 272 °C and a decomposition point of 297 °C.



Scheme 2. Synthesis of **1**

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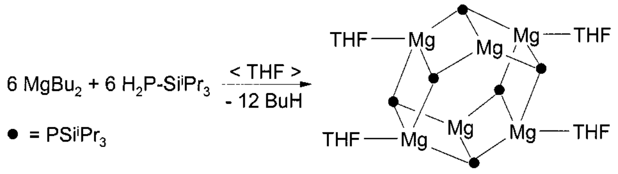
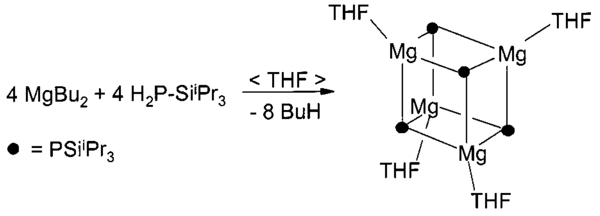
The ^{31}P NMR spectrum shows three chemically different phosphorus nuclei; however, the coupling pattern was not resolved and the assignment was not obvious. The resonance at $\delta = -265$ shows a doublet splitting due to a $^{1}J(P-H)$ coupling, whereas the other two signals originate from phosphandiide ligands. For these reasons a crystal structure determination was performed at -80°C (see below). The central moiety is a hexagonal Mg_6P_6 prism with two $Mg[P(H)Si^iPr_3]_2$ molecules coordinating above two opposite square planes. These magnesium bis(phosphanide) molecules can be substituted by Lewis bases such as THF. If a small amount of this ether is present during the magnesiation reaction compound **2** is instead obtained (Scheme 3). Again the Mg_6P_6 prism is formed; however, in this case, four THF molecules are bonded to the magnesium atoms of the two opposite square planes.



Scheme 3. Synthesis of **2**

Whereas ladder structures were reported for the hexamer $[LiP(SiMe_3)_2]_6$[7] and the polymeric compounds $[AP(SiMe_3)_2]_\infty$ (A = K, Rb, Cs),[8] the hexagonal prism of **2** can be described as a closed (cyclic) ladder structure. Open ladder structures such as those observed for the alkali metal bis(trimethylsilyl)phosphanides have not yet been found in alkaline earth metal phosphanide and phosphandiide complexes. The $^{31}P\{^1H\}$ NMR spectrum of **2** shows a single resonance due to a rapid interchange of the THF molecules on the NMR time scale. If the magnesiation of triisopropylsilylphosphane is performed in THF, the formation of $[(THF)MgPSi^iPr_3]_4$ **(3)** is observed (Scheme 4).



Scheme 4. Sythesis of **3**

Molecular Structures

The molecular structure of **1** and the atom numbering scheme is shown in Figure 1. The molecule has a crystallographic C_2 axis through the atoms Mg2 and Mg5; the symmetry-related atoms are marked with apostrophes. Selected bond lengths are summarized in Table 1.

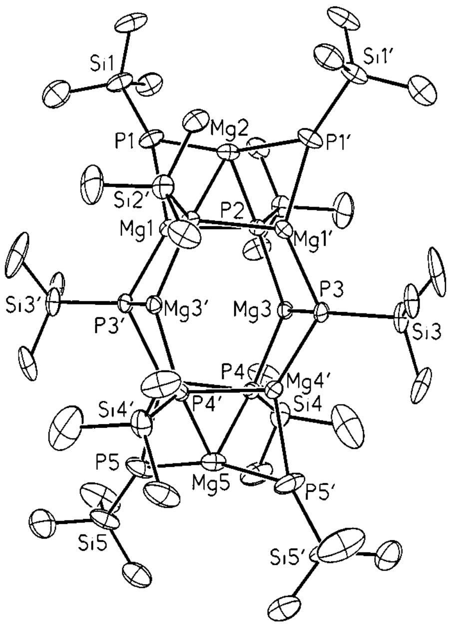


Figure 1. Molecular structure and numbering scheme of **1**; the methyl groups and the hydrogen atoms are omitted for clarity; the ellipsoids represent a probability of 40%; the atoms marked with an apostrophe are generated by C_2 symmetry; selected bond angles [°]: P1−Mg1−P2 100.59(7), P1−Mg1−P2′ 87.71(6), P1−Mg1−P3′ 139.0(1), P2−Mg1−P2′ 79.48(6), P2−Mg1−P3′ 120.40(7), P1−Mg2−P2 99.18(5), P1−Mg2−P1′ 163.0(1), P1−Mg2−P2′ 93.63(5), P2−Mg2−P2′ 82.46(8), P2−Mg3−P3 107.12(6), P2−Mg3−P4 134.59(8), P3−Mg3−P4 106.25(7), P4−Mg4−P5 98.17(8), P4−Mg4−P3′ 123.00(8), P4−Mg4−P4′ 80.21(7), P5−Mg4−P3′ 138.8(1), P5−Mg4−P4′ 89.02(7), P4−Mg5−P5 96.70(6), P4−Mg5−P4′84.29(8), P4−Mg5−P5′ 95.87(6), Mg1−P1−Mg2 71.05(7), Mg1−P2−Mg2 69.88(5), Mg1−P2−Mg3 107.12(7), Mg2−P2−Mg3 135.89(6), Mg1−P2−Mg1′ 100.22(6), Mg2−P2−Mg1′ 65.21(4), Mg3−P2−Mg1′ 72.56(5), Mg3−P3−Mg1′ 79.97(6), Mg3−P3−Mg4′ 81.22(7), Mg1′−P3−Mg4′ 123.65(9), Mg3−P4−Mg4 105.22(7), Mg3−P4−Mg5 135.82(7), Mg4−P4−Mg5 70.11(6), Mg3−P4−Mg4′ 73.12(6), Mg4−P4−Mg4′99.30(7), Mg5−P4−Mg4′ 64.87(5), Mg4−P5−Mg5 71.40(7)

Table 1. Selected bond lengths of **1**[a]

Atom	C.N.[b]	Mg1	Mg2	Mg3	Mg4	Mg5
P1	4	257.8(2)	254.8(2)			
P2	5	255.8(2)	264.2(2)	252.7(2)		
P3	4			253.2(2)		
P4	5			251.6(2)	255.9(2)	263.4(2)
P5	4				256.5(2)	254.8(2)
P1′	4		254.8(2)			
P2′	5	287.5(2)	264.2(2)			
P3′	4	246.1(2)			245.8(2)	
P4′	5				291.2(2)	263.4(2)
P5′	4					298.3(2)
n		1	2	3	4	5
P(n)−Si(n)		225.1(2)	223.8(2)	221.3(2)	223.6(2)	225.5(2)

[a] Atoms marked with an apostrophe are generated by C_2 symmetry ($-x + 1, y, -z + 0.5$). − [b] Coordination number.

The central moiety is a hexagonal Mg_6P_6 prism as already described for the hexamer $[MgPSi^tBu_3]_6$.[2] Due to the fact that the triisopropylsilyl groups are less effective in shielding the metal atoms than tri(*tert*-butyl)silyl substituents, coordination gaps appear at the magnesium centers. Two molecules of $Mg[P(H)Si^iPr_3]_2$ are bonded above two opposite Mg_2P_2 planes. These magnesium bis(phosphanide) units have P1−Mg2−P1′ and P5−Mg5−P5′ bond angles of 163.0(1)°. The Mg2−P1−Si1 and Mg5−P5−Si5 values amount to 137.5(1) and 139.6(1)°, respectively. These structural data, together with the rather short Mg2−P1 and Mg5−P5 bond lengths of 254.8(2) pm, allow us to consider the idea of coordinated magnesium bis(phosphanide) molecules.

Another description of the structure can be derived from considering the trigonal bipyramid with the magnesium atoms in apical positions as the basic polyhedron. Two bipyramids are joined through common faces (Mg2, P2, P2′, and Mg5, P4, P4′, respectively); two of these polyhedra are joined again through two $MgPSi^iPr_3$ units. Regarding the structure of **1** in this way, the similarity to the barium compound **D** is obvious; in **D** the $MPSiR_3$ moieties are missing and the dimerization occurs through M_2P_2 planes. The molecule has three- and four-coordinate magnesium atoms.

From this structure we can now identify the three different kinds of phosphorus atoms already found in the $^{31}P\{^1H\}$ NMR spectrum: the four-coordinate phosphorus atoms of the phosphanide ligands bound to two Mg atoms, one Si and one H atom (P1 and P5); the hexagonal prism containing one fourfold- (P3) and two fivefold coordinated P atoms (P2 and P4).

Figure 2 shows the molecular structure of **2** and the atom numbering scheme. Although the molecule displays no crystallographically enforced symmetry, the central moiety is very similar to the Mg_6P_6 polyhedron of **1**. Selected structural parameters are summarized in Table 2. The substitution of both $Mg[P(H)Si^iPr_3]_2$ molecules by four THF ligands leads to steric relief at the metal center; consequently the Mg−P bond lengths become more equal varying between 248.7 and 259.9 pm; bond lengths of this magnitude are already known for magnesium bis(phosphanides).[9] The Mg−O bond lengths are characteristic[10][11] of four-coordinate magnesium.

Figure 3 shows a comparison of the central moieties of the structures of **1**, **2** and $[MgPSi^tBu_3]_6$ ignoring the carbon and hydrogen atoms. The distortions of the hexagonal prism due to the coordination of two additional molecules of $Mg[P(H)Si^iPr_3]_2$ or THF are rather small. Whereas in the hexamer $[MgPSi^tBu_3]_6$ the Mg−P bond lengths vary in the rather narrow range of 247 to 260 pm, in **1** Mg−P distances of up to 298 pm are observed.

Figure 4 shows the molecular structure of **3** and the atom numbering scheme. The central moiety consists of a slightly distorted Mg_4P_4 cube with four-coordinate magnesium and phosphorus atoms. Table 3 contains selected bond lengths. In this polyhedron the Mg−P distances vary in a very narrow range around 254 pm.

The P(n)−Si(n) bond lengths differ in a characteristic manner. The P3−Si3 distance in **1** is the smallest due to the low coordination number of four at P3, whereas the P2−Si2 and P4−Si4 bond lengths are elongated due to the higher coordination number at the phosphorus atoms P2 and P4. The phosphanide ligands show further elongated bond lengths because the lower charge on P1 and P5 leads to a reduced electrostatic attraction between the negative phosphorus and the positively polarized silicon atoms. In **2** the P−Si bond lengths lie in a narrow range around 221 pm. In **3** the P−Si values of 218.4 pm are clearly smaller due to the reduced steric strain as a consequence of small Mg−P−Mg angles. The negative charge on the phosphorus atoms leads to decreased P−Si bond lengths relative to tris(trialkylsilyl)phosphanes[12−14] and bis(triisopropylsilyl)phosphane.[6]

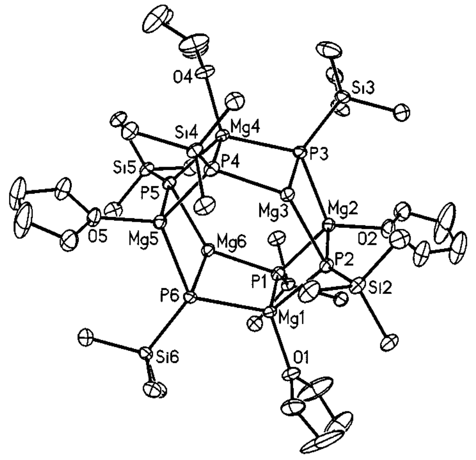


Figure 2. Molecular structure and numbering scheme of **2**; the methyl groups of the triisopropylsilyl substituents and the hydrogen atoms are omitted for clarity; the ellipsoids are drawn on a 40% probability level; selected bond angles [°]: P1−Mg1−P2 94.71(4), P1−Mg1−P6 99.75(4), P2−Mg1−P6 118.83(4), P1−Mg2−P2 94.76(4), P1−Mg2−P3 115.85(4), P2−Mg2−P3 100.88(4), P2−Mg3−P3 102.68(4), P2−Mg3−P4 138.58(4),P3−Mg3−P4 103.01(5), P3−Mg4−P4 100.44(4), P3−Mg4−P5 116.91(5), P4−Mg4−P5 94.96(4), P4−Mg5−P5 94.88(4), P4−Mg5−P6 117.33(4), P5−Mg5−P6 100.22(4), P1−Mg6−P5 139.70(4), P1−Mg6−P6 102.56(4), P5−Mg6−P6 102.37(4), Mg1−P1−Mg2 84.75(4), Mg1−P1−Mg6 78.07(4), Mg2−P1−Mg6 104.88(4), Mg1−P2−Mg2 85.52(4), Mg1−P2−Mg3 104.50(4), Mg2−P2−Mg3 78.00(4), Mg2−P3−Mg3 77.43(4), Mg2−P3−Mg4 125.39(4), Mg3−P3−Mg4 77.57(4), Mg3−P4−Mg4 77.84(4), Mg3−P4−Mg5 104.93(4), Mg4−P4−Mg5 84.37(4), Mg4−P5−Mg5 85.55(4), Mg4−P5−Mg6 104.38(4), Mg5−P5−Mg6 78.26(4), Mg1−P6−Mg5 123.08(4), Mg1−P6−Mg6 77.90(4), Mg5−P6−Mg6 77.62(4)

Table 2. Selected bond lengths of **2**

Atom	Mg1	Mg2	Mg3	Mg4	Mg5	Mg6	Si(n)
P1	259.9(1)	253.9(1)				249.4(1)	221.0(1)
P2	252.1(1)	258.0(1)	249.3(1)				220.1(1)
P3		254.1(1)	256.3(2)	254.2(1)			220.8(1)
P4			248.7(1)	260.2(1)	255.1(1)		221.0(1)
P5				252.0(1)	257.5(1)	250.0(1)	220.5(1)
P6	255.1(1)				255.8(1)	255.3(1)	221.6(1)
O(n)	204.6(2)	205.8(2)		204.8(2)	205.9(2)		

$Mg_{2n}P_{2m}$ Polyhedra

These new $Mg_{2n}P_{2m}$ polyhedra are missing links in a series of phosphandiides of divalent metals such as the alkaline earth metals and tin(II). An overview is given in

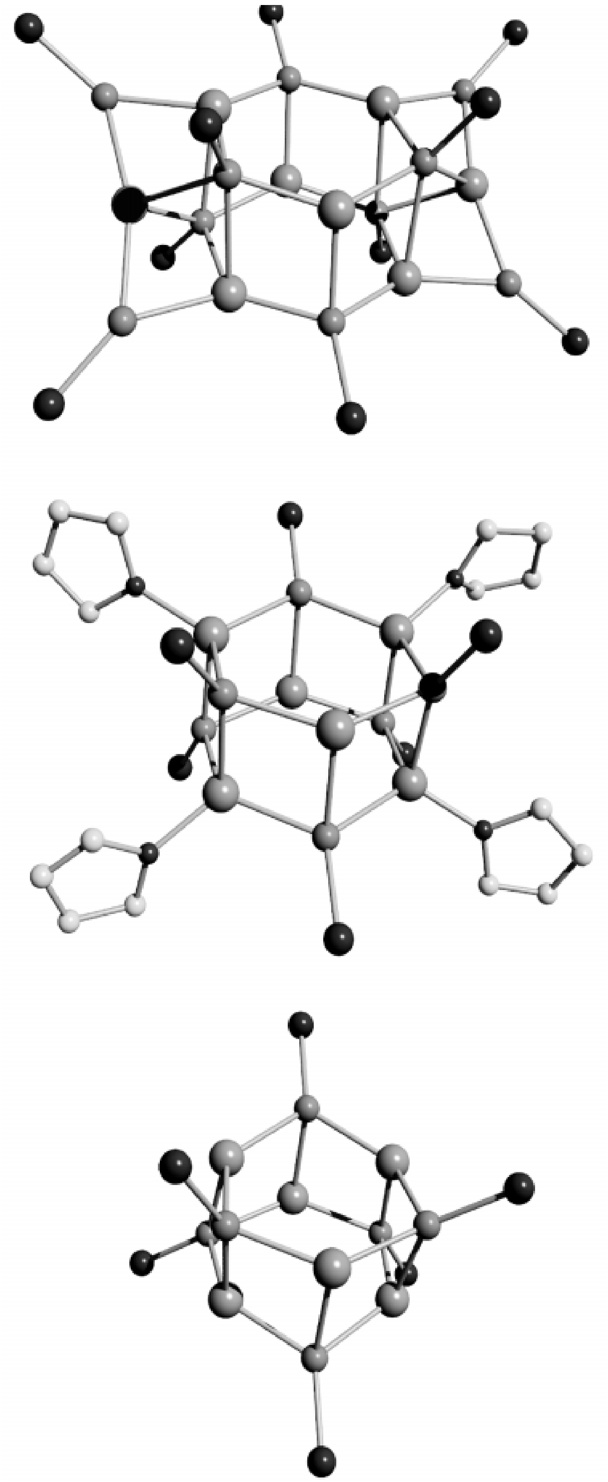


Figure 3. Comparison of the hexagonal prisms of **1** (on the top), **2** (in the middle) and hexakis(magnesium tri-*tert*-butylsilylphosphandiide) $[MgP{-}Si^tBu_3]_6$ (on the bottom); all hydrogen atoms are omitted for clarity; carbon atoms are omitted with the exception of those of the THF ligands; the atoms are shown with arbitrary radii

Scheme 5, where two basic types of polyhedra with m = n and $m = n + 1$ are shown, namely $M_{2n}P_{2n}$ ($n = 2$ and 3) and $M_{2n}P_{2n+2}$ ($n = 3$ and 4). The class of the $M_{2n}P_{2n}$ polyhedra consists of oligomeric alkaline earth metal phosphandiides where the dimer $[MgPSiR_3]_2$ with $n = 1$ − which would be the smallest unit − is still unknown. Dimerization leads to the formation of a cube ($n = 2$) and trimerization to the hexagonal prism ($n = 3$). These oligomeric alkaline earth metal phosphandiides are represented in the bottom row of Scheme 2.

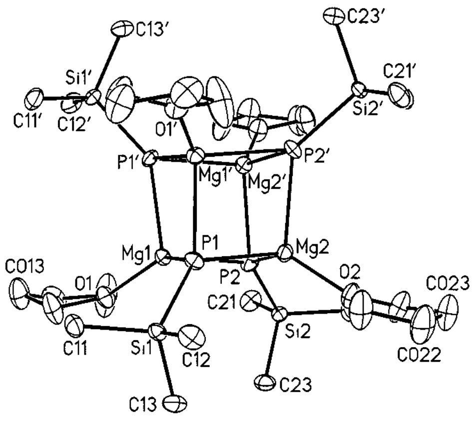


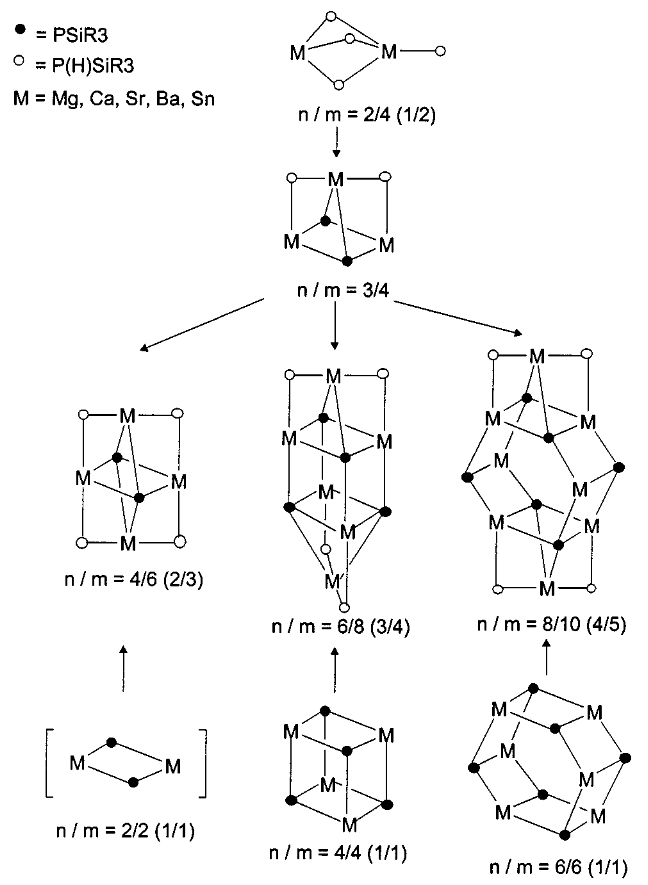
Figure 4. Molecular structure and numbering scheme of **3**. The methyl groups and the H atoms are omitted for clarity. The ellipsoids represent a probability of 40%. The atoms marked with an apostrophe are generated by C_2 symmetry. Selected bond angles [°]: P1−Mg1−P2 98.87(2), P1−Mg1−P1′ 98.78(2), P2−Mg1−P1′ 97.83(2), P1−Mg2−P2 99.16(2), P1−Mg2−P2′ 97.70(2), P2−Mg2−P2′ 97.78(2), Mg1−P1−Mg2 80.37(2), Mg1−P1−Mg1′ 80.54(2), Mg2−P1−Mg1′ 81.46(2), Mg1−P2−Mg2 80.57(2), Mg1−P2−Mg2′ 81.35(2), Mg2−P2−Mg2′ 81.53(2)

Table 3. Selected bond lengths of **3**[a]

Atom	Mg1	Mg2	Si(n)
P1	254.16(7)	253.97(7)	218.39(6)
P2	253.99(7)	253.08(7)	218.37(6)
P1′	254.66(7)		
P2′		255.19(7)	
O(n)	203.5(1)	203.0(1)	

[a] Atoms marked with an apostrophe are generated by C_2 symmetry ($-x$, y, $-z + 0.5$).

In the group of $M_{2n}P_{2n+2}$ polyhedra the molecules contain both phosphanide and phosphandiide ligands, however the compound with $n = 2$ cannot be stabilized with triisopropylsilyl groups at the phosphorus atoms, although the steric strain introduced by tri(*tert*-butyl)silyl substituents is enough to allow the isolation of a dimer with the formula $Mg_4(PSi^tBu_3)_2[P(H)Si^tBu_3]_4$[15] whose structure is shown in Scheme 5. The upper part of Scheme 5 shows the alkaline earth metal bis(phosphanides) with n = 1 which contain only phosphanide substituents. These molecules are bicyclic in the case of the heavier alkaline earth metals with small groups at the phosphorus atoms.[4,9,14,16,17] In Scheme 5 the M/P ratio changes from 1:2 on the top to 1:1 on the bottom, which are the extreme values in this substance class. The middle row of Scheme 5 shows the compounds with M/P ratios of 2:3, 3:4 and 4:5, which crystallize as dimers.



Scheme 5. Schematic construction of $Mg_{2n}P_{2n}$ polyhedra starting from a dimeric alkaline earth metal bis(phosphanide) on the top (Mg/P ratio of 1:2) or starting from the alkaline earth metal phosphandiide at the bottom (Mg/P ratio of 1:1); the compounds in the middle row belong to polyhedra of the type $Mg_{2n}P_{2n+2}$ (see text)

Conclusion

The steric strain incorporated by the trialkylsilyl substituents and/or by the coordination of Lewis bases such as THF to the metal dications defines the polyhedron which is formed in the magnesiation of bulky trialkylsilylphosphanes. Tri(*tert*-butyl)silyl groups lead to the formation of a hexagonal Mg_6P_6 prism. If the less crowded triisopropylsilylphosphane is magnesiated in the absence of Lewis bases, two $Mg[P(H)Si^iPr_3]_2$ molecules cap two opposite square Mg_2P_2 planes of a hexagonal prismatic $(MgPSi^iPr_3)_6$ and **1** precipitates. The presence of Lewis bases such as THF is necessary to achieve a complete deprotonation of triisopropylsilylphosphane. The magnesium bis(phosphanide) molecules of **1** can be substituted by four THF ligands to yield **2**. Coordination of a THF molecule to each magnesium atom allows the isolation of $[(THF)MgPSi^iPr_3]_4$ with a slightly distorted Mg_4P_4 cube.

Experimental Section

General Remarks: All experiments and manipulations were carried out under argon or nitrogen purified by passage through BTS catalyst and P_4O_{10}. Reactions were performed with standard Schlenk techniques and dried, thoroughly deoxygenated solvents. $H_2PSi^iPr_3$[6] was prepared by a literature procedure. NMR spectra were recorded on Jeol spectrometers GSX270 and EX400. A Perkin−Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra; solid substances were measured in nujol between KBr plates (vs very strong, s strong, m medium strong, w weak, vw very weak, sh shoulder). The low carbon values for the elemental analysis result from carbide and carbonate formation as well as loss of neutral coligands during handling and combustion of the compounds.

$Mg_8(PSi^iPr_3)_6[P(H)Si^iPr_3]_4$ (1): Triisopropylsilylphosphane (1.12 mL, 5.0 mmol) was dissolved in 40 mL of toluene. A heptane solution of dibutylmagnesium (4.0 mL of a 1M solution) was dropped into this solution and a yellow precipitate formed immediately. Heating to approximately 100 °C for 15 min. and subsequent cooling to 6 °C led to the crystallization of 1.03 g of colorless **1** (0.49 mmol, 97%); m.p. 272 °C, dec. above 297 °C. − ^1H NMR ([D$_8$]toluene, 30 °C): δ = 0.65 (m), 1.06 (m), 1.23 (m), 1.28 (m), 1.35 (m). − $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 30 °C): δ = −265.0 (br, PH), −266.8 (br, P with C.N. = 4), −331.2 (br, P with C.N. = 3). − IR: $\tilde{\nu}$ = 316 vw, 372 w, 427 w, 444 w, 482 m, 515 m, 539 w, 576 m, 636 w, 656 m, 732 w, 784 vw, 802 vw, 819 vw, 882 s, 918 m, 993 s, 1015 m, 1064 s, 1161 w, 1197 w, 1230 w, 1289 w, 1313 w, 1368 w, 1386 w, 1465 m, 1686 w, 1768 w, 2300 m, 2364 vw, 2719 vw, 2732 vw, 2869 s, 2893 m, 2946 s. − $C_{90}H_{214}Mg_8P_{10}Si_{10}$ (2081.69): calcd. C 51.97, H 10.36; found C 51.23, H 10.35.

$(THF)_4Mg_6(PSi^iPr_3)_6$ (2): To a solution of triisopropylsilylphosphane (1.12 mL, 5.0 mmol) and 0.41 mL of THF in 30 mL of toluene a 1M heptane solution of dibutylmagnesium (5.0 mL, 5.0 mmol) was added dropwise. A yellow solution forms. During stirring for additional 19 h at room temp. a colorless solid precipitated which redissolved upon heating to approximately 80 °C. Cooling to 6 °C led to the crystallization of 1.18 g of **2**·$2C_7H_8$ (0.67 mmol, 81%); dec. above 300 °C. − ^1H NMR ([D$_8$]toluene, 30 °C): δ = 1.16 [sept, ^3J(H,H) = 7.0 Hz, C*H*Me$_2$], 1.37 (d, CH*Me*$_2$), 1.51 and 4.20 (br, THF). − $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 30 °C): δ = 15.89 (m, CH), 20.58 (m, CH$_3$), 24.89 and 69.97 (m, THF). − $^{29}Si\{^1H\}$ NMR ([D$_8$]toluene, 30 °C): δ = 24.13 (m). − $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 30 °C): δ = −331.59 (s). − IR: $\tilde{\nu}$ = 327 w, 337 w, 462 m, 477 m, 487 m, 558 m, 678 m, 806 w,820 w, 884 s, 921 w, 991 m, 1013 s, 1061 m, 1093 s, 1162 m, 1193 m, 1260 w, 1366 w, 1386 w, 1465 m, 1631 w, 1638 w, 2865 s, 2894 m, 2953 s. − $C_{84}H_{174}Mg_6O_4P_6Si_6$ (1748.48): calcd. C 57.70, H 10.03; found C 57.48, H 10.04.

$[(THF)Mg]_4(PSi^iPr_3)_4$ (3): Dibutylmagnesium in heptane (5.0 mL of a 1M solution) was added dropwise to a solution of triisopropylsilylphosphane (1.12 mL, 5.0 mmol) in 25 mL of THF. After stirring for an additional 15 h at room temp. the volatile materials were removed in vacuum and the residue recrystallized from toluene at 90 °C. Storage of this solution at 6 °C led to the precipitation of 0.75 g of large colorless cuboids of **3** (0.66 mmol, 53%); dec. above 320 °C. − ^1H NMR ([D$_8$]toluene, 30 °C): δ = 1.21 [sept, ^3J(H,H) = 7.2 Hz, C*H*Me$_2$], 1.37 (d, CH*Me*$_2$), 1.51 and 4.20 (br, THF). − $^{13}C\{^1H\}$ NMR ([D$_8$]toluene, 30 °C): δ = 15.86 (s, CH), 20.52 (s, CH$_3$), 25.46 and 67.77 (THF). − $^{29}Si\{^1H\}$ NMR ([D$_8$]toluene, 30 °C): δ = 23.37 (m). − $^{31}P\{^1H\}$ NMR ([D$_8$]toluene, 30 °C): δ = −330.8 (s). − IR: $\tilde{\nu}$ = 466 m, 485 m, 496 m, 557 m, 615 w, 680 m, 804 w, 819 w, 884 m, 921 w, 994 m, 1012 s, 1060 s, 1089 s, 1160 m, 1262 w, 1367 w, 1384 w, 1465 m, 1632 m, 1638 m, 2865 s, 2894 m, 2945 s. − $C_{36}H_{84}Mg_4P_4Si_4$ (850.51, THF-free compound): calcd. C 50.84, H 9.95; found C 50.46, H 9.87.

X-ray Crystal Structure Determinations of 1, 2 and 3:[18] Data were collected on a Siemens P4 diffractometer with a Siemens SMART-CCD area detector (**1** and **2**) or on a STOE-IPDS diffractometer

Table 4. Crystallographic data of **1**, **2**, and **3**, details of the structure solution and refinement procedures

Compound	**1**	2·**2**C_7H_8	3
Formula	$C_{90}H_{214}Mg_8P_{10}Si_{10}$	$C_{84}H_{174}Mg_6O_4P_6Si_6$	$C_{52}H_{116}Mg_4O_4P_4Si_4$
Formula mass [g·mol^{-1}]	2081.69	1748.45	1138.93
T [K]	193(2)	173(2)	173(2)
Space group[21]	$C2/c$ (No. 15)	P1bar (No. 2)	$C2/c$ (No. 15)
a [pm]	1414.9(2)	1485.2(3)	2627.2(2)
b [pm]	3407.1(5)	1582.5(3)	1252.40(8)
c [pm]	2740.3(4)	2261.1(5)	2408.5(2)
α [°]	90	83.00(3)	90
β [°]	101.576(3)	84.71(3)	120.29(1)
γ [°]	90	88.54(3)	90
V [nm^3]	12.942(3)	5.251(2)	6.8428(9)
Z	4	2	4
$d_{\text{calcd.}}$ [g·cm^{-3}]	1.068	1.106	1.106
μ [mm^{-1}]	0.299	0.248	0.254
F(000)	4560	1912	2496
Scan range [°]	$2.4 < 2\theta < 55.5$	$5.1 < 2\theta < 56.1$	$4.7 < 2\theta < 52.0$
Measured data	35657	86377	29590
Unique data (R_{int})	9840 (0.1285)	23166 (0.0324)	6618 (0.0288)
Parameters	537	964	307
wR_2[a] (all data, on F^2)	0.2024	0.2110	0.0975
R_1[a] (all data)	0.1216	0.0871	0.0396
Data [$I > 2\sigma(I)$]	4939	16343	6069
R_1[a] [$I > 2\sigma(I)$]	0.0614	0.0657	0.0366
GOF[b] on F^2	1.028	1.077	1.029
Residual density [e·Å^{-3}]	1.19; −0.38	1.60; −0.68	0.48; −0.42

[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] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

(**3**) with graphite monochromated Mo-K_α radiation (λ = 71.073 pm) from oil-coated[19][20] rapidly cooled single crystals. Crystallographic parameters, details of data collection and refinement procedures are summarized in Table 4.

All structures were solved by direct methods and refined with the software packages SHELXL-93 and SHELXL-97.[22] The asymmetric unit of **2** contains two toluene molecules without coordination to magnesium atoms. Neutral scattering factors were taken from Cromer and Mann[23] and for the hydrogen atoms from Stewart et al.[24] The non-hydrogen atoms were refined anisotropically. The H-atoms were considered with a riding model under restriction of ideal symmetry at the corresponding atoms.

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[18] Crystallographic data (excluding structure factors) for the structures included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133694 **(1)**, -133695 **(2)** and -133696 **(3)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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