Oligomeric Solvent-Free Magnesium Bis(phosphanides) − Molecular Structure of Trimeric Magnesium Bis[bis(trimethylsilyl)phosphanide]☆

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The metathesis reaction of (dme)$LiPH_2$ and chlorodiisopropylsilane yields $HP(SiH\textit{i}Pr_2)_2$ (**1**) and $P(SiH\textit{i}Pr_2)_3$ (**2**). The metalation of **1** by *n*/*sec*-dibutylmagnesium in heptane leads to the formation of dimeric magnesium bis[bis(diisopropylsilyl)phosphanide] [(**3**)$_2$]. A toluene solution of magnesium bis[bis(trimethylsilyl)phosphanide] (**4**) shows a dimer-trimer equilibrium in the $^{31}P\{^1H\}$-NMR spectrum at −40°C with an increasing amount of the dimer with increasing temperature. A molecular mass determination by freezing-point depression in benzene yields a value of 516 $g\cdot mol^{-1}$, which lies between a monomeric and a dimeric molecule. Cooling of the toluene solution to −30°C leads to the precipitation of single crystals of monoclinic $\{(Me_3Si)_2P{-}Mg[\mu\text{-}P(SiMe_3)_2]_2\}_2Mg$ [(**4**)$_3$].

Several possibilities for the synthesis of the alkaline earth metal bis[bis(trialkylsilyl)amides] justified the vastly growing interest in the molecular chemistry of the heavier alkaline earth metals.[1][2] The alkaline earth metal bis(phosphanides) are easily accessible by the metalation of bis(trialkylsilyl)phosphane with the above-mentioned bis(trialkylsilyl)amides in toluene, where they precipitate, or in ethers such as tetrahydrofuran (thf) or 1,2-dimethoxyethane (dme), where ether adducts are formed.[3] Eq. (1) shows the preparation of the thf complexes of the alkaline earth metal bis[bis(trimethylsilyl)phosphanides].

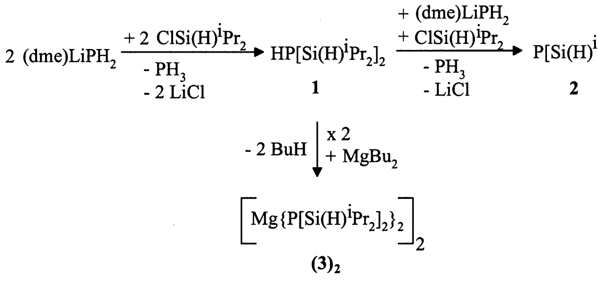
$$M[N(SiMe_3)_2]_2 + 2\ HP(SiMe_3)_2 \xrightarrow{\text{thf}} (thf)_nM[P(SiMe_3)_2]_2 \qquad (1)$$
$$M/n = Mg/2,\ Ca/4,\ Sr/4,\ Ba/4$$

The bis(trialkylsilyl)phosphanides of the heavier alkaline earth metals precipitate in the absence of neutral coligands such as ethers or amines. Therefore, the soluble ether adducts of the trialkylsilyl-substituted phosphanides[4] and a tmeda complex of $Mg[P(H)Ph]_2$[5] were investigated by solution NMR as well as X-ray crystallography. Further enhancement of the steric demand of the silyl groups reduces the reactivity of the phosphanes. For example, the metalation of bis(triisopropylsilyl)phosphane[6] by calcium bis[bis(trimethylsilyl)amide] is neither possible in boiling toluene nor in refluxing thf nor a mixture of both.

Solvent-poor alkaline earth metal bis(phosphanides) are gaining interest especially due to the unexpected structures of the dimers in solution as well as the solid state. Ab-initio SCF calculations for $M_2(PH_2)_4$ show for magnesium the "conventional" monocyclic structure $H_2P{-}Mg(\mu\text{-}PH_2)_2Mg{-}PH_2$[6] whereas for calcium or strontium the bicyclic structure $H_2P{-}M(\mu\text{-}PH_2)_3M$ is the lowest in energy.[4d] In the case of dimeric barium bis(phosphanide) even the tricyclic isomer $Ba(\mu\text{-}PH_2)_4Ba$ has to be taken into consideration. Here, the synthesis of the first solvent-free dimeric and trimeric magnesium bis(phosphanides) is presented and the X-ray structure of trimeric magnesium bis[bis(trimethylsilyl)phosphanide] is discussed in detail.

Preparation

To raise the reactivity of the P−H fragment compared to bis(triisopropylsilyl)phosphane[6][7] the diisopropylsilyl substituents are chosen. The second advantage of this substituent is the basicity of the Si−H moiety which allows an electrostatic attraction to the metal center as well as an agostic interaction between the metal atom and the Si−H bond. The metathesis reaction of (dme)$LiPH_2$ and chlordiisopropylsilane offers an easy approach to bis(diisopropylsilyl)phosphane (**1**), which is obtained together with tris(diisopropylsilyl)phosphane (**2**) according to eq. (2). The metalation of **1** in toluene with dibutylmagnesium, dissolved in heptane, yields quantitatively dimeric magnesium bis[bis(diisopropylsilyl)phosphanide] [(**3**)$_2$]. However, the efforts of crystallization failed, and an oil remained after the work-up procedures.



$$2\ (dme)LiPH_2 \xrightarrow[\substack{-\ PH_3 \\ -\ 2\ LiCl}]{+\ 2\ ClSi(H)^iPr_2} \underset{\mathbf{1}}{HP[Si(H)^iPr_2]_2} \xrightarrow[\substack{-\ PH_3 \\ -\ LiCl}]{\substack{+\ (dme)LiPH_2 \\ +\ ClSi(H)^iPr_2}} \underset{\mathbf{2}}{P[Si(H)^iPr_2]_3}$$
$$\mathbf{1}\ \xrightarrow[\times 2,\ +\ MgBu_2]{-\ 2\ BuH}\ [Mg\{P[Si(H)^iPr_2]_2\}_2]_2 \qquad (2)$$

(**3**)$_2$

During the metalation of bis(trimethylsilyl)phosphane with commercially available *n*/*sec*-dibutylmagnesium a col-

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[+] X-ray structure analysis.

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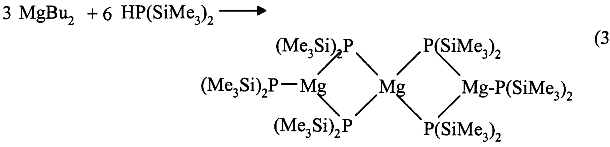
orless solid precipitates, however, stirring for several hours at room temperature leads to a clear solution. Upon cooling to −30°C crystalline trimeric magnesium bis[bis(trimethylsilyl)phosphanide] [**(4)**$_3$], formed according to eq. (3), precipitates in the shape of colorless cuboids.


(3)

(4)$_3$

The addition of tetrahydrofuran yields the already well-known bis(tetrahydrofuran)magnesium bis[bis(trimethylsilyl)phosphanide] (**4**·2 thf).[8] All these magnesium bis(phosphanides) are colorless and very moisture-sensitive.

Spectroscopic Characterization

The NMR data of the phosphanes **1** and **2** clearly show the existence of two chemically different methyl groups. This observation proves that the inversion of the phosphorus atom is very slow on the NMR time scale and the inversion barrier higher than at least 70 kJ·mol^{-1}. No line broadening is observable at room temperature.

The comparison between **1** and **2** shows the influence of the substitution of a hydrogen atom by a diisopropylsilyl group (Table 1). The effects are similar as described for $HP(SiMe_3)_2$/$P(SiMe_3)_3$.[9] The high-field shift of the ^{31}P signal is accompanied by a low-field shift of the ^{29}Si signal. The $^1J(P,Si)$ coupling constants of approximately 36 Hz are nearly not affected by this change in the ligand sphere of the phosphorus atom.

For compound **(3)**$_2$ the coupling pattern of two triplets between the bridging and the terminal phosphorus atoms clearly proves its dimeric appearance (Figure 1). Even at elevated temperatures up to 70°C the ligand-exchange processes are very slow on the NMR time scale. The $^2J(P_b,P_t)$ coupling constant of 22.2 Hz lies in the expected range. The $^1J(P,Si)$ coupling constant within the terminal ligand amounts nearly 39 Hz, whereas for the bridging ligand a value is not deducible, only a line broadening is observed.

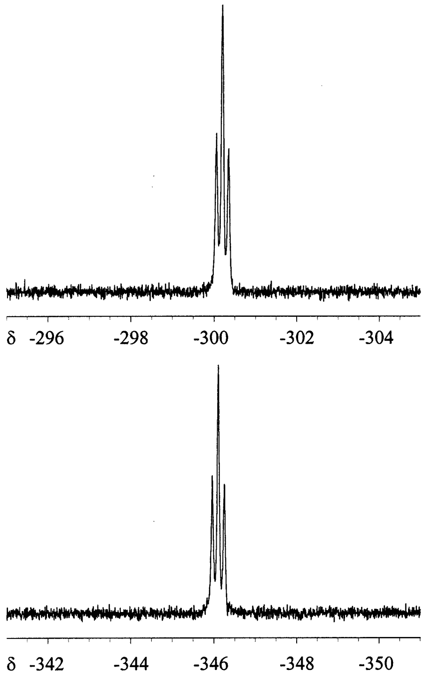
For the $^1J(Si,H)$ coupling constants only a rough estimation can be given due to overlapping of the signals in the ^{29}Si-NMR spectrum and the expected pattern of higher order. For the bridging phosphanide ligand a line separation of approximately 140 Hz can be seen, whereas the $^1J(Si,H)$ coupling constant of the terminal ligand is clearly larger than 200 Hz. This difference could result from an agostic interaction between the magnesium atom and the Si−H bond[10] or from the different coordination numbers of the phosphorus atoms, in particular under consideration of the strongly differing $^1J(P,Si)$ coupling constants for the terminal and the bridging substituents. However, only one strong Si−H stretching vibration at 2101 cm^{-1} is observed in the characteristic region for Si−H moieties.

Table 1. NMR parameters of the phosphanes **1** and **2** as well as magnesium bis[bis(diisopropylsilyl)phosphanide] [**(3)**$_2$] ([D$_6$]benzene, 30°C, t and b name the terminal and bridging position of the considered atom)

		1	**2**	**(3)**$_2$
^1H	$\delta(Me_{Pr})$	1.10	1.22	1.3[a]
	$\delta(Me_{Pr})$	1.10	1.19	
	$\delta(CH_{Pr})$	1.09	1.16	1.3[a]
	$\delta(PH)$	0.41	−	−
	$^1J(P,H)$	187.3	−	−
	$\delta(Si_tH)$	4.23	4.32	4.53
	$^1J(Si_t,H)$	188.2	188.1	
	$^2J(P_t,H)$	8.8	14.7	16.9
	$^3J(H_P,H_{Si})$	3.1	−	−
	$\delta(Si_bH)$	−	−	4.42
	$^2J(P_b,H)$	−	−	18.3
$^{13}C\{^1H\}$	$\delta(Me_{Pr})$	19.39	20.37	[b]
	$^3J(P,C)$	2.4	3.7	
	$\delta(Me_{Pr})$	19.22	19.62	
	$^3J(P,C)$	3.2	3.0	
	$\delta(CH_{Pr})$	13.28	14.56	15.78[c]
	$^2J(P,C)$	9.4	10.0	[c]
$^{29}Si\{^1H\}$	$\delta(Si_t)$	10.29	7.46	9.19
	$^1J(P_t,Si_t)$	36.3	36.1	38.7
	$\delta(Si_b)$	−	−	6.92
	$^1J(P_b,Si_b)$	−	−	< 4 Hz
$^{31}P\{^1H\}$	$\delta(P_t)$	−307.49	−314.31	−347.00
	$\delta(P_b)$	−	−	−301.41
	$^2J(P_t,P_b)$	−	−	22.2

[a] Broad signal. − [b] Four broad signals at δ = 19.7, 19.8, 20.7, and 21.4; assignment to terminal or bridging phosphanide ligands not possible − [c] Very broad signal due to overlapping of the dublets of the CH groups of the terminal and bridging phosphanide ligands; coupling constants not deducible.

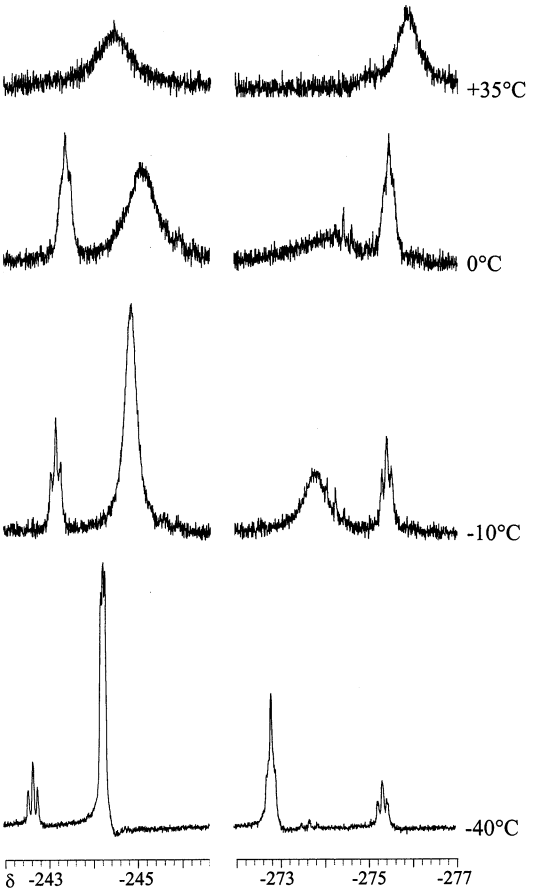
Figure 1. $^{31}P\{^1H\}$-NMR spectrum of a [D$_8$]toluene solution of magnesium bis[bis(diisopropylsilyl)phosphanide] [**(3)**$_2$] at 25°C; signals of the bridging (top) and terminal (bottom) $(iPr_2HSi)_2P$ ligands (109.365 MHz)



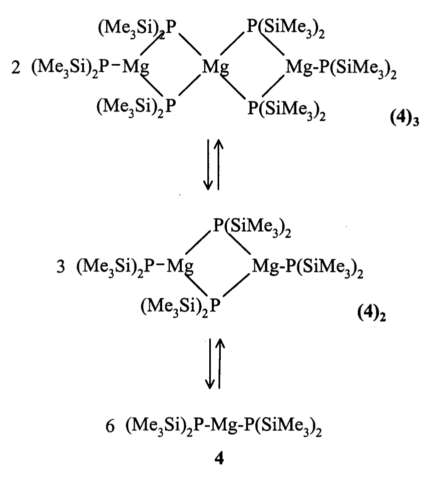
For magnesium bis[bis(trimethylsilyl)phosphanide] (**4**) the determination of the molecular mass by freezing-point depression in benzene yields a value of 516 g·mol^{-1} for a diluted solution, which lies between the mass of a monomer (379 g·mol^{-1}) and a dimer (758 g·mol^{-1}). The ^1H- and

$^{13}C\{^1H\}$-NMR spectra show broad and overlapping signals, an assignment to certain oligomers is not possible. The $^{31}P\{^1H\}$-NMR spectrum recorded at −40°C shows two triplets at $\delta = -242.55$ and -275.44 for the bridging and the terminal $(Me_3Si)_2P$ ligands with a $^2J(P,P)$ coupling constant of 17.9 Hz (Figure 2). In addition to this dimer another isomer with an intensity ratio for the bridging to terminal phosphanide ligands of 2:1 is observed and assigned to the trimer of the type $\{(Me_3Si)_2P{-}Mg[\mu\text{-}P(SiMe_3)_2]_2\}_2Mg$. This trimer can be crystallized from toluene at −30°C, and its structure is discussed below. Raising of the temperature (Figure 2) leads to an increasing concentration of the dimer at the expense of the trimer. At −40°C the amount of the trimer is 2.5 times higher than the one of the dimer, whereas at 0°C the dimer is 1.1 times more concentrated in solution. The equilibrium is shown in eq. (4), however, at room temperature and higher temperatures coalescence is observed, and the different oligomers are indistinguishable by $^{31}P\{^1H\}$-NMR spectroscopy.

Figure 2. Temperature-dependent $^{31}P\{^1H\}$-NMR spectra of a 0.5 M $[D_8]$toluene solution of magnesium bis[bis(trimethylsilyl)phosphanide] (**4**); all spectra are internally referenced to a small signal of $P(SiMe_3)_3$ at $\delta = -251.07$ (161.835 MHz); at −40°C the dimeric and trimeric molecules coexist in toluene solution (see text)



Magnesium bis[bis(trimethylsilyl)phosphanide] is monomeric in the gaseous phase as could be shown by mass spectrometry. The found isotopic pattern of the M^+ peak confirms the assignment.

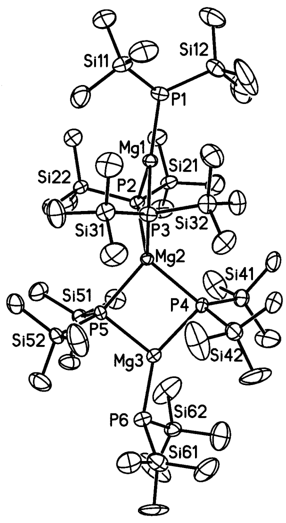


(4)

Molecular Structure of (4)$_3$

The molecular structure and numbering scheme of trimeric magnesium bis[bis(trimethylsilyl)phosphanide] [(**4**)$_3$] is shown in Figure 3. The coordination sphere around the magnesium atom Mg2 is a distorted tetrahedron, whereas Mg1 and Mg3 are surrounded by a trigonal planar coordination sphere. The four bridging phosphorus atoms are four-coordinate, and the angle sums of the terminal atoms P1 and P6 are 334.3° and 331.6°, respectively. Selected bond lengths and angles of (**4**)$_3$ are summarized in Table 2.

Figure 3. Molecular structure and the numbering scheme of trimeric magnesium bis[bis(trimethylsilyl)phosphanide] [(**4**)$_3$]; the ellipsoids represent a probability of 40%; the hydrogen atoms and the labelling of the carbon atoms are omitted for clarity



The influence of the coordination number is clearly seen. The terminal phosphanides show Mg−P bond lengths of approximately 245 pm, whereas the bridging phosphorus atoms show Mg−P distances to the triply coordinated magnesium atoms of 255 pm. A further increase of approximately 10 pm is observed for the bond lengths to the quadruply coordinated magnesium atom Mg2, however, the values lie in a wide range between 260 and 268 pm. The intramolecular strain due to the steric demand of the trimethylsilyl groups leads to a bending of the phosphanide

Table 2. Selected bond lengths [pm] and angles [°] of trimeric magnesium bis[bis(trimethylsilyl)phosphanide] [**(4)**$_3$]

n	1	2	3	4	5	6
Mg1−P(*n*)	245.1(2)	253.6(3)	255.3(2)			
Mg2−P(*n*)		261.7(2)	267.0(2)	267.8(2)	260.5(2)	
Mg3−P(*n*)				255.5(3)	254.1(3)	245.9(3)
P(*n*)−Si(*n*1)	221.6(3)	224.2(2)	224.8(2)	225.0(3)	224.9(2)	220.1(3)
P(*n*)−Si(*n*2)	221.2(3)	224.1(2)	223.6(3)	223.5(3)	223.7(2)	221.4(3)
Mg1−P(*n*)−Si(*n*1)	105.12(9)	107.68(9)	119.62(9)			
Mg1−P(*n*)−Si(*n*2)	121.3(1)	100.43(8)	96.75(9)			
Mg2−P(*n*)−Si(*n*1)		130.91(9)	128.04(9)	126.27(9)	114.75(9)	
Mg2−P(*n*)−Si(*n*2)		116.69(8)	114.90(9)	117.67(9)	129.17(9)	
Mg3−P(*n*)−Si(*n*1)				120.1(1)	95.55(8)	115.6(1)
Mg3−P(*n*)−Si(*n*2)				95.40(9)	113.79(9)	107.99(9)
Si(*n*1)−P(*n*)−Si(*n*2)	107.9(1)	106.04(9)	106.16(9)	105.6(1)	107.76(9)	108.0(1)
Mg1−P(*n*)−Mg2		87.89(7)	86.38(7)			
Mg2−P(*n*)−Mg3				87.10(7)	88.96(7)	

ligands towards the triply coordinated magnesium atoms Mg1 and Mg3. The bis(tetrahydrofuran)[8] as well as 1,2-dimethoxyethane complexes[11] show Mg−P bond lengths of approximately 250 pm between a triply coordinated phosphorus atom and a fourfold coordinated magnesium center.

The steric strain destabilizes the polymeric structures which presumingly lead to the precipitation of the magnesium bis[bis(trimethylsilyl)phosphanide] right after the metalation reaction. The polymeric structure breaks apart into trimers, which can then be crystallized. Due to longer M−P bonds for the heavier alkaline earth metals and consequently reduced intramolecular steric strain, solvent-free and soluble derivatives of oligomeric bis[bis(trimethylsilyl)phosphanides] are unknown thus far.

Conclusion

Solvent-free magnesium bis[bis(diisopropylsilyl)phosphanide] is soluble in common organic solvents such as toluene or benzene and dimeric in solution. In contrast to this derivative magnesium bis[bis(trimethylsilyl)phosphanide] shows monomeric molecules besides dimers by molecular-mass determination in benzene and a dimer-trimer equilibrium at −40°C in toluene in the $^{31}P\{^1H\}$-NMR spectrum at a 40 times more concentrated solution. Crystallization at −30°C from toluene solution yields single crystals of $\{(Me_3Si)_2P{-}Mg[\mu\text{-}P(SiMe_3)_2]_2\}_2Mg$. The Mg−P bond lengths vary between 245 and 268 pm depending on the coordination numbers of the metal and phosphorus atoms. In the gaseous phase monomeric magnesium bis[bis(trimethylsilyl)phosphanide] is observed.

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Experimental Section

All experiments and manipulations were carried out under argon purified by passage through BTS catalyst and P_4O_{10}. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. The starting materials (1,2-dimethoxyethane-O,O′)lithium phosphanide[12] and bis(trimethylsilyl)phosphane[13] were prepared by literature procedures. − NMR spectra were recorded with Bruker spectrometers AM200, AC250, and AM400 or 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 CsBr windows (vs very strong, s strong, m medium, w weak, vw very weak, sh shoulder). The frequencies in the region of the Nujol vibrations are not listed.

Bis(diisopropylsilyl)phosphane (**1**) *and Tris(diisopropylsilyl)phosphane* (**2**): 5.0 g of $ClSi(H)iPr_2$ (33 mmol) were slowly added at −20°C to a solution of 4.3 g of $(dme)LiPH_2$ (33.2 mmol) in 80 ml of 1,2-dimethoxyethane. After complete addition, the reaction mixture was stirred for additional 2 h at room temperature. All volatile materials were removed in vacuum at room temperature and a subsequent vacuum distillation gave 2.5 g of $HP[Si(H)iPr_2]_2$ (**1**) (9.5 mmol, 57%) at 73°C/0.02 Torr. The residue was dissolved in 10 ml of *n*-pentane. Cooling to −60°C led to the crystallization of 1.3 g of $P[Si(H)iPr_2]_3$ (**2**) (3.5 mmol, 31%). At −60°C the mother liquor was decanted and the crystals which show a melting point of approximately −10°C were dried in vacuum. The NMR data of both compounds are summarized in Table 1.

Physical Data of **1**: IR (CsBr): $\tilde{\nu}$ = 2940 cm^{-1} vs, 2887 s, 2862 vs, 2722 vw, 2287 m (νPH), 2103 vs (νSiH), 1469 s, 1391 m, 1373 m, 1241 w, 1164 w, 1078 m, 1012 s, 922 m, 885 s, 783 vs, 764 vs, 706 w, 648 m, 612 m, 588 w, 563 vw, 482 m, 458 m, 409 w, 351 vw. − Raman: $\tilde{\nu}$ = 2941 cm^{-1} sh, 2919 s, 2889 s, 2863 vs, 2758 vw, 2716 vw, 2327 m, 2106 s, 1465 m, 1446 m, 1386 w, 1366 vw, 1290 w, 1234 s, 1160 w, 1076 m, 971 m, 920 vw, 882 s, 783 m, 761 w, 645 m, 618 s, 590 s, 565 m, 484 vs, 460 s, 408 m, 391 s, 361 w, 270 vs, 153 s. − MS (20 eV, source 490 K, sample 295 K); *m/z* (%): 262 (62.6) [M$^+$], 246 (19.8), 220 (60.0), 203 (100), 178 (16.5), 115 (12.7). − $C_{12}H_{31}PSi_2$ (262.52): calcd. C 54.90, H 11.90; found C 53.78, H 11.86.

Physical Data of **2**: IR (CsBr): $\tilde{\nu}$ = 2951 cm^{-1} vs, 2887 s, 2862 vs, 2098 vs (νSiH), 1469 s, 1390 m, 1373 m, 1241 w, 1163 vw, 1080 m, 1010 s, 972 vw, 922 m, 880 s, 795 sh, 760 vs, 649 m, 610 m, 592 w, 562 vw, 512 m, 361 vw. − MS (70 eV, source 470 K, sample 320 K); *m/z* (%): 376 (71.0) [M$^+$], 334 (48.3), 292 (55.9), 262 (7.6), 250 (36.3), 249 (37.9), 219 (13.2), 207 (18.8), 203 (17.6), 177 (19.8), 147 (9.6), 135 (21.2), 133 (23.8), 115 (10.2), 105 (15.3), 87 (20.0), 73 (44.3), 59 (100). − $C_{18}H_{45}PSi_3$ (376.78): calcd. C 57.38, H 12.04; found C 55.46, H 11.76.

Magnesium Bis[bis(diisopropylsilyl)phosphanide] (**3**): 1 ml of a 1.0 M solution of *n*/*sec*-dibutylmagnesium in heptane was added dropwise slowly at 0°C to a solution of 530 mg of bis(diisopropylsilyl)phosphane (2.0 mmol) in 5 ml of toluene. After stirring for 5 additional hours at room temperature, all volatile materials were removed at reduced pressure at room temperature. Residues of toluene were removed at 60°C/10^{-2} mbar. A colorless pyrophoric oil remains, crystallization efforts from various solvents at −20°C and −60°C failed. The elemental analysis showed a low magnesium content and on the other hand high carbon and hydrogen values due to the grease still present in the sample. NMR data are listed in Table 1. − IR (CsBr): $\tilde{\nu}$ = 2940 cm^{-1} vs, 2886 sh, 2865 vs, 2755 vw, 2719 vw, 2101 vs (νSiH), 1462 vs, 1383 m, 1364 m, 1289 w, 1235 m, 1159 vw, 1069 s, 1006 vs, 969 w, 919 m, 879 s, 792 sh, 763 vs, 700 vw, 644 m, 611 s, 590 s, 566 w, 512 s, 483 sh, 410 w.

Magnesium Bis[bis(trimethylsilyl)phosphanide] (**4**): 1.75 ml of bis(trimethylsilyl)phosphane (8.03 mmol) was dissolved in 60 ml of toluene and 4.0 ml of a 1 M heptane solution of *n*/*sec*-dibutylmagnesium was added at room temperature. The precipitation of a colorless solid was observed immediately after complete addition, which dissolved within the next 12 h at room temperature. Reduction of the solution to 20 ml and storage at −30°C yielded 0.43 g of crystalline trimeric $(\mathbf{4})_3$ (0.38 mmol, 29%), m.p. 191°C. − NMR ([D_8]toluene, 0.5 mol/l, 25°C); ^{1}H: δ = 0.52 and 0.47 (broad, overlapping signals); $^{13}C\{^1H\}$: δ = 5.65, 6.82, and 7.08 (broad overlapping signals); $^{29}Si\{^1H\}$: δ = 3.74; $^{31}P\{^1H\}$: see text above and Figure 2. − IR (Nujol, CsBr): $\tilde{\nu}$ = 1313 cm^{-1} vw, 1247 vs, 1073 vw, 1028 vw, 855 sh, 829 vs, 749 s, 683 s, 628 vs, 473 s, 460 s, 447 s, 419 s, 370 m, 314 m, 282 w. − MS (70 eV); *m*/*z* (%): 378 (17.0) [M^+], 305 (8.0) [$M^+ - SiMe_3$], 250 (35.1) [$PSi_3Me_9^+$], 178 (53.4) [$HPSi_2Me_6^+$], 163 (40.3) [$HPSi_2Me_5^+$], 147 (100) [$PSi_2Me_4^+$], 73 (89.5) [$SiMe_3^+$]. − $C_{12}H_{36}MgP_2Si_4$ (379.02): calcd. C 38.02, H 9.57; found C 36.93, H 9.22. − Molecular mass: calcd. for monomer: 379; found 516 (by freezing-point depression in benzene, 0.012 mol/l).

Table 3. Crystallographic data of $(\mathbf{4})_3$ as well as details of the structure solution and refinement procedures

	$(\mathbf{4})_3$
Empirical formula	$C_{36}H_{108}Mg_3P_6Si_{12}$
Molecular mass (g·mol^{-1})	1137.05
T [K]	193
Crystal system	monoclinic
Space group[15]	$P2_1/n$
Unit cell dimensions:	
a [pm]	1290.65(1)
b [pm]	3529.33(5)
c [pm]	1633.51(1)
β [°]	99.46(1)
V [nm^3]	7.3397(1)
Z	4
$d_{calcd.}$ [g·cm^{-3}]	1.029
μ [mm^{-1}]	0.390
F(000)	2472
Scan range	1.2° ≤ θ ≤ 20.0°
Indices	$-13 \le h \le 13$; $-35 \le k \le 36$; $-17 \le l \le 17$
Measured data	22718
Unique data	6840 (R_{int} = 0.0809)
Number of parameters	533
R indices[a] with $I > -\sigma(I)$, data	6376
wR_2	0.0928
R_1	0.1067
R indices[a] with $I > 2\sigma(I)$, data	5099
wR_2	0.0899
R_1	0.0821
Goodness-of-fit σ[b] on F^2	1.946
Residual density [e·nm^{-3}]	354; −325

[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 $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.[16] − [b] $\sigma = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

X-ray Crystallographic Study of $(\mathbf{4})_3$:[14] A suitable single crystal of $(\mathbf{4})_3$ was covered with nujol, sealed in a thin-walled capillary and mounted on a four-circle diffractometer Siemens P4 (graphite-monochromated Mo-K_α radiation and SMART area detector). Crystallographic parameters and details of data collection performed at −80°C are summarized in Table 3. No absorption or extinction corrections were applied. The structure was solved by direct methods with the software package SHELXTL Plus[17] and refined with the program SHELXL-93.[16] Neutral atom scattering factors were taken from Cromer and Mann[18] and for the hydrogen atoms from Stewart et al.[19] The non-hydrogen atoms were refined anisotropically whereas the hydrogen atoms were calculated in ideal positions. One of the trimethylsilyl groups shows a two-site disorder (C612, C613/C614, C615) with an occupation ratio of 0.59(3)/0.41(3).

☆ Dedicated to Professor Dr. *Hanns-Peter Boehm* on the occasion of his 70th birthday.

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