

Synthesis and Structure of Solvent-Free Hexameric Magnesium Tri(*tert*-butyl)silylphosphandiide

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Introduction

Geminal dimetalated amines, phosphanes, and arsanes gained increasing attention due to the expectation of a high reactivity and unique solid-state structures. Power et al.¹ reported the molecular structure of a hexameric ether complex of a magnesium imide. The aryl substituent at the nitrogen atom has been a phenyl¹ or a naphthyl group.² Furthermore, the high reactivity allows the synthesis of a wide variety of derivatives.² Dilithiated phosphanes and arsanes are already published;³ however, they are centered by an oxygen-centered lithium octahedron. The tmeda complex of magnesium bis(phenylphosphanide) has been known since 1987.⁴ Solvent-free magnesium bis[bis(trimethylsilyl)phosphanide] is trimeric in the solid state, but monomeric and dimeric species are present in the gaseous phase and in solution.⁵ This equilibrium explains the high reactivity for example toward multiple bonds such as of nitriles and alkynes.⁶ The ether adducts are monomeric in solution and the solid state.⁷ Here, we report a solvent-free magnesium phosphandiide.

Results and Discussion

Magnesium dibutanide metalates quantitatively tri(*tert*-butyl)silylphosphane⁸ in a solvent mixture of heptane and toluene according to eq 1. During the metalation reaction the solution



turns bright yellow. From this solution yellow cuboids precipi-

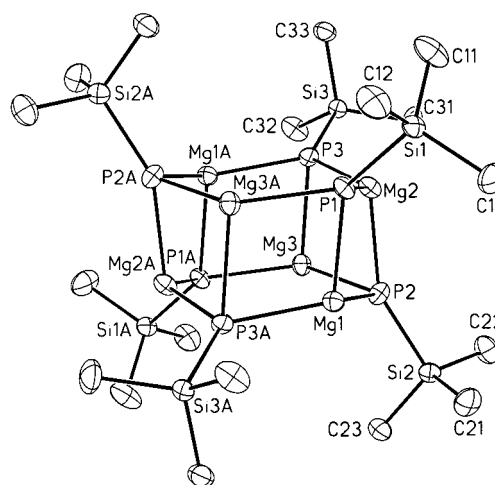


Figure 1. Molecular structure and numbering scheme of hexameric magnesium tri(*tert*-butyl)silylphosphandiide **1**. The ellipsoids represent a probability of 40%. All methyl groups are omitted for clarity. The atoms generated by the inversion center ($-x + 1, -y, -z + 1$) are marked with an "A". Selected bond lengths [Å]: Mg1–P1, 2.555(2); Mg1–P2, 2.509(2); Mg1–P3A, 2.487(2); Mg2–P1, 2.486(2); Mg2–P2, 2.503(2); Mg2–P3, 2.474(2); Mg3–P1A, 2.475(2); Mg3–P2, 2.473(2); Mg3–P3, 2.596(2); P1–Si1, 2.237(1); P2–Si2, 2.201(2); P3–Si3, 2.235(1). Selected bond angles [deg]: P1–Mg1–P2, 100.58(7); P1–Mg1–P3A, 102.14(8); P2–Mg1–P3A, 125.70(7); P1–Mg2–P2, 102.70(7); P1–Mg2–P3, 127.20(8); P2–Mg2–P3, 100.49(7); P1A–Mg3–P2, 133.93(8); P1A–Mg3–P3, 101.31(7).

tate which are thermochromic. On heating, the yellow crystals turn colorless at about 200–250 °C, whereas up to approximately 400 °C no melting of **1** is observed. The high symmetry of the oligomeric compound is already shown NMR spectroscopically since all P*Si*^tBu₃ moieties are chemically and magnetically equivalent in a benzene-*d*₆ solution. The ³¹P singlet at $\delta = -263.8$ as well as the absence of P–H stretching frequencies in the IR spectrum prove the preparation of a dimetalated phosphane.

Figure 1 shows the molecular structure and the numbering scheme of hexameric **1**. The central core is a slightly distorted hexagonal Mg₆P₆ prism shielded by the sterically demanding tri(*tert*-butyl)silyl substituents. The benzene molecule originating from the recrystallization is not shown. The trigonal pyramidal coordination sphere of the magnesium atoms is responsible for the high reactivity of this compound as for example the extreme sensitivity against moisture and air. The phosphorus atoms display a distorted tetrahedral coordination sphere. A similar Sn₆P₆ prism was published by Driess et al.⁹ for hexameric tin-(II) triisopropylsilylphosphandiide.

The hexagonal Mg₆P₆ prism of **1** is disordered in the ratio of 0.824(3)/0.176(3) as stereoscopically displayed in Figure 2 with the same orientation of the major product as shown in Figure 1. This static disordering of the Mg₆P₆ fragment occurs without great influence on the aliphatic periphery. It can be best described as an octahedral arrangement of the bulky tri(*tert*-butyl)silyl substituents bonded to the phosphorus atoms. Above of six of the octahedron faces the magnesium atoms are positioned. Two opposite faces remain uncapped by metal

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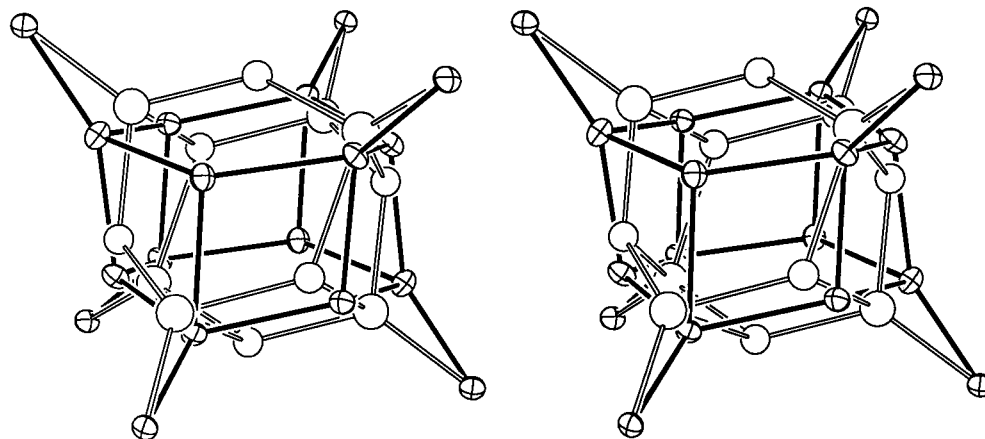


Figure 2. Representation of the disordering model of **1**. Stereoscopic representation of the overlapping major (ellipsoids, solid bonds) and minor components (empty balls, empty bonds) with the same orientation as shown in Figure 1. The population ratio of these molecules amounts to 0.824(3)/0.176(3).

atoms. The difference of these two molecules is the orientation of the capped faces of the P_6 octahedron.

For the following discussion the structural parameters of the major component are considered. The Mg–P distances vary in the narrow range between 2.473(2) and 2.509(2) Å within the six-membered Mg_3P_3 cycle and between 2.503(2) and 2.596(2) Å for the bond lengths between both the Mg_3P_3 cycles. These values are similar to those observed for magnesium bis-(phosphanides) with a four-coordinated metal center. The P–Si bond lengths with a mean value of 2.224 Å lie in the expected region and are approximately 4 pm shorter than in tetrameric tin(II) tri(*tert*-butyl)silylphosphandiide with a central Sn_4P_4 heterocubane.¹⁰

Due to the solubility of **1** in common organic solvents reactivity studies are in progress. The isolation of **1** provides a well-characterized source for the dianion ${}^tBu_3SiP^{2-}$ in aromatic hydrocarbons even in the absence of solvents with Lewis basicity such as ethers. Therefore, no limitations such as the handling at very low temperatures is necessary to avoid ether cleavage reactions.

Experimental Section

Synthesis of 1. To a solution of 0.56 g of ${}^tBu_3Si-PH_2$ (2.4 mmol) in 20 mL of toluene, a 1M heptane solution of dibutylmagnesium was added slowly. The clear solution turned yellow within the next 2 h. After several days 1.43 g of yellow crystals of **1** (0.94 mmol; yield 39%) precipitate at rt. Recrystallization from benzene yields a benzene solvate. Mp > 400 °C. 1H NMR (benzene- d_6 , 30 °C): δ 1.36. ${}^{13}C\{{}^1H\}$ NMR (benzene- d_6 , 30 °C): δ 24.06 (SiC), 32.34 (Me). ${}^{31}P\{{}^1H\}$ NMR (toluene, 30 °C): δ -293.8. IR (CsBr, Nujol): 1262 vw, 1179 vw, 1097 w, 1064 w, 1030 w, 1012 m, 932 w, 816 s, 759 vw, 727 w, 693 w, 647 vw, 627 w, 600 m, 565 s, 511 vs, 463 m, 458 m, 430 w, 410 w, 371 w, 329 vw, 302 vw. Elem. Anal. Calcd for $Mg_6P_6Si_6C_72H_{162}$ (1528.26): C, 56.59; H, 10.68. Found: C, 55.90; H, 10.68.

Structure Determination of $1 \cdot C_6H_6$. Data were collected on a STOE-IPDS diffractometer with graphite-monochromated Mo $K\alpha$ radiation at -100 °C using an oil-coated¹¹ rapidly cooled crystal ($2.18 < \theta < 25.92^\circ$). Selected crystallographic data are summarized in Table

Table 1. Crystallographic Data for $1 \cdot C_6H_6$

empirical formula	$C_{78}H_{168}Mg_6P_6Si_6$
fw (g mol ⁻¹)	1606.35
<i>T</i> (°C)	-100
space group	$P2_1/c$ (No. 14)
unit cell dimens	
<i>a</i> (Å)	13.594(1)
<i>b</i> (Å)	23.177(2)
<i>c</i> (Å)	16.351(1)
β (deg)	104.59(1)
<i>V</i> (Å ³)	4985.6(6)
<i>Z</i>	2
ρ_{calcd} (g cm ⁻³)	1.070
λ (Å)	0.710 73
μ (cm ⁻¹)	0.253
goodness-of-fit on F^2 ^a	1.062
wR2 indices [on F^2 , all data] ^b	0.2263
R1 [on F^2 , $I > 2\sigma(I)$]	0.0756
residual dens (e Å ⁻³)	1.23; -0.62

^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 $w^{-1} = \sigma^2(F_o^2) + (aP)^2$.

1. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using all data.¹² All non-hydrogen atoms were refined anisotropically with the exception of the minor Mg_3P_3 unit with a population factor of 0.176(3) (no restraints, 459 parameters). The asymmetric unit also contains half of a benzene molecule. The hydrogen atoms were considered on ideal positions at the corresponding carbon atoms.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available free of charge via the Internet at <http://pubs.acs.org>.

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