

Synthesis and Structure of $P_7[Si(SiMe_3)_3]_3$ (Tri(hypersilyl)heptaphosphanortricyclane)

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Summary. By reaction of sodium-potassium phosphide (prepared from white or red phosphorus and sodium-potassium alloy) and chloro*tris*(trimethylsilyl)silane, $P_7[Si(SiMe_3)_3]_3$ has been prepared in high yields. An X-ray analysis proved that the molecule is composed of a P_7 -nortricyclane cage substituted with three $Si(SiMe_3)_3$ groups and that two enantiomers are present in crystals grown from benzene. The ^{31}P NMR spectrum shows the complex splitting pattern of an $A[MX]_3$ spin system. ^{31}P chemical shifts and ^{31}P , ^{31}P one-bond and two-bond coupling constants have been calculated by numerical simulation of the spectrum.

Keywords. Tri(hypersilyl)heptaphosphanortricyclane; Synthesis; Crystal structure; $^{31}P\{^1H\}$ NMR data.

Synthese und Struktur von $P_7[Si(SiMe_3)_3]_3$ (Tri(hypersilyl)heptaphosphanortricyclan)

Zusammenfassung. Durch die Reaktion von Natrium-Kalium-Phosphid (darstellt aus rotem oder weißem Phosphor und Natrium-Kalium-Legierung) mit Chlor*tris*(trimethylsilyl)silan konnte $P_7[Si(SiMe_3)_3]_3$ in hoher Ausbeute dargestellt werden. Die Charakterisierung des mit drei $Si(SiMe_3)_3$ -Gruppen substituierten P_7 -Nortricyclan-Käfigs erfolgte mit Hilfe der Röntgenstrukturanalyse. In aus Benzol gezüchteten Kristallen sind beide Enantiomere enthalten. Das ^{31}P -NMR-Spektrum zeigt das komplexe Aufspaltungsmuster eines $A[MX]_3$ -Spinsystems. Die ^{31}P Verschiebungen und die ^{31}P , ^{31}P Kopplungskonstanten über eine oder zwei Bindungen wurden durch numerische Simulation des Spektrums berechnet.

Introduction

Due to its steric and electronic properties and facile availability, the *tris*(trimethylsilyl)silyl group (hypersilyl group) has been extensively used for the stabilization of exceptional structures comprising not only main group elements but also transition metals. Typical examples of main group compounds are $[(Me_3Si)_3Si]_2Sn \cdot LiCl(THF)_3$ [1], $[(Me_3Si)_3Si]_2Sn$ [2], $(Me_3Si)_3SiBMe_2$ [3], $(Me_3Si)_3SiB = NCMe_3$ [4], and $(Me_3Si)_3SiSi(SiMe_3)_3$ [5]. *Tris*(trimethylsilyl)-acylsilanes have been found to rearrange to the corresponding silaethylenes [6], and formylsilanes ($(R_3Si)_3SiCHO$) are stabilized considerably [7]. Transition metal

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compounds comprise $(\text{Me}_3\text{Si})_3\text{SiRe}(\text{CO})_5$ [8] or $(\text{Me}_3\text{Si})_3\text{SiAuPPh}_2\text{Me}$ [9], just to name a few. It has been argued that *van der Waals* bonding contributions within the peripheral methyl groups of $(\text{Me}_3\text{Si})_3\text{SiSi}(\text{SiMe}_3)_3$ compensate the reduced bond order of 0.83 of the central Si-Si-bond, an effect which is even more pronounced for hexa(*tert*-butyl)disilane with a Si-Si bond order of merely 0.26 [10, 11].

These unique properties of the hypersilyl group prompted us to investigate its potential use for the stabilization of structures contained in *Zintl* phases and *Zintl* ions composed of elements of groups 14 and 15. In the course of these experiments, we also developed a synthesis for the title compound, a molecule containing three weakly interacting hypersilyl groups which decrease the reactivity of the Si-P-bonds substantially. We will report on the reactions of $\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3$ with H_2O , BuLi, and KO^tBu as well as on the stabilization of Sb_7 and Bi_7 by the hypersilyl group in a forthcoming paper.

Results and Discussion

Molecular structure of tri(hypersilyl)heptaphosphanortricyclane

Colourless single crystals of $\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3 \cdot \text{solv}$ suitable for X-ray diffraction analysis were grown from benzene. Space group P-1 was suggested and later confirmed by a successful structure solution. As it is characterized by a centre of symmetry, the unit cell contains both enantiomers of $\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3$, along with two molecules of benzene. This is in contrast to $\text{P}_7(\text{SiMe}_3)_3$ which crystallizes enantiomorphically [12].

The molecular structure is shown in Fig. 1. The molecule possesses C_3 -symmetry to a very good approximation, the small deviations being caused by packing effects within the crystal.

Apart from a large number of organosubstituted P_7 -cages [15] as well as lithiated derivatives [16] that have been described in the literature, the molecular structures of three silyl substituted P_7 -nortricyclane cages have been determined so far. Table 1 compares their relevant structural parameters with those of the title compound, their definition being given in Fig. 2. The P-P interatomic distances *a*, *b*, and *c* as well as the Si-P distance do not vary much with the bulkiness of the silyl group which increases in the order $\text{SiMe}_3 < \text{SiPh}_3 < \text{Si}(\text{SiMe}_3)_3 < \text{Si}^t\text{Bu}_3$. The

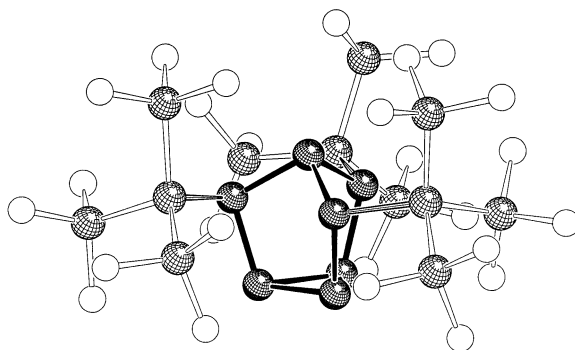


Fig. 1. Molecular structure of $\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3$; hydrogen atoms have been omitted

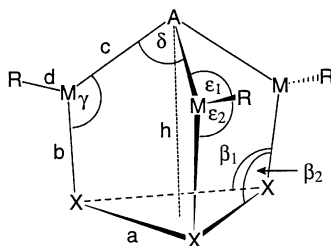


Fig. 2. Notation for the structural parameters and the $A[MX]_3$ spin system of P_7R_3

twisting of the cage with respect to the threefold axis of rotation, measured as the difference $\beta_1 - \beta_2$ of the bond angles β_1 and β_2 (Table 1), increases moderately in the order $Si^iBu_3 > Si(SiMe_3)_3 > SiMe_3$, but surprisingly assumes its smallest value for $SiPh_3$. Notable changes occur within the exocyclic bond angles ϵ_1 and ϵ_2 (and to a lesser extent γ) of the equatorial phosphorus atoms. Increasing bulkiness forces the SiR_3 -groups to rotate away from the apical P-atom (thereby increasing ϵ_1) and away from the neighbouring equatorial P-atom, thereby increasing not only ϵ_2 but also the nonbonded $Si \cdots P$ distance. The hypersilyl groups effectively surround and shield the P_7 -cage as can be anticipated from Fig. 1. The smallest $H \cdots H$ nonbonded distances between two $Si(SiMe_3)_3$ groups range from 2.4 to 2.9 Å which is quite close to the twofold value of the *van der Waals* radius for hydrogen, given in the literature as 1.20–1.45 Å [17]. Therefore, the elongation observed for the P_7 -cage of hypersilylheptaphosphane as expressed by the parameter h (Table 1) can be explained by *van der Waals* interactions within the hypersilyl groups, reducing slightly the distance between the equatorial P-atoms.

Table 1. Comparison of important intramolecular distances (Å) and bond angles (°) for silyl substituted heptaphosphanortricyclanes; for the meaning of the parameters, cf. Fig. 2

	$P_7(SiMe_3)_3$ [12]	$P_7(SiPh_3)_3$ [13]	$P_7[Si(SiMe_3)_3]_3$ [this work]	$P_7(Si^iBu_3)_3$ [14]
a	2.214(4)	2.217(3)	2.2176(11)	2.224(2)
b	2.192(4)	2.182(3)	2.1983(11)	2.185(2)
c	2.180(4)	2.180(6)	2.1836(9)	2.174(2)
d	2.288	2.286(6)	2.2884(10)	2.304(2)
h	3.154	3.144 ^a	3.184	3.158
ϵ_1	107.6(4)	109.3(6)	111.27(4)	118.34(7)
ϵ_2	102.2(4)	101.6(7)	103.71(4)	109.90
γ	101.2(2)	102.2(2)	103.11(4)	102.59(7)
δ	98.3(2)	98.5(9)	97.52(4)	96.88
β_1	101.0(2)	101.9(5)	100.42(4)	99.55(7)
β_2	107.1(2)	106.5(2)	106.94(4)	107.35(7)
$\beta_1 - \beta_2$	6.1	4.6	6.52	7.8

^a Calculated by the authors

NMR-Spectroscopy

The P₇-cage was also characterized by ³¹P and ²⁹Si NMR spectroscopy. The proton decoupled ³¹P NMR spectrum shows the complex splitting pattern of an A[MX]₃ system, very similar to that of the analogous supersilyl compound [14]. It consists of three groups of signals corresponding to the spins A, M and X (as illustrated in Fig. 2) centred at $\delta = -100.6$, -7.3 , and -161.6 ppm, respectively. From the symmetry of the spectrum it can be concluded that only the symmetric isomer (all hypersilyl groups possessing the same sense of rotation with respect to the threefold axis of rotation) is present. In order to determine the seven ³¹P, ³¹P-coupling constants characterizing the spin system, (¹J_{AM}, ¹J_{MX}, ¹J_{XX'}, ²J_{AX}, ²J_{MM'}, ²J_{MX'}, and ²J_{MX''}), a simulation of the spectrum using the parameters published for P₇[Si^tBu₃]₃ as a starting point and a subsequent iteration was performed. The calculated and the experimental spectra are presented in Fig. 3. The final chemical shifts and coupling constants are summarized in Table 2 and compared with the values reported for the analogous Si^tBu₃-substituted cage. The one-bond coupling constants between the equatorial and the apical as well as basal P-atoms (¹J_{AM} and ¹J_{MX}) are smaller than those of the supersilyl compound but larger than the values

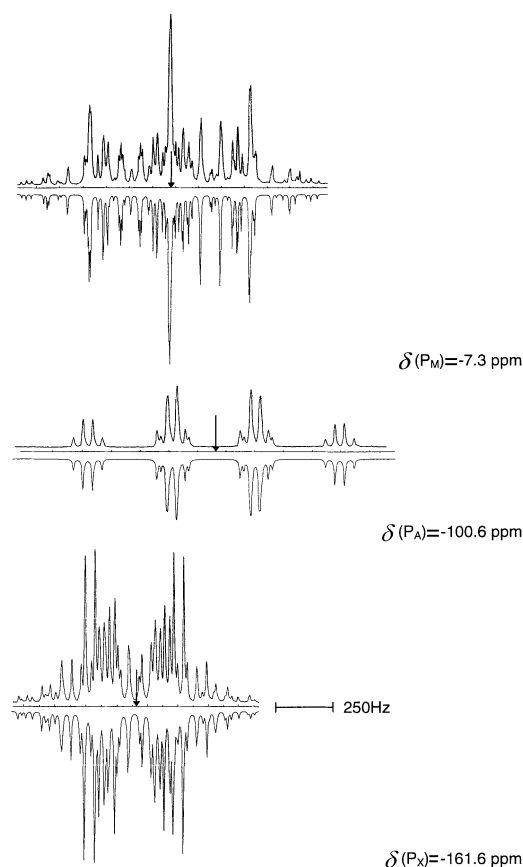


Fig. 3. A comparison of the measured ³¹P{H} NMR spectrum (top) with the calculated one (bottom)

Table 2. ^{29}Si and ^{31}P NMR shifts (ppm relative to *TMS* for ^{29}Si and relative to H_3PO_4 for ^{31}P and coupling constants (Hz) of $\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3$ and $\text{P}_7(\text{Si}^i\text{Bu}_3)_3$ ^a

	$\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3$	$\text{P}_7(\text{Si}^i\text{Bu}_3)_3$ [14]
$\delta(\text{P}_A)$	-100.6	-113.0
$\delta(\text{P}_M)$	-7.3	-31.2
$\delta(\text{P}_X)$	-161.6	-175.6
$^1J_{\text{AM}}$	-349.2	-401.7
$^1J_{\text{MX}}$	-364.9	-431.1
$^1J_{\text{XX}'}$	-213.7	-205.0
$^2J_{\text{AX}}$	39.4	33.3
$^2J_{\text{MM}'}$	-13.7	-12.1
$^2J_{\text{MX}'}$	-14.6	-12.3
$^2J_{\text{MX}''}$	27.8	22.1
$\delta(^{29}\text{Si})$	-92.5	
$\delta(^{29}\text{SiMe}_3)$	-7.8	
$^1J_{\text{SiP}}^b$	99	

^a Recorded in benzene- d_6 ; ^b due to long-range coupling with other ^{31}P nuclei there was a significant peak broadening which could not be resolved any further and which reduced the accuracy of $^1J_{\text{SiP}}$ to ± 5 Hz

reported for $\text{P}_7(\text{SiMe}_3)_3$, indicating that the exocyclic bond angles of the equatorial P-atoms (ε_1 and ε_2 , Fig. 2) lie between these two extremes.

Experimental

General remarks

All operations with sodium, potassium, and phosphorus-silicon compounds were carried out under a nitrogen atmosphere. Solvents were distilled from potassium. The NMR experiments were performed in C_6D_6 at ambient temperature on a Bruker 300 MSL spectrometer. $^{29}\text{Si}\{^1\text{H}\}$ spectra were recorded at 59.6 MHz using the INEPT pulse sequence, $^{31}\text{P}\{^1\text{H}\}$ spectra at 121.4 MHz.

X-ray structure solution

The data collection was performed under a stream of N_2 at -70°C using a Siemens diffractometer with a CCD SMART detector and graphite monochromated molybdenum K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal was mounted on the tip of a glass fibre in an inert oil. A summary of the crystal data, data collection, and data refinement is given below. Detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, Cambridge, U.K., under the deposition number 102248.

Crystal data for $\text{P}_7[\text{Si}(\text{SiMe}_3)_3]_3$: $\text{C}_{27}\text{H}_{81}\text{P}_7\text{Si}_{12} + \text{C}_6\text{H}_6$, $M = 1037.9 \text{ g/mol}$, triclinic (P-1), $a = 1400.72(1) \text{ pm}$, $b = 1414.31(2) \text{ pm}$, $c = 1825.98(3) \text{ pm}$, $\alpha = 84.216(1)^\circ$, $\beta = 77.639(1)^\circ$, $\gamma = 63.401(1)^\circ$, $V = 3159.48 \times 10^6 \text{ pm}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.091 \text{ g} \cdot \text{cm}^{-3}$; 27108 reflections (18895 independent, $1.14^\circ < 2\theta < 30.52^\circ$; $h = -19$ to 20, $k = -19$ to 20, $l = -13$ to 26) were collected from a crystal of $0.4 \times 0.4 \times 0.3 \text{ mm}$ size; $F(000) = 1116$, $R_1[I > 2\sigma(I)] = 0.0385$ ($R = (\sum ||F_0| - |F_c||) / \sum |F_0|$), $wR_2 = 0.1149$ ($wR_2 = (\sum (w(|F_0|^2 - |F_c|^2)^2) / \sum (w(F_0^4)))^{1/2}$), $GOF = 0.463$ ($GOF = (\sum w(|F_0|^2 - |F_c|^2)^2 / (n - m))^{1/2}$). The structure was solved by direct methods using XS [18] and

refined by full-matrix least squares with SHELXL-93 [19] minimizing the residuals for F^2 . No absorption correction was applied. Hydrogen atoms were included in the model at their calculated positions. The torsion angle of a methyl group was set to maximize the sum of the electron density at the three calculated hydrogen positions. Anisotropic displacement parameters were assigned to all non-hydrogen atoms and isotropic parameters used for the hydrogen atoms.

Synthesis of $P_7[Si(SiMe_3)_3]_3$

1.42 g (45.7 mmol) of red phosphorus [20] (or equivalently white phosphorus P_4 [21]) are placed in a 100 ml three-necked round bottom flask and dried carefully by repeatedly evacuating and flushing the flask with dry nitrogen. The phosphorus is then suspended in 60 ml of dry dimethoxyethane (DME), and 1.04 ml (24.8 mmol) of liquid sodium potassium alloy (prepared by melting together 0.1 g of Na and 0.81 g of K in DME) are added. The mixture is then refluxed for 24 h. Subsequently, the solvent is removed by evaporation *in vacuo*, and the phosphide is suspended in 50 ml of dry toluene. 6 g (21.3 mmol) of $(Me_3Si)_3SiCl$ (prepared from $(Me_3Si)_3SiH$ and CCl_4 [22]) and 5 ml of dry DME are added, and the reaction mixture is refluxed for 72 h. Without the addition of a few ml of dry DME, no reaction occurs even with prolonged refluxing. The salts are then separated by filtration and washed with dry toluene. The volume of the combined filtrates is then reduced to about 50 ml, and the clear yellow solution is cooled to $-30^\circ C$. A colourless crystalline product separates in a total yield of 4.3 g (68.7%).

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