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[11] After 12 days at room temperature a ^{31}P NMR analysis of a solution of **7** in a sealed NMR tube prepared under dinitrogen had the following composition: **7**, 35%; **8**, 28%; **6**, 12%; unknown iridium compounds 25%. The NMR spectroscopic properties of **8** are virtually the same as those for **3**. $^{31}P\{^1H\}$ NMR ([D$_8$]THF, 25 °C, 202.42 MHz): ABCDEFG spin system, $\delta_A = -19.60$, $\delta_B = -30.73$, $\delta_C = -45.63$, $\delta_D = -268.33$ (transforms into a doublet of multiplets in the proton-coupled ^{31}P spectrum: $^1J(HP) \approx 118$ Hz), $\delta_E = -217.65$, $\delta_F = -221.72$, $\delta_G = 28.87$

[12] On hydrogenation of **7**, the reductive elimination of P_4 with formation of the trihydride **2** becomes competitive with respect to the hydrogenation reaction of P_4. This finding supports the hypothesis that hydrogen migration from the metal to one of the P atoms of P_4 is mandatory to bring about the final dihydrogen transfer to give PH_3 and *cyclo*-P_3.

[13] Homolytic P–P bond cleavage of P_4 has been considered recently in the photochemical reaction of P_4 with $[Cp''(CO)_2Fe]_2$ ($Cp'' = 1,3\text{-}t Bu_2C_5H_3$): O. J. Scherer, G. Schwarz, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **1996**, *622*, 951.

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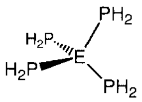
Synthesis and Crystal Structure Analysis of Tetraphosphanylsilane and Identification of Tetraphosphanylgermane[**]

Matthias Driess,[*] Christian Monsé, Roland Boese, and Dieter Bläser

Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday

The ease with which the phosphanyl group (PH_2) can be functionalized by electrophilic and nucleophilic reagents provides facile access to a wide range of molecular phosphorus compounds. Polyphosphanyl–element compounds without organic substituents are also very promising as potential single-source precursors for chemical vapor deposition (CVD) for the synthesis of metastable element phosphides and for surface refining. Element hydrides substituted solely by PH_2 groups are not yet known, however. We have therefore been concerned with the synthesis of tetraphosphanyl compounds with elements of Group 14 (**1**–**5**). Whereas nothing is yet known about the existence of these (expectedly) extremely reactive molecules, in the case of the polyphosphanylsilanes only $HSi(PH_2)_3$[1] and related organotriphosphanylsilanes[2] could be isolated. An excellent nucleophilic transfer reagent for the PH_2 group is the tetraphosphanylalanato ion in $[LiAl(PH_2)_4]$, which reacts even at −80 °C with halogen–element compounds under halogen/PH_2 exchange.[1, 3] According to earlier studies, the reaction of SiX_4 and GeX_4 (X = halide) with $[LiAl(PH_2)_4]$ does not lead to **2** and **3**, but to a mixture of SiH- and GeH-containing phosphanyl derivatives.[4] In contrast, we ascertained that the title compounds **2** and **3** are indeed accessible when mild reaction conditions are employed and the reaction products rapidly worked-up. Whereas **2** was for the first time isolated and characterized by means of NMR and IR spectroscopy as well as by X-ray structure analysis, **3** has only been identified by gas chromatography and mass spectrometry as yet.



	1	2	3	4	5
E	C	Si	Ge	Sn	Pb

The reaction of $SiCl_4$ with $[LiAl(PH_2)_4]$ in tetraethylene glycol dimethyl ether at −30 °C leads to an orange solution,

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from which **2** can be isolated in 18% yield. Compound **2** is colorless with a melting point of −25 °C, and can be stored without problem under vacuum or inert gas at temperatures below −10 °C. Contact with atmospheric oxygen leads to spontaneous combustion or even explosion. In the EI mass spectrum the molecular ion was detected at $m/z = 160$ with a relative intensity of approximately 30%. The ^{1}H NMR spectrum shows a doublet of multiplets of higher order at $\delta = 2.04$. The M part of the $A[MX_2]_4$ spin system ($A = {}^{29}Si$, $M = {}^{31}P$, $X = {}^1H$) in the ^{31}P NMR spectrum (Figure 1) is a triplet of complex multiplets at characteristic high field ($\delta = -205.0$). The ^{31}P nuclei in **2** are somewhat more strongly shielded than those in $HSi(PH_2)_3$ ($\delta = -216$).[4] Analysis of the multiplet by spectrum simulation[5] results in coupling constants of $^1J(P,H) = 185.51$, $^2J(P,P) = 14.28$, $^2J(H,H) = 0.37$, and $^4J(P,H) = 4.35$ Hz. As expected, the $^{29}Si\{^1H\}$ NMR spectrum (Figure 2) has a quintet at $\delta = -12.17$ ($^1J(Si,P) = 52.5$ Hz), which in the ^{1}H-coupled spectrum is additionally split into a nonet of quintets ($^2J(Si,H) = 7.5$ Hz).

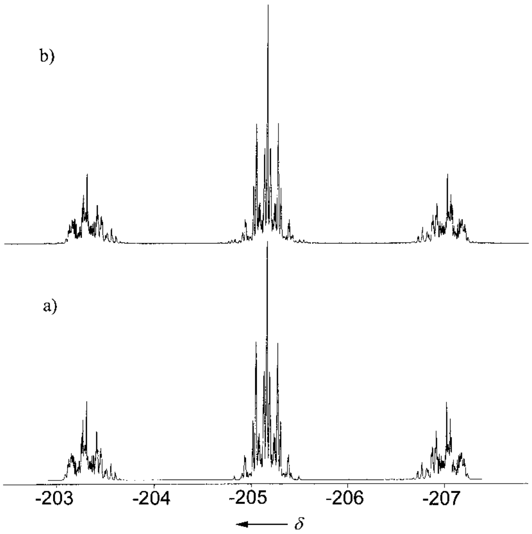

Figure 1. ^{31}P NMR spectra of **2**. a) measured; b) simulated.

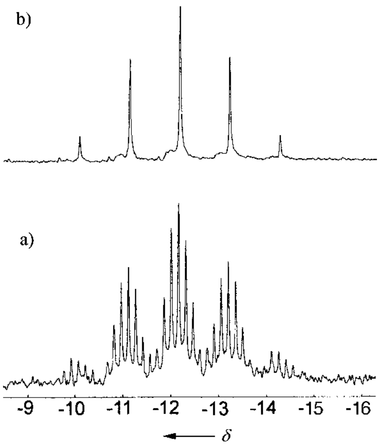

Figure 2. ^{29}Si NMR spectra of **2**. a) ^{29}Si NMR spectrum; b) $^{29}Si\{^1H\}$ NMR spectrum.

A single crystal of **2** suitable for X-ray structure analysis was obtained by in situ crystallization on a diffractometer at −30 °C.[6] Compound **2** crystallized in the monoclinic space group $P2_1/c$ with four independent molecules in the unit cell. In the structure refinement, the H atoms on the pyramidally coordinated phosphorus atom were initially localized by a difference Fourier synthesis, but then refined with restrictions.[6] This resulted in a local C_1 symmetry, with the P atoms forming an ideal tetrahedron around the Si atom (av P-Si-P 109.46(5)°, Figure 3). The sum of the bond angles at phosphorus amounts to 277°. The average Si−P bond length of 2.240(1) Å is practically identical with that found in other silylphosphanes.[8] The structure calculated with the B3LYP density function without symmetry restrictions has C_1 symmetry, and the bond lengths and angles are in excellent agreement with the experimental values (Si−P 2.227, 2.225, and 2.230 Å; av P-Si-P 109.4°; H−P 1.43 Å). However, conformations with higher symmetry (D_2, D_{2d}, or S_4) are almost identical in energy with the C_1-symmetrical form and the rotation barriers of the PH_2 groups are only about 3–5 kcal mol^{-1}. This implies that various conformations that may be present in solution cannot be observed on the NMR time scale. The ^{1}H and ^{31}P NMR spectra of **2** in [D$_8$]toluene do indeed remain identical between −80 and 80 °C. In contrast, the packing of **2** in the crystal (Figure 4) favors local C_1 symmetry, and inversion-symmetrical molecule pairs are formed with two P(3)-H⋯P(4′) or P(4)-H⋯P(3′) interactions. The longer H⋯P distances of 2.97 Å lie in the range of the sum of the van der Waals radii of 3.0 Å, the P-H⋯P angles are 154° and the P⋯P′ distances about 4.3 Å.

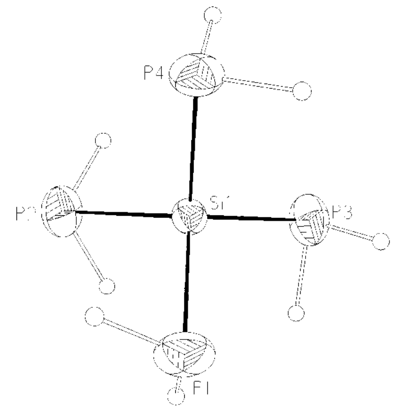

Figure 3. Structure of **2** in the crystal (50% probability ellipsoids). Bond lengths [Å] and angles [°]: Si1−P1 2.239(1), Si1−P2 2.243(1), Si1−P3 2.241(1), Si1−P4 2.237(1); P4-Si1-P1 109.75(5), P1-Si1-P3 111.59(5), P1-Si1-P2 109.60(5), P4-Si1-P3 108.81(5), P4-Si1-P2 108.28(5), P3-Si1-P2 108.74(5).

Calculations at the MP2/6-31G* level[7] of the gas-phase structure of such a dimer resulted, however, in weak *repulsive* Gibbs energies of association, irrespective of whether they were based on the crystallographically determined or geometrically optimized atomic sites for the H atoms on phosphorus, while at the same time holding the (experimental) distances of the Si and P atoms. In agreement with this, vibrational spectroscopy studies on **2** in an argon matrix at the

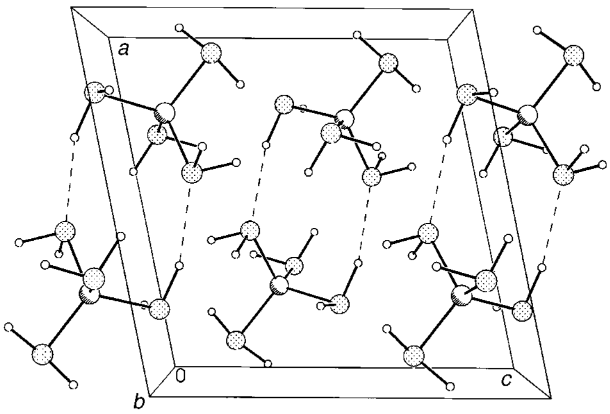

Figure 4. Packing and pair formation of **2** in the crystal.

temperature interval from 8 to 55 K gave no indication of the voluntary formation of a dimer.

Owing to the strongly oxidizing effect of tetravalent germanium, PH_3 and an insoluble yellow solid are formed spontaneously on reaction of $GeCl_4$ with $Li[Al(PH_2)_4]$ in ethylene glycol dimethyl ether at $-45\,^{\circ}C$. After filtration and removal of PH_3, the clear reaction solution contains only tetraphosphanylgermane (**3**) and triphosphanylgermane ($HGe(PH_2)_3$, **6**) in the ratio 1:2.5, as determined by GC-MS. In the EI mass spectrum of **3**, the molecular ion peak is at $m/z = 206$ with a relative intensity of 10% and a correct isotope distribution. The new compounds **2**, **3**, and **6** are indeed thermolabile single-source precursors for CVD processes. They react at the relatively low temperature of 80 °C under cleavage of PH_3 to readily form Si and Ge phosphides. We will report on these elsewhere.

Experimental Section

2: $SiCl_4$ (11.46 g, 67.4 mmol) was added to a solution of $Li[Al(PH_2)_4]$ (0.25 M, 75 mmol) in tetraethylene glycol dimethyl ether (300 mL) at $-30\,^{\circ}C$ over a period of 10 min under continuous stirring. The solution turned orange. The volatile components (PH_3, $HSi(PH_2)_3$, and **2**) were removed under vacuum (10^{-3} Torr) at 20 °C and collected in a cold trap at $-196\,^{\circ}C$. These were then fractionated by condensation in a series of cold traps at -10, -60, and $-196\,^{\circ}C$. Compound **2** was collected in the trap at $-10\,^{\circ}C$, $HSi(PH_2)_3$ at $-60\,^{\circ}C$, and PH_3 at $-196\,^{\circ}C$. Yield: 1.94 g (12.1 mmol, 18%); m.p. $-25\,^{\circ}C$; ^1H NMR (250 MHz, C_6D_6, 25 °C): $\delta = 2.04$ (dm); ^{31}P NMR (101 MHz, C_6D_6, 25 °C): $\delta = -205.0$ (tm, $^1J(P,H) = 185.51$, $^2J(P,P) = 14.28$, $^2J(H,H) = 0.37$, $^4J(P,H) = 4.35$ Hz); ^{29}Si NMR (49 MHz, C_6D_6, 25 °C): $\delta = -12.17$ (n of quint, $^1J(Si,P) = 52.5$, $^2J(Si,H) = 7.5$ Hz); IR (Ar matrix, $-218\,^{\circ}C$): $\tilde{\nu} = 2289$ (vs), 1183 (vs), 840 (w), 721 (m), 633 (m), 566 (w), 478 cm^{-1} (vs); MS (EI): m/z (%): 160 (30) $[M^+]$, 127 (100) $[M^+ - PH_2]$, 93 (61) $[SiPH(PH_2)^+]$, 61 (17) $[SiPH_2^+]$.

3/6: $GeCl_4$ (0.60 g, 2.8 mmol) was added dropwise under stirring to a solution of $Li[Al(PH_2)_4]$ (0.31 M, 3.1 mmol) in ethylene glycol dimethyl ether (10 mL) at $-45\,^{\circ}C$. The release of gas (PH_3) was accompanied by formation of a yellow suspension, which was filtered. According to GC-MS, the clear filtrate contained only **3** and **6** in the ratio 1:2.5. **3**: MS(EI): m/z (%) = 206 (10) $[M^+]$, 173 (100) $[M^+ - PH_2]$, 137 (100) $[GeP_2H^+]$, 107 (82) $[GePH^+]$, 74 (19) $[Ge^+]$, 67 (19) $[P_2H_3^+]$. **6**: MS(EI): m/z (%): 174 (23) $[M^+]$, 140 (90) $[M^+ - PH_3]$, 107 (100) $[M^+ - PH_2PH_3]$, 74 (40) $[Ge^+]$.

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[5] The spectrum simulation was carried out with the program Perch, Version 1/96, University of Kuopio (Finland).

[6] A single crystal of **2** was formed in a capillary tube with a diameter of 0.3 mm on a four-circle diffractometer at 242 K by miniaturized zone melting with focused infra-red radiation.[9] **2**: monoclinic, space group $P2_1/c$, $a = 10.659(3)$, $b = 7.137(2)$, $c = 10.832(3)$ Å, $\beta = 101.72(2)^{\circ}$, $V = 806.8(4)$ Å^3, $Z = 4$, $\rho = 1.318\ g\,cm^{-3}$, $\Theta_{max} = 30^{\circ}$; of 2464 measured reflections, 2316 were independent ($R_{merg} = 0.0379$) and 1752 observed ($I > 2\sigma(I)$). The intensities were measured on a Nicolet R3m/V four-circle diffractometer (MoK_{α} radiation, $\lambda = 0.71073$ Å, ω scan, $T = 123$ K). The structure was solved by direct methods,[10a] and refined with all measured reflections against F^2.[10b] The Si and P atoms were anisotropic, and hydrogen-atom positions were determined from a difference Fourier and refined as riding groups with P–H distances taken from the sum of the covalent radii (1.42 Å) with group isotropic temperature factors. A refinement without imposing certain restrictions led to unreasonably small P–H distances. $R1 = 0.0479$, $wR2 = 0.1306$ (all data), 50 parameters. Models with higher local symmetry (D_{2d} or S_4) led to significantly higher R values ($R1 > 0.10$). Further details on the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408423.

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Rate Enhancement of the Radical 1,2-Acyloxy Shift (Surzur–Tanner Rearrangement) by Complexation with Lewis Acids**

Emmanuel Lacôte and Philippe Renaud*

Owing to their mildness and their compatibility with many functional groups, radical reactions have become a very powerful tool for organic synthesis.[1] For instance, unique

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