DOI: 10.1002/ejic.200800446

Staudinger Reaction as a Way Out To Avoid Cyclization in the Reaction of Silylated Dichloro(hydrazino)phosphane with Trimethylsilyl Azide

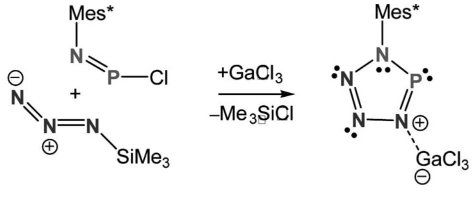
Axel Schulz*[a,b] and Alexander Villinger[a]

Keywords: Gallium / Azides / NBO analysis / Phosphorus heterocycles / Nitrogen heterocycles / Structure elucidation

Reaction of dichloro-*N*,*N*′,*N*′-[tris(trimethylsilyl)]hydrazinophosphane (**1**) with Me_3SiN_3 leads after an initial chlorine/azide exchange in a Staudinger reaction to a new phosphorus azide. The in situ formed phosphoranimine reacts with $GaCl_3$ by Me_3SiCl elimination, resulting in a phosphoranimino–dichlorogallane, which dimerizes to a Ga_2N_2-four-membered ring. The overall reaction at ambient temperature represents a fast and clean high-yielding reaction (reaction time 2 h). The dimer of the formed azido–phosphoranimino–dichlorogallane was fully characterized and shown to be stable to temperatures above 103 °C.

Introduction

Recently, we reported on the successful preparation of the first binary members of the neutral azaphosphole series, triazadiphospholes, RN_3P_2 [R = $(TMS)_2N$, Mes*; TMS = trimethylsilyl, Mes* = 2,4,6-tri-*tert*-butylphenyl] and tetrazaphospholes, Mes^*N_4P, stabilized as $GaCl_3$ adducts.[1] Access to this new class of neutral binary nitrogen–phosphorus heterocycles was gained by $GaCl_3$ assisted [3+2] cycloaddition reactions, in which $GaCl_3$ triggers TMSCl elimination in suitable precursors, releasing the dipolarophile and/or the 1,3-dipole, and finally stabilizes the formed, labile heterocycle by adduct formation.[2] For instance, the $GaCl_3$ assisted [2+3] cycloaddition of Mes*–N=P–Cl with trimethylsilyl azide ($TMSN_3$) results in the formation of a tetrazaphosphole kinetically stabilized as a $GaCl_3$ adduct in high yields (Scheme 1).[1b] Similar to this reaction, we tried to react dichloro-*N*,*N*′,*N*′-[tris(trimethylsilyl)]hydrazinophosphane (**1**) and $(TMS)_2N(TMS)NPCl_2$[3] with $TMSN_3$ in the presence of $GaCl_3$, which is the typical set up for a $GaCl_3$ assisted [2+3] cycloaddition. According to the concept of a $GaCl_3$ assisted [2+3] cycloaddition, a bis(trimethylsilylamino)tetrazaphosphole–$GaCl_3$ adduct should have formed but instead a new phosphorus azide attached to a four-membered binary gallium nitrogen ring, bis[azido{*N*,*N*′,*N*′-[tris(trimethylsilyl)]hydrazino}(chloro)phosphoranimino(dichloro)gallane] (**2**), was observed.



Scheme 1. Formation of a tetrazaphosphole in $GaCl_3$ assisted [2+3] cycloaddition.

Results and Discussion

Synthesis

Immediately after adding a solution of **1** in benzene to a solution of $TMSN_3$ and $GaCl_3$, the release of molecular nitrogen was observed at 5 °C and the colourless solution turned light green. According to ^{31}P NMR spectroscopic studies, the reaction was finished after 60 min at ambient temperature, resulting in the formation of a single new compound, **2**. Owing to the presence of two stereogenic phosphorus centres, two resonances {**2**: $\delta[^{31}P]$ = 34.49, 34.81 (s); cf. **1**: $\delta[^{31}P]$ = 166.6 ppm}, which can be assigned to the diastereomeric pairs (*S*,*S*/*R*,*R*) and (*R*,*S*/*S*,*R*) (*meso* compound) were detected. The (*S*,*S*/*R*,*R*) enantiomers could not be distinguished by means of NMR spectroscopy. The two new ^{31}P NMR resonances lie in the typical range of four-coordinate phosphorus(V) compounds {cf. $\delta[^{31}P]$ = 33.4 ppm for $(iPr)_2N{-}P(Cl)(N_3){=}N(Ph){\cdot}AlCl_3$}.[4] The existence of monomeric **2** in solution can be ruled out, as only one resonance should be observed in a ^{31}P NMR study (*R* and *S* enantiomers are indistinguishable.). Removal of the solvent in vacuo results in a yellowish polycrystalline powder. ^{31}P MAS NMR studies proved the existence of the same species in the solid state as that observed in the solvent ^{31}P NMR experiment. Because a (*S*,*S*/*R*,*R*/*R*,*S*/*S*,*R*)

---

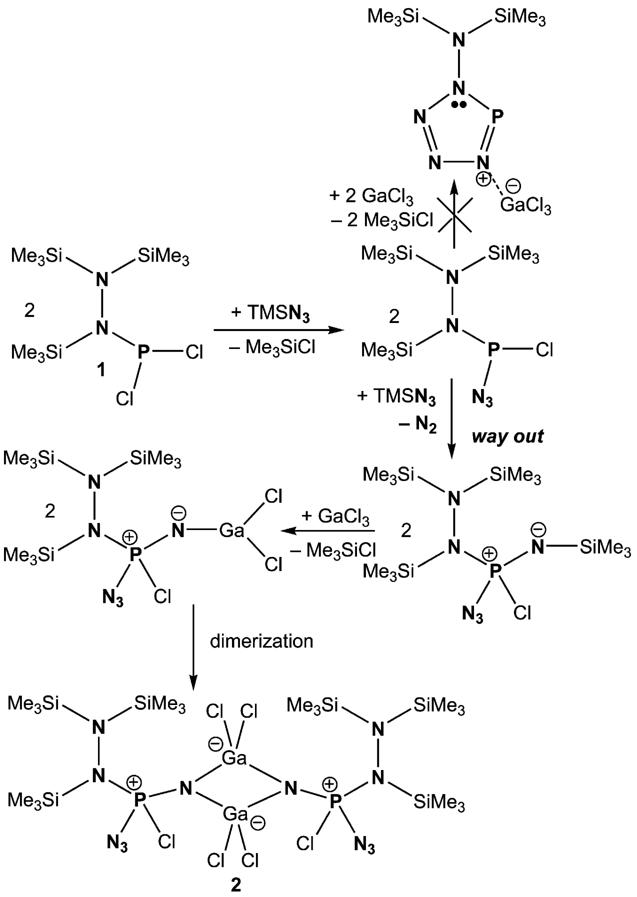
[a] Universität Rostock, Institut für Chemie,
Albert-Einstein-Str.3a, 18059 Rostock, Germany
[b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock,
Albert-Einstein-Str. 29a, 18059 Rostock, Germany
Fax: +49-381-4986382
E-mail: axel.schulz@uni-rostock.de
www.chemie.uni-rostock.de/ac/schulz

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

mixture of **2** was studied (see above), two resonances at δ_{iso}[^{31}P MAS] = 33.1 (s) and 36.0 (s) ppm were found in the ^{31}P MAS NMR spectrum.

Recrystallization from dichloromethane at 0 °C gave a colourless, crystalline solid. X-ray structure analysis confirmed the formation of **2**. Pure dry **2** is stable at temperature up to 103 °C (decomposition starting with the release of N_2), heat but not shock sensitive, easily prepared in bulk (yield $> 90\%$) and infinitely stable when stored in a sealed tube. This together with the very good solubility in almost all common organic solvents makes **2** a good precursor for further synthesis.

The intriguing formation of **2** can be explained by a halogen (Cl)/pseudohalogen (N_3) exchange in the first reaction step, followed by a Staudinger reaction (Scheme 2).[5] The Staudinger reaction describes an oxidation of phosphorus(III) to phosphorus(V) compounds, which is accompanied by a linkage of a P (phosphane) and a N (azide) atom of two different molecules upon N_2 release. With respect to the azide and phosphorus(III) compounds, the Staudinger reaction is very flexible. Therefore, a great diversity of iminophosphoranes and their application are well known.[6–10]



Scheme 2. Synthesis of **2** by the Staudinger reaction.

The complete mechanism of the formation of **2** according to Scheme 2 is still unknown although the release of molecular nitrogen was experimentally proven as an initial step. Presumably, after N_2 elimination, the in situ formed phosphoranimine reacts with $GaCl_3$, again by TMSCl elimination, leading to a phosphoranimino–dichlorogallane, which dimerizes to the Ga_2N_2 four-membered ring **2**. The overall reaction to **2** at ambient temperature represents a fast and clean high-yielding reaction (reaction time 2 h). A solution of **2** in CH_2Cl_2 is stable for at least four weeks (according to ^{31}P NMR spectroscopic experiments).

To the best of our knowledge, only two fully characterized dimers of phosphoranimino–dichlorogallane have been reported: $[GaCl_2(NPPh_3)]_2$[11] and $[GaCl_2\{NP(R)_2Br\}]_2$ (R = OCH_2CF_3),[12] which were synthesized from the according Me_3Si-substituted phosphoranimines and $GaCl_3$.

Structure

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The ORTEP drawing of **1** is depicted in Figure 1. In agreement with our computation,[3] the molecule adopts a staggered configuration with the two planes P–N1–Si1–N2 and N1–N2–Si2–Si3 [88.2(2) and 88.7(2)°] perpendicular to each other. According to our calculations, the rotation about the P–N1 axis is sterically hindered by ca. 10 kcal mol^{-1}. The phosphorus atom sits in a pyramidal environment with bond angles between 101 and 106°. In contrast to the P–Cl bond lengths [2.084(2), 2.120(2) Å], the experimentally determined P–N bond length of 1.656(3) Å is slightly shorter than expected for a typical P–N single bond [cf. $\Sigma r_{cov.}$ 1.80 (1.76) Å].[13,14]

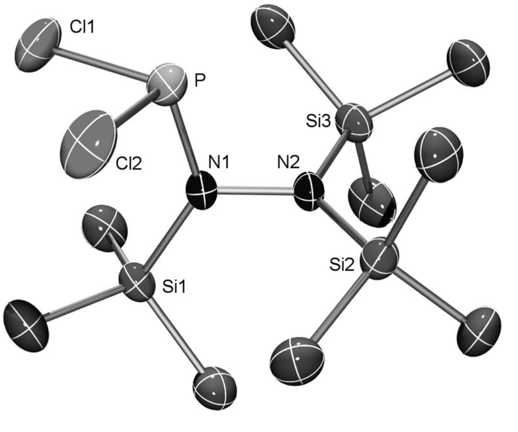


Figure 1. ORTEP drawing of the molecular structure of **1** in the crystal. Thermal ellipsoids with 50% probability at 200 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Cl1–P1, 2.084(2), Cl2–P1 2.120(2), P1–N1 1.656(3), Si1–N1 1.792(3), Si2–N2 1.768(3), Si3–N2 1.771(3), N1–N2 1.477(4); N1–P1–Cl1 101.6(1), N1–P1–Cl2 106.1(2), Cl1–P1–Cl2 95.3(6), N2–N1–P1 107.6(2), N2–N1–Si1 119.0(2), P1–N1–Si1 133.2(2), N1–N2–Si2 117.2(2), N1–N2–Si3 115.8(2).

Both nitrogen atoms sit in an almost planar environment [$\Sigma\angle$(N) = 360°]. Hence, as displayed by NBO analysis, the one lone pair on both nitrogen atoms is localized in a pure p-type atomic orbital. Both lone pairs are also perpendicular to each other. As a consequence, the p-type lone pair at the N1 atom (notation: p-LP) is slightly further delocalized resulting in intramolecular interactions (noncovalent effects). As indicated by an investigation of the noncovalent effects,[15] there are two significant interactions of the N1 lone pair (p-LP) with the two unoccupied, localized antibonding σ*(P–Cl) orbitals. Moreover, the lone pair localized at the P atom interacts with the unoccupied σ*(N–N) bond orbital. These intramolecular LP(N) → σ*(P–Cl) and LP(P) → σ*(N–N) donor–acceptor interactions account for the rather short P–N distance by introducing a small amount of π interaction. Similar structural features with short P–N distances (1.67 ± 3 Å) have already been observed in a series of amino–iminophosphanes ($R_2N–P=N–R'$).[16]

Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with four formula units in the unit cell (Figure S1, Table 1) including four solvent molecules (CH_2Cl_2). The ORTEP representation of **2** is depicted in Figure 2. The four-membered Ga_2N_2 is nearly planar [<(Ga2–N1–N4–Ga1) = 172.3°, <(N4–Ga1–Ga2–N1) = 172.0°]. Hence, deviation from local C_2 symmetry of the entire molecular unit is rather small. All four Ga–N bonds are in the range between d(Ga–N) = 1.942(5) and 1.957(5) Å, which is only slightly longer than the Ga–N distances found in phosphorane–iminato–$GaCl_2$ complex $[GaCl_2(NPPh_3)]_2$ [1.906(8)–1.91(1) Å].[11] However, these distances are significantly smaller than those found for a four-coordinated N atom attached to Ga {cf. $[GaCl_2(N(H)SiMe_2Ph)]_2$:[17] d(Ga–N) = 1.968(3)–1.988(4) Å, $[GaCl_2(N(H)t\text{Bu})]_2$:[18] d(Ga–N) = 1.973(2)–1.977(2) Å}. The Ga–N–Ga angles {87.5(2) and 87.2(2)°, cf. $[GaCl_2(NPPh_3)]_2$: 93.7°, $[GaCl_2(N(H)t\text{Bu})]_2$: 93.2(1)°} are rather small relative to the Ga–N–P angles [128.5(3)–132.1(3)°]. In agreement with three-coordinated N atoms, the NBO analysis[15] indicates an almost ideal sp^2-hybridized N ring atom with strongly polarized Ga–N bonds. The Ga···Ga distance of 2.808(1) Å is substantially longer than the sum of the covalent radii [d_{cov}(Ga–Ga) = 2.52 Å].[19] The P–N_{ring} distances [1.558(4) and 1.574(4) Å] are substantially shorter than the sum of the covalent radii [d_{cov}(N–P) = 1.8, d_{cov}(N=P) = 1.6 Å],[13,14] indicating partial double bond character for the P–N_{ring} bonds, whereas the P–$N_{hydrazine}$ bonds [1.624(5) and 1.632(6) Å] as well as the P–N_{azide} bonds [1.693(5) and 1.718(6) Å] are considerably elongated. The hydrazine N–N bond represents a typical single bond with 1.473(5) and 1.482(6) Å, respectively. As shown on numerous occasions,[20] both covalently bound azide groups display a *trans* bent configuration (regarding the P atom) with a N–N–N bond angle of 173.4(7) (N7–N8–N9) and 172(8)° (N10–N11–N12), respectively.

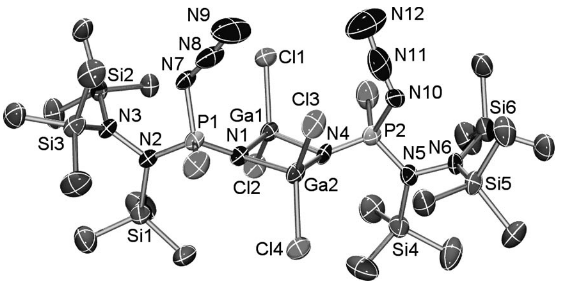


Figure 2. ORTEP drawing of the molecular structure of **2** in the crystal. Thermal ellipsoids with 50 % probability at 200 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]:Ga1–N4 1.942(4), Ga1N1 1.945(4), Ga1–Cl2 2.154(2), Ga1–Cl1 2.155(2), Ga1···Ga2 2.8083(9), Ga2–N1 1.947(4), Ga2–N4 1.950(4), Ga2–Cl4 2.147(2), Ga2–Cl3 2.165(2), Cl5–P1 2.031(2), Cl6–P2 2.043(2), P1–N1 1.558(4), P1–N2 1.634(5), P1–N7 1.698(5), P2–N4 1.574(4), P2–N5 1.628(5), P2–N10 1.715(5), N2–N3 1.473(5), N5–N6 1.482(6), N7–N8 1.173(7), N8–N9 1.150(8), N10–N11 1.076(8), N11–N12 1.230(9); N4–Ga1–N1 87.5(2), N4–Ga1–Ga2 43.9(1), N1–Ga1–Ga2 43.8(1), N1–Ga2–N4 87.2(2), N1–P1–N2 117.2(2), N1–P1–N7 116.5(2), N2–P1–N7 102.9(2), N1–P1–Cl5 106.8(2), N2–P1–Cl5 109.6(2), N7–P1–Cl5 102.9(2), N4–P2–N5 116.1(2), N4–P2–N10 116.1(3), N5–P2–N10 103.7(2), N4–P2–Cl6 107.6(2), N5–P2–Cl6 109.7(2), N10–P2–Cl6 102.7(2), N3–N2–P1 118.2(3), N8–N7–P1 118.8(4), N9–N8–N7 173.4(7), N11–N10–P2 119.3(5), N10–N11–N12 172.4(8).

Another interesting feature of this structure is the almost planar environment of both hydrazine nitrogen atoms [all N–N–X angles are between 114.1(3)–121.1(3)°, X = P, Si; Table S3]; however, both planes are almost perpendicular to each other. Hence, as displayed by NBO analysis, the lone pair at both nitrogen atoms is localized in a pure p-type atomic orbital.

Conclusions

We present here an easy, high-yielding (>90 %) synthetic procedure and full characterization of a new phosphorus azide[21] attached to a Ga_2N_2 ring. Because of the astonishing stability of **2** in solution as well as in the solid state, **2** may have great synthetic potential, for example, as a source for ternary PNGa species.

Experimental Section

General Information: All manipulations were carried out under oxygen- and moisture-free conditions by using standard Schlenk or dry box techniques. Dichloromethane was dried with P_4O_{10} and freshly distilled prior to use. Benzene was dried with Na/benzophenone and was freshly distilled prior to use. *N*,*N'*,*N'*-[tris(trimethylsilyl)]hydrazino(dichloro)phosphane (**1**) was prepared according to the procedure given in the literature,[3] and it was sublimed for purification. Trimethylsilyl azide (98 %, Fluka) was distilled freshly prior to use, $GaCl_3$ (99.99 %, Sigma–Aldrich) was used as received. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra were obtained with a JEOL EX 400 NMR spectrometer (400.2, 100.6, 162.0, and 79.5 MHz, respectively) and were referenced either to protic impurities in the deuterated solvent (^1H) or externally to $SiMe_4$ ($^{13}C\{^1H\}$,$^{29}Si\{^1H\}$, $^{31}P\{^1H\}$). Raman spectra were measured with a Perkin–Elmer Spectrum 2000 NIR FT equipped with a Nd:YAG laser (1064 nm). C, H and N analyses were performed with an Analysator Elementar Vario EL. Mass spectra were measured with a Jeol MStation JMS 700. Melting points are uncorrected (Büchi B540).

X-ray Structure Determination: A X-ray quality crystal of **2** was selected at –50 °C in Galden HT230 oil (Solvay Solexis) and mounted on a glass fibre in a low-temperature N_2 stream. A suitable crystal of compound **1** was selected in Kel-F oil (Riedel de Haen) at room temperature. The samples were cooled to 200(2)

Table 1. Crystallographic details.

	2	**1**
Chemical formula	$C_{18}H_{54}Cl_6Ga_2N_{12}P_2{\cdot}(CH_2Cl_2)_{0.94}$	$C_9H_{27}Cl_2N_2PSi_3$
Formula weight [$g\,mol^{-1}$]	1101.39	349.47
Colour	Colourless	Colourless
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (Nr. 14)	$P2_1/c$ (Nr. 14)
a [Å]	10.3989(8)	9.4252(19)
b [Å]	13.4213(8)	13.757(3)
c [Å]	36.808(2)	17.171(5)
β [°]	102.459(5)	119.69(2)
V [$Å^3$]	5016.2(6)	1934.1(8)
Z	4	4
$\rho_{calcd.}$ [$g\,cm^{-3}$]	1.465	1.200
μ [mm^{-1}]	1.738	0.591
λ(Mo-K_α) [Å]	0.71073	0.71073
T [K]	200(2)	200(2)
Measured reflections	29055	13826
Independent reflections	11469	2506
Reflections with $I > 2\sigma(I)$	6264	2287
$R_{int.}$	0.0786	0.0583
$F(000)$	2264	744
R_1 {R [$F^2 > 2\sigma(F^2)$]}	0.0648	0.0531
wR_2 (F^2)	0.1542	0.1228
GooF	1.004	1.159
Parameters	461	163

K during measurement. The data was collected with an Oxford Xcalibur3 CCD diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073). The structures were solved by direct methods (SHELXS-97)[22] and refined by full-matrix least-squares procedures (SHELXL-97).[23] Semiempirical absorption corrections were applied by using the ABSPACK program.[24] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the refinement at calculated positions by using a riding model. The position of the dichloromethane molecule in **1** was found to be partially occupied and the occupation factor was refined freely [0.943(6)]. Crystallographic details of compounds **1** and **2** are gathered in Table 1. CCDC-679123 (for **1**) and -679124 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Gallane Dimer 2: To a stirred solution of $TMSN_3$ (0.506 g, 4.4 mmol) in benzene (10 mL) was dropwise added a solution of $GaCl_3$ (0.387 g, 2.2 mmol) in benzene (10 mL) at 5 °C. To the resulting colourless solution was then dropwise added **1** (0.699 g, 2.0 mmol) in benzene (10 mL), resulting in a greenish solution, which was stirred for 2 h at ambient temperature, resulting in a yellow solution. The solvent was removed in vacuo, and the yellowish residue was recrystallized from dichloromethane at 0 °C. Removal of solvent and drying in vacuo yielded **2** (1.04 g, 94%) as a colourless, crystalline solid. M.p. 103 °C (decomp.). $C_{18}H_{54}Cl_6Ga_2N_{12}P_2Si_6{\cdot}CH_2Cl_2$ (1106.26): calcd. C 20.63, H 5.10, N 15.19; found C 19.27, H 4.97, N 15.59. Raman (200 mW, 25 °C): 2966 (45), 2905 (100), 2496 (2), 2170 (15), 1414 (22), 1269 (12), 1172 (9), 1050 (11), 991 (7), 850 (12), 779 (14), 747 (17), 685 (25), 654 (64), 592 (14), 520 (15), 477 (23), 422 (32), 395 (30), 382 (29), 353 (55), 297 (24), 224 (54), 202 (44) cm^{-1}. ^1H NMR (CD_2Cl_2, 25 °C): δ = 0.29 {s, 6 H, N[Si(CH_3)$_3$]$_2$}, 0.31 {s, 6 H, N[Si(CH_3)$_3$]$_2$}, 0.49 {s, 6 H, N[Si(CH_3)$_3$]} ppm. ^{13}C NMR (CD_2Cl_2, 25 °C): δ = 2.70, 2.75 {s, N[Si(CH$_3$)$_3$]$_2$}, 2.82, 2.86 {s, N[Si(CH$_3$)$_3$]$_2$}, 3.09, 3.14 {s, N[Si(CH$_3$)$_3$]} ppm. ^{31}P NMR (CD_2Cl_2, 25 °C): δ = 34.49, 34.81 (s) ppm. $^{29}Si\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ = 13.0, 13.1 {s, N[Si(CH$_3$)$_3$]$_2$}, 16.0, 16.1 {s, N[Si(CH$_3$)$_3$]$_2$}, 24.2 {d, $^2J_{SiP}$ = 3.9 Hz, N[Si(CH$_3$)$_3$]}, 24.5 {d, $^2J_{SiP}$ = 4.4 Hz, N[Si(CH$_3$)$_3$]} ppm. ^{31}P MAS NMR (25 °C, ω_{rot} = 15 kHz): δ_{iso} = 33.1 (s), 36.0 (s) ppm. MS (EI, 70 eV, 35 °C): m/z (%) = 508 (6.0) [M_{mono} – 2H]$^+$, 434 (17.5) [M_{mono} – 2H – TMS]$^+$, 401 (6.5) [M_{mono} – 2H – TMS – Cl]$^+$.

Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated dichloromethane solution of **2** to 0 °C.

Supporting Information (see footnote on the first page of this article): Further experimental details, selected bond lengths, angles and torsion angles of **1** and **2**; view along the a axis in the crystal of **2**; ^{31}P MAS spectra.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (SCHU117/4-1) for financial support. We are indebted to Prof. T. M. Klapötke for allocation of X-ray measurement time and Dr. Johannes Weber and Dr. J. Schmedt auf der Günne for the MAS NMR study. Prof. K. Karaghiosoff is gratefully acknowledged for helpful discussions with the ^{31}P NMR spectra. We also thank LANXESS Deutschland GmbH (Leverkusen) for generous gifts of chemicals.

---

[1] a) S. Herler, A. Villinger, P. Mayer, A. Schulz, J. J. Weigand, *Angew. Chem. Int. Ed.* **2005**, *44*, 7790–7793; b) P. Mayer, A. Schulz, A. Villinger, *Chem. Commun.* **2006**, 1236–1238; c) P. Mayer, A. Schulz, A. Villinger, *J. Organomet. Chem.* **2007**, *692*, 2839–2842.

[2] H. Brand, A. Schulz, A. Villinger, *Z. Anorg. Allg. Chem.* **2007**, *633*, 22–35.

[3] G. Fischer, S. Herler, P. Mayer, A. Schulz, A. Villinger, J. J. Weigand, *Inorg. Chem.* **2005**, *44*, 1740–1751.

[4] M. R. Marre-Mazières, M. Sanchez, R. Wolf, *Nouv. J. Chim.* **1985**, *9*, 605–615.

[5] H. Staudinger, E. Hauser, *Helv. Chim. Acta* **1919**, *2*, 635–646.

[6] a) K. Sasse in *Houben-Weyl*: *Methoden der Organischen Chemie, Bd. 12, Teil 1 (Organische-Phosphor-Verbindungen)*,

Thieme, Stuttgart, **1963**, p. 73; b) R. F. Hudson, *Structure and Mechanism in Organophosphorus Chemistry*, Academic Press, London, **1965**, p. 198; c) A. W. Johnson, *Ylid Chemistry*, Academic Press, London, **1966**, p. 219; d) H. J. Bestmann, J. Zimmermann in *Organic Phosphorus Compounds, Bd. 3*, (Eds.: G. M. Kosalapoff, L. Maier) Wiley-Interscience, New York, **1972**, p. 11; e) M. Regnitz (Ed.), *Houben-Weyl*: *Methoden der Organischen Chemie, Bd. E II (Phosphorverbindungen)*, Thieme, Stuttgart, **1982**, p. 96.

[7] A. W. Johnson, *Ylides and Imines of Phosphorus*, Wiley, New York **1993**.

[8] K. Dehnicke, F. Weller, *Coord. Chem. Rev.* **1997**, *158*, 103–169.

[9] K. Dehnicke, M. Krieger, W. Massa, *Coord. Chem. Rev.* **1999**, *182*, 19–65.

[10] M. Köhn, R. Breinbauer, *Angew. Chem. Int. Ed.* **2004**, *43*, 3106–3116.

[11] F. Heshmatpour, D. Nusshaer, R. Garbe, S. Wocadlo, W. Massa, K. Dehnicke, H. Goesmann, D. Fenske, *Z. Allg. Anorg. Chem.* **1995**, *621*, 443–450.

[12] K. Huynh, E. Rivard, A. J. Lough, I. Manners, *Inorg. Chem.* **2007**, *46*, 9979–9987.

[13] First value corresponds to the sum of covalent radii: $r(\mathrm{P}) = 1.1$ and $r(\mathrm{N}) = 0.7$; however, bond lengths between two elements with large differences in electronegativity are often corrected according to $d_{\mathrm{AB}} = r_{\mathrm{A}} + r_{\mathrm{B}} - c|\chi_{\mathrm{A}} - \chi_{\mathrm{B}}|$, (Schomaker-Steveson equation), A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, vol. 101, Walter de Gruyter, **1995**, Anhang V.

[14] E. Niecke, O. Altmeyer, M. Nieger, *J. Chem. Soc., Chem. Commun.* **1988**, 945–946.

[15] a) E. D Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, *NBO Version 3.1*; b) J. E. Carpenter, F. Weinhold, *THEOCHEM* **1988**, *169*, 41–62; c) F. Weinhold, J. E. Carpenter, *The Structure of Small Molecules and Ions*, Plenum, **1988**, p. 227; d) F. Weinhold, C. Landis, *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, **2005** and references cited therein; e) The NBO analysis was carried out with the experimental structural data by utilizing the B3LYP/6-31G(d,p) level of theory.

[16] E. Niecke, D. Gudat, *Angew. Chem.* **1991**, *103*, 251–270; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 217–237 and references cited therein.

[17] C. J. Carmalt, J. D. Mileham, A. J. P. White, D. J. Williams, J. W. Steed, *Inorg. Chem.* **2001**, *40*, 6035–6038.

[18] C. J. Carmalt, J. D. Mileham, A. J. P. White, D. J. Williams, *Dalton Trans.* **2003**, 4255–4260.

[19] Sum of covalent radii: $r(\mathrm{Ga}) = 1.26$; A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, vol. 101, Walter de Gruyter, **1995**, Anhang V.

[20] a) T. M. Klapötke, A. Schulz, R. D. Harcourt (Eds.), *Quantum Chemical Methods in Main Group Chemistry*, Wiley, New York, **1998**; b) A. Schulz, I. C. Tornieporth-Oetting, T. M. Klapötke, *Inorg. Chem.* **1995**, *34*, 4343 and references cited therein.

[21] N. Götz, S. Herler, P. Mayer, A. Schulz, A. Villinger, *Eur. J. Inorg. Chem.* **2006**, 2051–2057.

[22] G. M. Sheldrick, *SHELXS-97: Program for the Solution of Crystal Structures*, University of Göttingen, Germany **1997**.

[23] G. M. Sheldrick, *SHELXL-97: Program for the Refinement of Crystal Structures*, University of Göttingen, Germany **1997**.

[24] *ABSPACK*, Oxford Diffraction, **2005**.

Received: April 30, 2008