Formation of the spirocyclic, Si-centered cage cations [ClP(NSiMe3)2Si(NSiMe3)2P5]⁺ and [P5(NSiMe3)2Si(NSiMe3)2P5]2⁺

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On account of our interest in P₄ activation by phosphonium ion insertion into P–P bonds we have developed synthetic routes to bicyclic N–P–Si–heterocycle 7 and probed its reactivity towards GaCl₃ and P₄. A GaCl₃-induced rearrangement of 7 leads to the in situ formation of spirocyclic, Si-centered phosphonium ions. Their insertion into P–P bonds of one or two P₄ tetrahedra yields polyphosphorus cages [ClP(NSiMe3)2Si(NSiMe3)2P₃⁺ (19⁺) ] and [P₅(NSiMe3)₂Si(NSiMe₃)₂P₃]²⁺ (13²⁺). GaCl₃ while the isolobal Al-species 4 is the result of the reaction of phosphonium zwitterion Cl₂Al(NSiMe₃)₂P with P₄.⁹

Only recently, cationic polyphosphorus cages have emerged as valuable synthetic building blocks for three purposes. First, they can be selectively fragmented in reactions with carbenes which results in the formation of P₄⁻species (e.g. a P₅⁻cage cation yields a P₂⁻ and cationic P₃⁻ species).¹³ Second, they can be oxidized with selenium or sulphur which allows for the targeted preparation of cationic phosphorus–chalcogen cages.⁷c Third, they can be used for the controlled release of P₄ due to the reversibility of the phosphonium ion insertion.¹⁰b

With the intention to further expand the range of methods for the in situ generation of phosphonium ions for P₄ activation, we investigated the reactivity of bicyclic phosphorus–nitrogen–silicon heterocycle 7 with GaCl₃ and P₄. A GaCl₃-induced rearrangement reaction was observed which formally gives access to the spirocyclic, Si-centered compound Cl₅P₄(NSiMe₃)絮[Cl₅P₄(NSiMe₃)絮Si(NSiMe₃)₂PCl]. Chloride abstraction by GaCl₃ and insertion of the respective phosphonium ion in P–P bonds of one or two P₄ molecules yields the Si-centered polyphosphorus cages [ClP(NSiMe₃)₂Si(NSiMe₃)₂P₃]⁺ (19⁺) and [P₅(NSiMe₃)₂Si(NSiMe₃)₂P₃]²⁺ (13²⁺).

Fig. 1 P₅⁺-cages 1⁺, 2⁺, 3⁺ and 4 featuring a fused four-membered heterocycle.
Results and discussion

Synthetic routes towards and characterization of 7

As part of our ongoing interest in four-membered phosphorus–nitrogen-element heterocycles as precursors for phosphonium ions\(^\text{12}\) that can insert into a P–P bond of P\(_2\)\(^\text{10}\), we revisited the synthesis of heterocycle 6. This compound is synthesized by the reaction of iminophosphane \(5\) with SiCl\(_4\) according to a procedure reported by Niecke and co-workers (Scheme 1).\(^\text{13}\) Compound 6 was obtained from the reaction mixture by distillation (40 °C, 8 × 10\(^{-2}\) mbar) and isolated in 41% yield in accordance with the literature report. Surprisingly, however, a second fraction was obtained at higher temperatures (105 °C, 2 × 10\(^{-3}\) mbar) and identified as bicyclic compound 7 (18% yield).\(^\text{14}\) The \(^{31}\)P{\(^1\)H} NMR spectrum of 7 dissolved in C\(_6\)D\(_6\) shows a singlet resonance at \(\delta(P) = 211.8\) ppm which is in the typical chemical shift region of diphosphadiazanes featuring amino-groups on P.\(^\text{15}\)

The molecular structure of 7 is \(C_{2v}\)-symmetric and features an distorted planar four-membered [NP]\(_2\)-ring (largest deviation from the plane 0.195 Å, Fig. 2). All four N atoms exhibit a trigonal planar arrangement (angular sums range from 358.8 (3)° to 360.0(3)°) whereas the P atoms are involved in pyramidal bonding environments (angular sums P1: 286(3)° and P2: 286.2(2)°). The P1–N1 and P2–N2 bonds are almost orthogonal to the [NP]\(_2\)-plane (N1–P1⋯P2: 95.84(4)°, N2–P2⋯P1: 95.84 (4)°). The \(C_{2v}\)-symmetric arrangement of the N\(_2\)SiCl\(_2\)-moiety in 7 is rare\(^\text{16}\) and contrasts other known diamido-cyclodiphosphazane compounds featuring amino-groups on P.\(^\text{15}\)

Compounds of type (PNR)\(_n\)NR\(_n\)EX\(_n\) typically exhibit \(C_{2v}\)-symmetric, seco-heterocube type structures in which the main group element fragment (e.g. EX\(_n\) = Mg, BPh, AlCl, GaCl, Ge, Sn, SnCl\(_2\), SiCl\(_2\), AsCl, SbCl, BiCl, R = t-Bu, Ph) is coordinated by three N atoms and occupies the edge of a distorted cube.\(^\text{15}\)

The molecular arrangement observed for 7 in the solid state also persists in solution. The observation of two sets of resonances for its chemically inequivalent Me\(_3\)Si-groups in the \(^1\)H NMR spectrum (\(\delta(H) = 0.21\) and 0.40 ppm) confirm the \(C_{2v}\)-symmetry. The \(^{13}\)C\({^1}\)H NMR spectrum shows a triplet resonance which is assigned to the carbon atoms of the Me\(_3\)Si-groups attached to the [NP]\(_2\)-ring (\(\delta(C) = -0.1\) ppm, \(\delta(J(CP)) = 3.6\) Hz). A pseudo-triplet is observed for the Me\(_3\)Si-groups adjacent to the N\(_2\)SiCl\(_2\)-moiety (\(\delta(C) = 2.3\) ppm, \(\delta(J(CP)) + \delta(J(HP)) = 5.0\) Hz) and is a result of an AA'X,X' spin system (\(A = 31^P\), X = \(^{13}\)C) with a comparatively large \(\delta(J(CP))\) coupling constant.\(^\text{17}\) The same arguments account for the pseudo-triplet resonance in the \(^{29}\)Si\(^{1}\)H NMR spectrum of 7 (\(\delta(Si) = 7.7\) ppm) which is assigned to the Me\(_3\)Si-groups adjacent to the N\(_2\)SiCl\(_2\)-moiety (\(\delta(J(SiP)) + \delta(J(SiP')) = 12.5\) Hz). The triplet resonance corresponding to the Me\(_3\)Si-groups attached to the [PN]\(_2\)-ring (\(\delta(Si) = 1.8\) ppm, \(\delta(J(SiP)) = 11.7\) Hz) and the resonance of the SiCl\(_2\) moiety (\(\delta(Si) = -47.4\) ppm) are observed in the expected regions.\(^\text{18}\)

Due to the low isolated yield of 7, it was of interest to develop an alternative synthetic approach. Compound 8 is the head to tail dimer of iminophosphane 5 and was obtained according to a literature known procedure.\(^\text{17}\) The solvent free reaction of 8 with an excess of SiCl\(_4\) gave selectively and quantitatively compound 9 via Me\(_3\)SiCl elimination (Scheme 2).\(^\text{19}\)

Compound 9 is the trans-conformer of an unsymmetrically-substituted diphosphadiazane derivative and, thus, shows an AX spin system in its \(^{31}\)P\(^{1}\)H NMR spectrum (\(\delta(P_A) = 219.5\) ppm, \(\delta(P_X) = 232.3\) ppm, \(\delta(J(P_A P_X)) = 12.0\) Hz). The \(^1\)H NMR spectrum of 9 shows singlet resonances for the SiMe\(_3\)- groups on the [NP]\(_2\)-ring and for both pointing towards the plane of the four-membered ring. The SiMe\(_3\) group pointing away from the ring, however, shows a relatively large \(\delta(J(HP))\) coupling constant (\(\delta(H) = 0.27\) ppm, \(\delta(J(P_A H)) = 3.7\) Hz). For structurally related compounds, this was rationalized by the

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Scheme 1 Preparation of compounds 6 and 7; (a) +SiCl\(_4\), –Me\(_3\)SiCl, neat, 80 °C, 3 d.
close proximity of the CH3-groups to the lone pair of electrons on the adjacent P atom. 20 Due to the same reason, two relatively large $J_{(PH)}$ coupling constants (3.4 and 3.7 Hz) were observed for the isomer of 9 in which the SiCl3-group points towards the face of the four-membered ring (9'). 19 The chloro-substituted Si atom in 9 appears as doublet resonance in the typical range in the $^{29}$Si NMR spectrum ($\delta$(Si) = -27.3 ppm) 21 with a remarkably large coupling constant of $J$($\text{SiP}_9$) = 26.0 Hz. A coupling constant of similar magnitude is observed for the Me3Si-group pointing away from the four-membered ring ($\delta$(Si) = 7.8 ppm, $J$($\text{SiP}_9$) = 32.4 Hz), whereas those pointing to the faces of the [NP]2-ring exhibit rather small coupling constants ($\delta$(Si) = 4.9 and 0.2 ppm; $J$($\text{SiP}_9$) = 4.2 and 3.0 Hz). Similarly the $^{31}$P($^1$H) NMR spectrum reveals rather small coupling constants for the latter Me3Si-groups ($J$($\text{CP}$) = 8.0 and 10.5 Hz) and a large coupling constant for the Me3Si-group pointing away from the [NP]2-ring plane ($J$($\text{CP}$) = 19.8 Hz).

It is assumed, that 9 is obtained from 7 via an intermediate of type 10 which forms upon rotation 22 of the P–N bond involving the SiCl3-substituted N atom and inversion 23 of one of the P centers in 9 (Scheme 2). The arrangement of the SiCl3-group and one of the SiMe3-groups in intermediate 10 allows for Me3SiCl elimination yielding 7. Indeed, heating 9 for ten minutes to 185 °C results in conversion to 7 in 25% yield. 24

Reactivity of 7 towards GaCl3 and P4

Diphosphadiazanes and related compounds bearing chloro- and Me3Si-substituents are known to undergo a variety of distinct reactions with Lewis acids. Next to halide abstraction, 10 also elimination of Me3SiCl, 25 migration of Me3Si, 26 chloro- or methyl-substituents 27 and P–N bond cleavage reactions are reported. 28 Especially the latter reaction is of interest, since it is assumed to proceed via phosphonium ion intermediates. Thus, bicyclic compound 7 is a promising substrate for the generation of phosphonium ions and, subsequently, insertion of the latter into P–P bonds of P4.

Thus, the reaction of 7 with the Lewis acid GaCl3 was probed (Scheme 3). The addition of one equivalent of GaCl3 to a solution of 7 in C6H5F gave a reddish colored reaction mixture which was investigated by means of $^{31}$P($^1$H) NMR spectroscopy. The formation of the Lewis-acid/base adduct 11 is proposed on the basis of the observation of two broad resonances in an approximate ratio of 1 : 1 ($\delta$(P9) = 115 ppm, $\Delta$nu1/2 = 1200 Hz; $\delta$(P8) = 179.6 ppm, $\Delta$nu1/2 = 600 Hz). The coordination of GaCl3 to a P atom is very likely, since they have been identified as the most basic sites in related compounds. 29 The resonance at low field is tentatively assigned to the tri-coordinated P atom. Accordingly, the resonance at high field corresponds to the tetra-coordinated P atom and exhibits a stronger line broadening due to the coordination of GaCl3.

Interestingly, P4 does not react with 11 which indicates that the latter is not a suitable phosphonium ion source. Adding two equivalents of GaCl3 to a solution of 7 in C6H5F, however, results in the rapid consumption of in situ generated 11. This reaction yields a complex mixture of not identified products and bodes well for the generation of reactive intermediates that might be able to activate P4. Indeed, mixtures of 7, P4 and GaCl3 in 1:1:2 and 1:2:4 stoichiometries were bright red and the consumption of P4 accompanied by a color change to brown was observed. Subsequent investigation by means of $^{31}$P($^1$H) NMR spectroscopy revealed the formation of P5+$^+_2$ cage cation 12+$^+$ and bridged bis(P5+)-cage dication 13+$^{3+}$ by their characteristic A2MOX2 and A2MX2 spin systems (Scheme 4).

Scheme 3 Formation of Lewis-acid/base adduct 11 via the reaction of 7 and GaCl3; (a) +GaCl3, C6H5F, r.t., 1 h.

Scheme 4 Reaction of 7 with P4 and GaCl3 in various stoichiometries; (a) +P4, +2, GaCl3, C6H5F, r.t., 24 h; (b) +2, P4, +4, GaCl3, r.t., C6H5F, 24 h; the equation depicts the major products and is not balanced; anions of the products are not depicted.
In addition, both spectra reveal significant amounts of \( \text{P}_4 \) but neither remaining 7 nor the corresponding adduct 11 were observed which is attributed to unidentified side reactions. The products 12 and 13\(^{2+} \) are formally obtained by the insertion of phosphonium ions based on CIP[NSiMe\(_3\)]\(_2\)Si[NSiMe\(_3\)]\(_2\)PCl which features a Si-centered spiro[3.3]heptane-motif, into P-P bonds of \( \text{P}_4 \). Interestingly, both reactions yield 12\(^+ \) and 13\(^{2+} \) in comparable ratios (1:1.8 for (a) and 1:1.5 for (b), Scheme 4). This contrasts the anticipated increase of the amount of dication 13\(^{2+} \) in the presence of excess \( \text{P}_4 \) and \( \text{GaCl}_3 \). In addition, the formation of large quantities of 13\(^{2+} \) in the reaction of 1:1:2 stoichiometry indicates that the reaction rate of a \( \text{GaCl}_3 \)-induced rearrangement of 7 yielding the spiro-motif is slow compared to that of the subsequent phosphonium ion insertion.

A tentative mechanism for the formation of such a Si-centered spiro[3.3]heptane-type species from 7 is illustrated in Scheme 5. While the reaction of 7 with one equivalent \( \text{GaCl}_3 \) gives the Lewis-acid/base adduct 11 \((\text{vide supra})\), an excess of \( \text{GaCl}_3 \) is assumed to initiate a chloride abstraction from the \( \text{SiCl}_2 \)-moiety. This is facilitated by the tendency of bicyclic compounds of type 7 to form a \( \text{seco} \)-heterocube-type structure.\(^{15} \) Thus, compound 7 might be in equilibrium with the related derivative 7\(^{1} \). Compound 7\(^{1} \) features a hypervalent penta-coordinated Si-moieties which might favor the sequestering of a chloride anion. Thus, it is assumed that the reaction with \( \text{GaCl}_3 \) proceeds via chloride abstraction and formation of the cationic \( \text{seco} \)-heterocube 14\(^+ \) featuring a tetra-coordinated N atom. The next two steps constitute P-N bond cleavage and formation reactions yielding intermediates 15\(^+ \) and 16\(^+ \) via formal retention of the \( \text{seco} \)-heterocube-type structure. Similar P-N bond ruptures were reported as decomposition pathways of diamino-\( \text{cyclo} \)-diphosphadiazanes.\(^{28} \) Intermediate 16\(^+ \) features a diphosphadiazane [NP\(_3\)]\(_2\)-ring which is assumed to react via a \( \text{cyclo} \)-reversion reaction to intermediate 17\(^+ \). Cation 17\(^+ \) features an aminooiminophospho moiety similar to 5 which is tethered to a four-membered SiN\(_4\)-ring. Intramolecular nucleophilic attack of the imino-N atom on the chloro-substituted Si atom initiates a \( \text{GaCl}_3 \)-mediated transfer of a chloride anion from the Si atom to a di-coordinated P atom to give formally the phosphonium ion 18\(^+ \). Cation 18\(^+ \) features the Si-centered spiro[3.3]heptane-motif and, thus, is assumed to be accountable for the formation of cages cations 12\(^+ \) and 13\(^{2+} \) via insertion into a P-P bond of \( \text{P}_4 \), chloride abstraction by \( \text{GaCl}_3 \) and subsequent insertion into a P-P bond of a second \( \text{P}_4 \) tetrahedron.

Attempts to isolate a gallate salt of 12\(^+ \) from both reaction mixtures were unsuccessful, possibly due to the fluxional coordination behavior of the \( \text{GaCl}_3 \)-molecule to the \( \text{PCL} \)-func tion. However, slow diffusion of \( n \)-hexane into the reaction mixture of 1:1:2 stoichiometry yielded compound 19\([\text{GaCl}_4]\) in low yields (10%, Scheme 6). The \( ^{31} \text{P} \{^1 \text{H}\} \) NMR spectrum of 19\([\text{GaCl}_4]\) dissolved in \( \text{CD}_2\text{Cl}_2 \) shows an ABMX\(_2\)Y spin system which is in accordance with the \( C_2 \) symmetry of the molecule (Fig. 3). The mirror plane is defined by the tetra-coordinated P atom and the two adjacent P atoms. The P–Cl unit is included in the plane and exhibits a spatial proximity to one of the two bridge-head P atoms. The chemical shifts and coupling constants involving the \( \text{P}_5 \)-cage motif are similar to those observed for the cage cation 3.\(^{10a} \) The chloro-substituted P atom in 19 exhibits a singlet resonance (\( \delta(\text{P}_5) = 166.8 \) ppm) in the typical range of silyl-substituted diamino-chlorophospho sphanes.\(^{13,10} \) A \( J(\text{PP}) \) coupling between this P atom and the tetra-coordinated P atom of the \( \text{P}_5 \)-cage is not resolved. The \( ^1 \text{H} \) NMR spectrum of 19 reveals three singlet resonances assigned to the chemically different \( \text{Me}_3\text{Si} \)-groups which integrate in a 2:1:1 ratio. The high-field resonance (\( \delta(\text{H}) = 0.31 \) ppm) exhibits the highest intensity and is assigned to the two \( \text{Me}_3\text{Si} \)-groups bonded to the four-membered ring which incorporates the P–Cl moiety. The chemical shift is comparable to related four-membered ring compounds (6: \( \delta(\text{H}) = 0.18 \) ppm,\(^{11} \) 7: \( \delta(\text{H}) = 0.21 \) ppm). Both resonances assigned to the \( \text{Me}_3\text{Si} \)-groups bonded to the N atoms adjacent to the

![Scheme 5](image1)

Scheme 5  Suggested \( \text{GaCl}_3 \)-induced rearrangement mechanism of 7 to phosphonium ion 18\(^+ \) featuring a Si-centered spiro[3.3]heptane-type motif; \( R \) denotes \( \text{Me}_3\text{Si} \)-substituents; for reasons of simplification the reactions of intermediates or products possessing a di-coordinated P atom with \( \text{P}_4 \) as well as retransfer of a chloride ion to a di-coordinated P atom are not considered.

![Scheme 6](image2)

Scheme 6  Reaction of 19\([\text{GaCl}_4]\) with \( \text{GaCl}_3 \); (a) +\( \text{GaCl}_3 \), \( \text{CD}_2\text{Cl}_2 \), r.t., 30 min.
The molecular structure of 19⁺ is depicted in Fig. 4 and the P–P bond lengths and angles in the P₃⁺ moiety are comparable to those of 3⁺.¹⁰ The four-membered rings are almost planar (largest deviation from the planes N1: 0.026 Å and N3: 0.022 Å) and exhibit a perpendicular arrangement (angle between both planes: 89.79°). Due to the steric limitations of the four-membered heterocycles the spiro-Si atom exhibits a distorted tetrahedral arrangement with two rather small (N1–Si3–N2: 85.4(1), N3–Si3–N4: 87.7(1)°) and two widened (N1–Si3–N3: 122.9(1), N2–Si3–N4: 118.8(1)°) N–Si–N angles. Alternating bond lengths are observed within the two four-membered rings. The P–N bonds involving the tetra-coordinated P atom are shorter (N2–P1: 1.656(3) Å, N1–P1: 1.661(3) Å) than those involving the tri-coordinated P atom (N3–P6: 1.716(3) Å, N4–P6: 1.711(3) Å) and both magnitudes of bond lengths are also observed in the related cages 3⁺ and 2⁺. The Si–N bonds in the [SiNP₂]ring fused to the P₃⁺-cage (N1–Si3: 1.755(3) Å, N2–Si3: 1.751(3) Å) are of similar lengths as observed for 3⁺. In contrast, the Si–N bonds in the second [SiNP₂]-ring are shorter (N3–Si3: 1.711(3) Å, N4–Si3: 1.704(3) Å).

The addition of GaCl₃ to a solution of 19[GaCl₄] in CD₂Cl₂ yields the previously mentioned Lewis-acid base adduct 12⁺ (Scheme 6). The A₂M₂X₂ spin system observed in the ³¹P(¹H) NMR spectrum of 12⁺ suggests a time averaged Cᵥ-symmetry of the molecule in solution which can be explained by a fluxional behavior of the coordinated GaCl₃ molecule (Fig. 5). The A₂M₂X₂ part of the A₂M₂X₂ spin system corresponds to the P₃⁺-cage moiety and reveals comparable chemical shifts and coupling constants as observed for 3⁺. The resonance corresponding to the O part of the spin system is very broad (δ(P₃) =

144 ppm, Δν/ν = ∼1200 Hz) which is caused by the fluxional behavior of the coordinated GaCl₃ molecule and its quadrupole moment.

Dication 13⁺ was isolated as a [Ga₃Cl₇]⁺ salt from the reaction of 7, P₂ and GaCl₃ in a 1:2:4 stoichiometry (Scheme 4) by the addition of n-hexane. This gave a brown oil which was isolated by decanting the supernatant and upon addition of small amounts of 1,2-C₆H₄F₂ yielded a suspension containing a yellow microcrystalline material of 13[Ga₃Cl₇]. This compound was isolated by filtration in low yields (20%) in an approximate purity of 75%. Further purification by recrystallization from CH₂Cl₂/n-hexane leads to significantly decreased yields (7% yield in >90% purity). The ³¹P(¹H) NMR spectrum of 13[Ga₃Cl₇] dissolved in CD₂Cl₂ shows an A₂M₂X₂-spin system in accordance with the Cᵥ-symmetry of the molecule.
The bicyclic P–N–Si heterocycle 7 was targeted as source for the \textit{in situ} generation of phosphonium cations for P$_4$ activation. In this context, two distinct synthetic protocols for its preparation were thoroughly investigated and gave insights into the formation of the bicycle. The reaction of with GaCl$_3$ initially yields adduct 11. This adduct is not stable and subsequently rearranges to give \textit{in situ} spirocyclic, Si-centered compound ClP(NSiMe$_3$)$_3$Si(NSiMe$_3$)$_3$PCL. The latter species gives access to polyphosphorus cage cations [ClP(NSiMe$_3$)$_3$Si(NSiMe$_3$)$_3$P]$_3$ (19$^+$) and [P$_2$(NSiMe$_3$)$_3$Si(NSiMe$_3$)$_3$P$_2$]$_2$ (13$^{2+}$) in the presence of GaCl$_3$ and P$_4$. We are continuing to investigate the Lewis-acid mediated generation of phosphonium ions for P$_4$ activation from related phosphorus–nitrogen-element bicycloses. Furthermore, studies directed towards the utilization of 12$^+$, 19$^+$ and 13$^{2+}$ as synthetic building blocks will be the target of future efforts.

**Experimental**

**General**

General information on materials and methods as well as $^{31}$P($^1$H) NMR spectra of reaction mixtures are given in the ESI.$^\dagger$

**Synthesis of Cl$_3$Si(NSiMe$_3$)$_3$(PNSiMe$_3$)$_3$(7)**

\textbf{Method A:} The literature reported synthesis of 5 was performed on a 20 mmol scale.$^{13}$ Compound 5 was removed by distillation from the reaction mixture (40 °C, 8 × 10$^{-2}$ mbar). The remaining colorless, slushy residue was dissolved in C$_6$H$_5$F (5 mL) yielding a turbid suspension. The solvent was removed \textit{in vacuo} yielding a sludgy residue which was redistilled employing a short Vigreux column (5 cm). Compound 7 was obtained as colorless oil (1.789 g, 3.51 mmol, 18%, 105 °C, 2 × 10$^{-2}$ mbar) which solidified shortly after distillation. \textbf{Method B:} 9 (305 mg, 0.50 mmol, 1.0 eq.) was heated to 185 °C for 10 min. In the course of the reaction a colorless liquid is formed accompanied by the condensation of Me$_3$SiCl on

![Fig. 6](image-url) 3$^{13}$P($^1$H) NMR spectrum of 13$^{2+}$[GaCl$_3$(CD$_2$Cl)$_2$, r.t.]; unidentified side products are marked with asterisks: A$_2$MX$_3$ spin system of 13$^{2+}$: $\delta$(P$_4$) $=-320.4$ ppm, $\delta$(P$_5$) $=32.2$ ppm, $\delta$(P$_6$) $=158.8$ ppm, $^2$J(P$_5$P$_6$) $=−142.7$ Hz, $^3$J(P$_5$P$_6$) $=−259.1$ Hz, $^4$J(P$_5$P$_6$) $=20.0$ Hz.

colder parts of the reaction vessel. After cooling to ambient
temperature the reaction mixture remains a liquid.
Isolation of 7 from this mixture proceeds as described in method A.

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\begin{array}{c}
\text{m.p.: 55.6–57.8 °C; Raman (300 mW, [cm}^{-1}]): } \nu = 2959 \\
(390), 2899 (100), 1410 (11), 690 (10), 645 (22), 613 (51), 562 \\
(4), 349 (34), 185 (30), 141 (6), 75 (10); IR (ATR, [cm}^{-1}]): } \nu = \\
2956 (w), 1408 (w), 1249 (s), 1098 (w), 973 (w), 942 (w), 883 \\
(w), 830 (vs), 776 (wv), 754 (w), 713 (w), 682 (w), 643 (w), 556 \\
(s), 450 (m); ^1H NMR (C6D6, [ppm]): } \delta = 0.21 (18H, s, H1), 0.39 \\
(18H, s, H2); ^13C{^1H} NMR (C6D6, [ppm]): } \delta = -0.08 (6C, t, C1, \\
J(CP) = 3.6 Hz), 2.7 (6C, pseudo-t, C2, J(CP) = 5.0 Hz); ^29Si \\
{^1H} NMR (C6D6, [ppm]): } \delta = -4.74 (1Si, s, Si1), 1.8 (2Si, t, Si1, \\
J(SiP) = 11.7 Hz), 7.7 (2Si, pseudo-t, Si2, J(SiP) = 11.8 Hz); ^15N \\
NMR (C6D6, [ppm]): } \delta = -397 (t, N1, J(NP) = 55 Hz), -374 (d, \\
N2, J(NP) = 75 Hz); ^31P{^1H} NMR (C6D6, [ppm]): } \delta = 211.8 (s); \\
elemental analysis for C12H36Cl2N4P2Si5 \\
\text{N} 11.0; found: C 28.5, H 7.3, N 10.6;
\end{array}
\]

**Synthesis of (SiMe3)2(N(PNSiMe3)2(N(SiMe3))(SiCl3) (9)**

Compound 8 (1.114 g, 2.00 mmol, 1.0 eq.) was suspended in
SiCl4 (6.796 g, 40.0 mmol, 40.0 eq.) and stirred for 12 h at
ambient temperature. After removal of all volatiles in vacuo 9
was isolated in quantitative yields as colorless solid (1.187 g, 
1.92 mmol, 96%).

\[
\begin{array}{c}
m.p.: 180.2–182.5 °C; Raman (300 mW, [cm}^{-1}]): } \nu = 2957 \\
(37), 2906 (100), 1410 (15), 686 (13), 651 (4), 641 (64), 586 (21), 
488 (4), 436 (35), 351 (21), 206 (37), 107 (27), 78 (18); IR (ATR, 
[cm}^{-1}]): } \nu = 3139 (vw), 3047 (m), 2958 (vw), 1406 (m), 1251 \\
(s), 1060 (m), 923 (m), 834 (vs), 778 (wv), 755 (w), 712 (w), 677 \\
wv), 572 (wv), 559 (m), 506 (w), 432 (vw); ^1H NMR (C6D6, [ppm]): } \\
\delta = 0.17 (18H, s, H5), 0.27 (9H, d, H3,4 \\
J(H3,4) = 7.4 Hz), 4.5 (1Si, d, Si2,2 \\
J(SiP) = 11.8 Hz), 7.7 (2Si, pseudo-t, Si2, J(SiP) = 11.8 Hz); ^15N \\
NMR (C6D6, [ppm]): } \delta = -397 (t, N1, J(NP) = 55 Hz), -374 (d, \\
N2, J(NP) = 75 Hz); ^31P{^1H} NMR (C6D6, [ppm]): } \delta = 211.8 (s); 
\end{array}
\]

**Reaction of 7, P4 and GaCl3 in 1 : 1 : 2 and 1 : 2 : 4 stoichiometries**

1 : 1 : 2: Compound 7 (256 mg, 0.50 mmol, 1.0 eq.) was added to a suspension of P4 (62 mg, 0.50 mmol, 1.0 eq.) in C6H5F 
(5 mL). A solution of GaCl3 (176 mg, 1.00 mmol, 2.0 eq.) in C6H5F (2 mL) was added dropwise to the suspension giving a 
red colored reaction mixture which was stirred for 12 h at ambient temperature. In the course of the reaction the color of the reaction mixture changed to yellow and the dissolving of P4 was observed. The reaction mixture was investigated by means of ^31P{^1H} NMR spectroscopy (see ESI†). 1 : 2 : 4: Compound 7 (256 mg, 0.50 mmol, 1.0 eq.) was added to a suspension of P4 (124 mg, 1.00 mmol, 2.0 eq.) in C6H5F (5 mL). A solution of GaCl3 (352 mg, 2.00 mmol, 4 eq.) in C6H5F (4 mL) 
was added dropwise to the suspension giving a red colored reaction mixture which was stirred for 12 h at ambient temperature. In the course of the reaction the color of the reaction mixture changed to brown and the dissolving of P4 was observed. The reaction mixture was investigated by means of ^31P{^1H} NMR spectroscopy (see ESI†). n-Hexane (2 mL) was added leading to the formation of a brown oil. The supernatant was removed, diluted with C6H5F (6 mL) and layered 
with n-hexane (3 mL) at −35 °C. Small amounts of crystalline material of 19[GaCl4] (41 mg, 10%), suitable for X-ray single 
crystal structure determination, were obtained within a few 
days. The remaining oil was washed with n-hexane (3 × 3 mL) 
transforming it into a brown sludge. All volatiles were removed 
in vacuo and the sludge was suspended in 1,2-C6H4F2 (2 mL) 
leading to the formation of a yellow, microcrystalline solid. 
The supernatant was removed and the yellow powder was 
was washed with 1,2-C6H4F2/3-hexane (1 : 1 mixture, 2 × 2 mL). The obtained yellow powder consisting of 13[Ga2Cl7]2 was in an 
approximate purity of 75% (determined by ^31P{^1H} NMR spectroscopy, 20% yield, 145 mg) was isolated by filtration and 
dried in vacuo. Recrystallization from a CH2Cl2 solution by 
slow diffusion of n-hexane yielded crystalline material of 19 
[Ga2Cl7]2 (purity > 90%) which was suitable for single crystal 
structure determination. Isolation was conducted via filtration 
and removal of all volatiles in vacuo (7% yield, 55 mg). Single 
crystals of 13[Ga2Cl7]2/[GaCl4] were obtained by layering the 
diluted supernatant of the reaction mixture with n-hexane at 
−35 °C.

\[
\begin{array}{c}
m.p.: 115.0–116.9 °C; Raman (300 mW, [cm}^{-1}]): } \nu = 2961 \\
(37), 2998 (100), 1412 (24), 636 (37), 552 (63), 442 (22), 398 \\
(24), 376 (14), 344 (43), 152 (44), 121 (13); IR (ATR, [cm}^{-1}]): 
\end{array}
\]
1H NMR (CD2Cl2, [ppm]): δ = 0.37 (18H, s, H2), 0.75 (18H, s, H1); 31P{1H} NMR (CD2Cl2, [ppm]): ABM0X3 spin system: δ(P) = −318.3, δ(PM) = 30.4, δ(PX) = 155.5, δ(PA) = 166.8, 1J(PMX) = −189.8 Hz, 1J(PAPX) = −143.4 Hz, 1J(PAPM) = −147.7 Hz, 2J(PAPX) = −245.1 Hz, 2J(PAPM) = 18.5 Hz, 3J(PMX) = 18.8 Hz, 3J(PAX) = 19.0 Hz. Compound 12[GaCl4] was independently synthesized by addition of GaCl3 (18 mg, 0.10 mmol, 1.0 eq.) to a solution of 19[GaCl4] (64 mg, 0.10 mmol, 1.0 eq.) in CD2Cl2 (1 mL). The obtained colourless solution was stirred for 30 min at ambient temperature and subsequently investigated by 1H and 31P{1H} NMR spectroscopy.

m.p.: 164.5–167.5 °C (decomposition); Raman (250 mW, cm−1): ν = 2962 (10), 2898 (17), 1095 (10), 633 (13), 549 (100), 441 (11), 397 (17), 384 (10), 354 (10), 138 (81) The Raman measurement was hampered by strong fluorescence effects; IR (ATR, cm−1): ν = 2956 (ww), 2898 (vw), 1409 (w), 1257 (s), 994 (vs), 899 (m), 814 (vs), 759 (vw), 729 (w), 692 (w), 637 (w), 544 (w), 490 (w), 441 (vw), 409 (w); 1H NMR (CD3COCD3, [ppm]): δ = 0.72 (36H, s, CH3), 13C{1H} NMR (CD3COCD3, [ppm]): δ = 2.7 (12C, s, CH3); 29Si{1H} NMR (CD3COCD3, [ppm]): δ = 13.7 (s, Si(CH3)3), the Si atom of the SiN4-moiety was not detected; 15N NMR (CD3COCD3, [ppm]): δ = 115 (s); 31P{1H} NMR (CD3COCD3, [ppm]): A3MX2 spin system: δ(P) = −320.4, δ(PM) = 32.2, δ(PX) = 158.8, 1J(PPX) = −142.7 Hz, 1J(PXM) = −259.1 Hz, 2J(PMX) = 20.0 Hz; elemental analysis for C12H36GaCl5P6N4Si5: calcld: C 17.1, H 4.4, N 5.5; found: C 17.8, H 4.2, N 5.5.

Acknowledgements

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Notes and references

3 P-rich cations Rn+ (n < m) were also prepared from P1-sources, however in most cases the reaction outcome is unpredictable, see: (a) M. Donath, E. Conrad, P. Jerabek, G. Frenking, R. Fröhlich, N. Burford and J. J. Weigand, Angew. Chem., Int. Ed., 2012, 51, 2964; (b) K.-O. Feldmann and J. J. Weigand, Angew. Chem., Int. Ed., 2012, 51, 7545; (c) M. Donath, M. Bodenhausen and J. J. Weigand, Chem. – Eur. J., 2014, 20, 17306.
Next to main species 7, also minor amounts of compounds 8, 9 and 9’ were observed in the $^1$H and $^{31}$P($^1$H) NMR spectra of the residue described in ref. 14, see ESI† for more information.


22 This rotation is not observed at ambient temperature due to the high barrier of rotation reported for exocyclic P-N bonds in amino-substituted diphosphadiazines (e.g. 8: $\Delta G > 27$ kcal mol$^{-1}$, ref. 17).


24 Next to 7 (25%), compounds 5 (33%) and 6 (42%) are main products of this reaction. It is assumed, that 5 and Me$_2$SiN═PO(SiCl$_3$(SiMe$_3$) form upon cyclo-reversion of 9. Compound Me$_5$SiCl yielding four-membered heterocycle 6.


