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Formation of the spirocyclic, Si-centered cage
cations $[\text{ClP}(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}_5]^+$ and
 $[\text{P}_5(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}_5]^{2+}$

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On account of our interest in P_4 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 GaCl_3 and P_4 . A GaCl_3 -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 P_4 tetrahedra yields polyphosphorus cages $[\text{ClP}(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}_5]^+$ (**19**⁺) and $[\text{P}_5(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}_5]^{2+}$ (**13**²⁺).

Introduction

White phosphorus (P_4) is an archetypal building block for the syntheses of polyphosphorus cations featuring a high P to substituent ratio.¹ In contrast to highly substituted cations R_nP_m ($n > m$), which are obtained *via* synthetic methods based on *catena* or *cyclic* polyphosphanes,² the targeted preparation of P-rich cations R_nP_m ($n < m$) is achieved by taking advantage of the tetrahedral P_4 framework.^{1,3} In a seminal paper, Krossing *et al.* reported that dicoordinated phosphonium ions, like other predominantly electrophilic ambiphiles,⁴ are able to insert into a P–P bond of the P_4 tetrahedron.⁵ This was exploited for the preparation of a series of P_5X_2^+ -cages ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).^{5,6} We expanded this methodology and prepared a series of symmetrically and unsymmetrically-substituted R_2P_5^+ - and RP_5Cl^+ -cations ($\text{R} = \text{aryl}, \text{alkyl}, \text{R}_2\text{N}$).⁷ The additional stability added by organo-substituents allowed for the stepwise insertion of up to three $[\text{Ph}_2\text{P}]^+$ phosphonium ions into P–P bonds of one P_4 molecule yielding mono- to tri-cationic $[\text{Ph}_2\text{P}_5]^+$, $[\text{Ph}_4\text{P}_6]^{2+}$ - and $[\text{Ph}_6\text{P}_7]^{3+}$ -cages.⁸ A complementary study exploited 1,3-dichloro-*cyclo*-1,3-diphosphadiazane $\text{ClP}(\text{NDipp})_2\text{P}(\text{Cl})$ ($\text{Dipp} = 2,6\text{-diisopropylphenyl}$), as a twofold phosphonium ion source for the stepwise activation of two P_4 tetrahedra which yielded the mono- and dicationic species $[\text{ClP}(\text{NDipp})_2\text{P}_5]^+$ (**1**⁺) and $[\text{P}_5(\text{NDipp})_2\text{P}_5]^{2+}$ (**2**²⁺, Fig. 1).⁹ The related P_5^+ -species **3** $[\text{GaCl}_4]$ was obtained by the reaction of P_4 with the four-membered heterocycle $\text{Cl}_2\text{Si}(\text{NSiMe}_3)_2\text{P}(\text{Cl})$ and

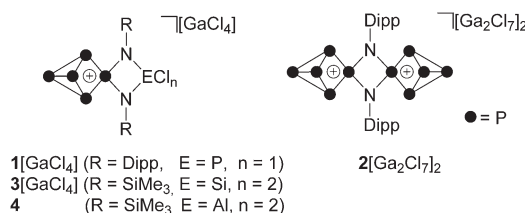


Fig. 1 P_5^+ -cages **1**⁺, **2**²⁺, **3**⁺ and **4** featuring a fused four-membered heterocycle.

GaCl_3 while the isolobale Al-species **4** is the result of the reaction of phosphonium zwitterion $\text{Cl}_2\text{Al}(\text{NSiMe}_3)_2\text{P}$ with P_4 .¹⁰

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 P_n -species (*e.g.* a P_5^+ -cage cation yields a P_2^- - and cationic P_3^+ -species).¹¹ 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 P_4 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 P_4 activation, we investigated the reactivity of bicyclic phosphorus–nitrogen–silicon heterocycle **7** with GaCl_3 and P_4 . A GaCl_3 -induced rearrangement reaction was observed which formally gives access to the spirocyclic, Si-centered compound $\text{ClP}(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}(\text{Cl})$. Chloride abstraction by GaCl_3 and insertion of the respective phosphonium ion in P–P bonds of one or two P_4 molecules yields the Si-centered polyphosphorus cages $[\text{ClP}(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}_5]^+$ (**19**⁺) and $[\text{P}_5(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}_5]^{2+}$ (**13**²⁺).

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† Electronic supplementary information (ESI) available: Crystallographic data,
³¹P NMR spectra of reaction mixtures and general experimental information.
CCDC 1060461–1060464. For ESI and crystallographic data in CIF or other elec-
tronic format see DOI: 10.1039/c5dt01512j

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 ions¹² that can insert into a P–P bond of P_4^{10a} 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).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).¹⁴ The $^{31}P\{^1H\}$ NMR spectrum of 7 dissolved in C_6D_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.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_2SiCl_2 -moiety in 7 is rare¹⁶ and contrasts other known diamido-cyclodiphosphazane compounds coordinating main group fragments.¹⁵ Compounds of type $(PNR)_2NR_2EX_n$ typically exhibit C_s -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.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_3Si -groups in the 1H NMR spectrum ($\delta(H) = 0.21$ and 0.40 ppm) confirm the C_{2v} -symmetry. The $^{13}C\{^1H\}$ NMR spectrum shows a triplet resonance which is assigned to the carbon atoms of the Me_3Si -groups attached to the $[PN]_2$ -ring ($\delta(C) = -0.1$ ppm, $^3J(CP) = 3.6$ Hz). A *pseudo*-triplet is observed for the Me_3Si -groups adjacent to the N_2SiCl_2 -moiety ($\delta(C) = 2.3$ ppm, $|^3J(CP) + ^5J(CP)| = 5.0$ Hz) and is a result of an $AA'X_3X'_3$ spin system ($A = ^{31}P$,

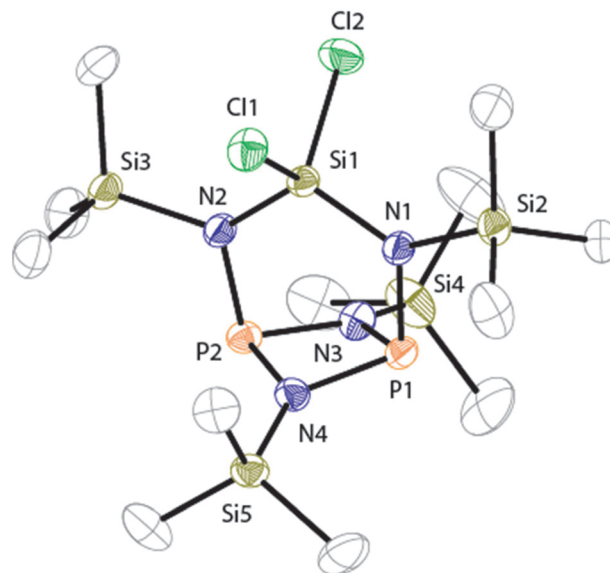
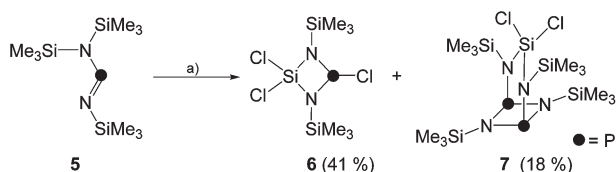


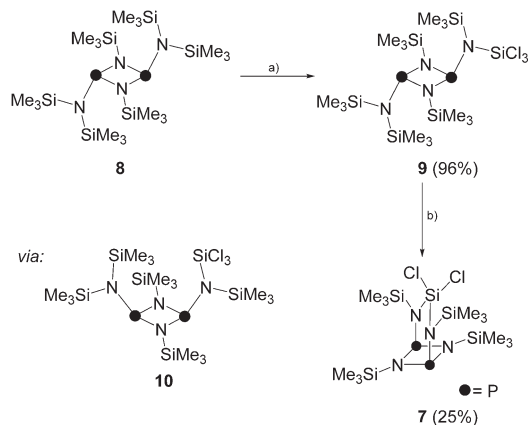
Fig. 2 Molecular structure of 7 (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected bond lengths [Å] and angles [°]: N1–P1 1.734(1), N3–P1 1.721(1), N4–P1 1.719(4), N2–P2 1.738(1), N3–P2 1.724(1), N4–P2 1.720(1), P1...P2 2.5235(6), N1–Si1 1.708(1), N1–Si2 1.773(1), N2–Si1 1.710(1), N2–Si3 1.774(1), N3–Si4 1.728(1), N4–Si5 1.740(1), Si1–Cl2 2.0554(6), Si2–Cl1 2.5235(6); P1–N4–P2 94.39(6), P1–N3–P2 94.19(7), N3–P1–N4 84.06(7), N3–P2–N4 83.96(7), N1–P1–N3 100.48(6), N1–P1–N4 102.10(6), N2–P2–N3 100.29(7), N2–P2–N4 101.91(6), N1–P1...P2 95.84(4), N2–P2...P1 95.58(4), Si1–N1–P1 117.14(7), Si1–N2–P2 117.18(8), N1–Si1–N2 114.19(6), Cl1–Si1–Cl2 104.35(2).

$X = ^{13}C$) with a comparatively large $^2J(P_AP_A)$ coupling constant.¹⁷ The same arguments account for the *pseudo*-triplet resonance in the $^{29}Si\{^1H\}$ NMR spectrum of 7 ($\delta(Si) = 7.7$ ppm) which is assigned to the Me_3Si -groups adjacent to the N_2SiCl_2 -moiety ($|^2J(SiP) + ^4J(SiP)| = 12.5$ Hz). The triplet resonance corresponding to the Me_3Si -groups attached to the $[PN]_2$ -ring ($\delta(Si) = 1.8$ ppm, $^3J(SiP) = 11.7$ Hz) and the resonance of the $SiCl_2$ moiety ($\delta(Si) = -47.4$ ppm) are observed in the expected regions.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.¹⁷ The solvent free reaction of 8 with an excess of $SiCl_4$ gave selectively and quantitatively compound 9 *via* Me_3SiCl elimination (Scheme 2).¹⁹ Compound 9 is the *trans*-conformer of an unsymmetrically-substituted diphosphadiazane derivative and, thus, shows an AX spin system in its $^{31}P\{^1H\}$ NMR spectrum ($\delta(P_A) = 219.5$ ppm, $\delta(P_X) = 232.3$ ppm, $^2J(P_AP_X) = 12.0$ Hz). The 1H 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 $^4J(HP)$ coupling constant ($\delta(H) = 0.27$ ppm, $^4J(P_AH) = 3.7$ Hz). For structurally related compounds, this was rationalized by the



Scheme 1 Preparation of compounds 6 and 7; (a) $+SiCl_4$, $-Me_3SiCl$, neat, 80 °C, 3 d.



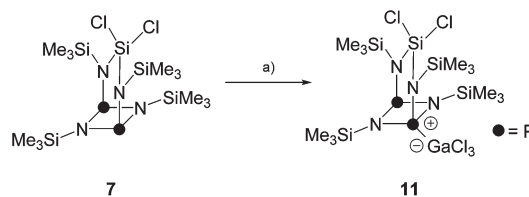
Scheme 2 Synthesis of **9** via reaction of **8** and SiCl_4 : (a) $+\text{SiCl}_4$, $-\text{Me}_3\text{SiCl}$, rt, 12 h, 96%; and subsequent transformation to **7**; (b) neat, 185°C , 10 min, 25%.

close proximity of the CH_3 -groups to the lone pair of electrons on the adjacent P atom.²⁰ Due to the same reason, two relatively large $^4J(\text{PH})$ coupling constants (3.4 and 3.7 Hz) were observed for the isomer of **9** in which the SiCl_3 -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 ($\delta(\text{Si}) = -27.3$ ppm)²¹ with a remarkably large coupling constant of $^2J(\text{SiP}_\text{x}) = 26.0$ Hz. A coupling constant of similar magnitude is observed for the Me_3Si -group pointing away from the four-membered ring ($\delta(\text{Si}) = 7.8$ ppm, $^2J(\text{SiP}_\text{A}) = 32.4$ Hz), whereas those pointing to the faces of the $[\text{NP}]_2$ -ring exhibit rather small coupling constants ($\delta(\text{Si}) = 4.9$ and 0.2 ppm; $^2J(\text{SiP}) = 4.2$ and 3.0 Hz). Similarly the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum reveals rather small coupling constants for the latter Me_3Si -groups ($^3J(\text{CP}) = 8.0$ and 10.5 Hz) and a large coupling constant for the Me_3Si -group pointing away from the $[\text{NP}]_2$ -ring plane ($^3J(\text{CP}_\text{A}) = 19.8$ Hz).

It is assumed, that **7** is obtained from **9** via an intermediate of type **10** which forms upon rotation²² of the P–N bond involving the SiCl_3 -substituted N atom and inversion²³ of one of the P centers in **9** (Scheme 2). The arrangement of the SiCl_3 -group and one of the SiMe_3 -groups in intermediate **10** allows for Me_3SiCl 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 GaCl_3 and P_4

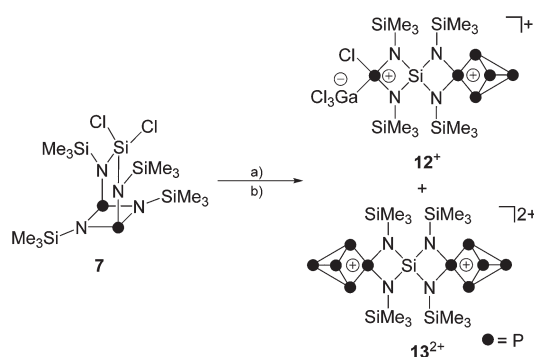
Diphosphadiazanes and related compounds bearing chloro- and Me_3Si -substituents are known to undergo a variety of distinct reactions with Lewis acids. Next to halide abstraction,¹⁰ also elimination of Me_3SiCl ,²⁵ migration of Me_3Si -,²⁶ chloro- or methyl-substituents²⁷ and P–N bond cleavage reactions 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 P_4 .



Scheme 3 Formation of Lewis-acid/base adduct **11** via the reaction of **7** and GaCl_3 ; (a) $+\text{GaCl}_3$, $\text{C}_6\text{H}_5\text{F}$, r.t., 1 h.

Thus, the reaction of **7** with the Lewis acid GaCl_3 was probed (Scheme 3). The addition of one equivalent of GaCl_3 to a solution of **7** in $\text{C}_6\text{H}_5\text{F}$ gave a reddish colored reaction mixture which was investigated by means of $^{31}\text{P}\{^1\text{H}\}$ 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 ($\delta(\text{P}_\text{A}) = 115$ ppm, $\Delta\nu_{1/2} = 1200$ Hz; $\delta(\text{P}_\text{x}) = 179.6$ ppm, $\Delta\nu_{1/2} = 600$ Hz). The coordination of GaCl_3 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 GaCl_3 .

Interestingly, P_4 does not react with **11** which indicates that the latter is not a suitable phosphonium ion source. Adding two equivalents of GaCl_3 to a solution of **7** in $\text{C}_6\text{H}_5\text{F}$, 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 P_4 . Indeed, mixtures of **7**, P_4 and GaCl_3 in 1 : 1 : 2 and 1 : 2 : 4 stoichiometries were bright red and the consumption of P_4 accompanied by a color change to brown was observed. Subsequent investigation by means of $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed the formation of P_5^+ cage cation **12**⁺ and bridged *bis*(P_5^+)-cage dication **13**²⁺ by their characteristic A_2MOX_2 and A_2MX_2 spin systems (Scheme 4).



Scheme 4 Reaction of **7** with P_4 and GaCl_3 in various stoichiometries; (a) $+\text{P}_4$, $+2$, GaCl_3 , $\text{C}_6\text{H}_5\text{F}$, r.t., 24 h; (b) $+2$, P_4 , $+4$, GaCl_3 , r.t., $\text{C}_6\text{H}_5\text{F}$, 24 h; the equation depicts the major products and is not balanced; anions of the products are not depicted.

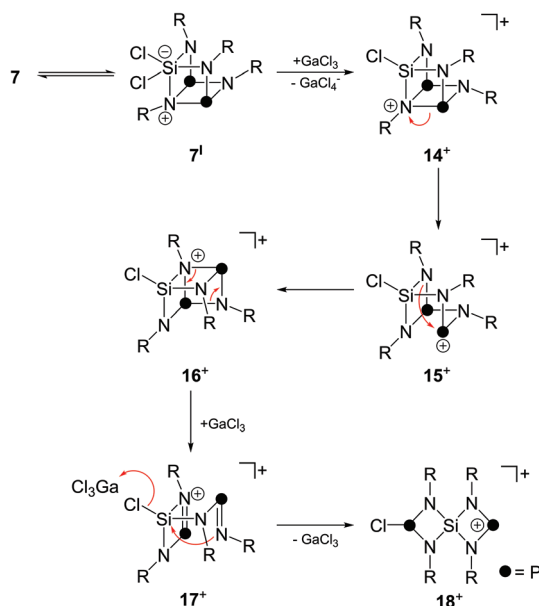


In addition, both spectra reveal significant amounts of P_4 but neither remaining **7** nor the corresponding adduct **11** were observed which is attributed to unidentified side reactions. The products 12^+ and 13^{2+} are formally obtained by the insertion of phosphonium ions based on $ClP(NSiMe_3)_2Si(NSiMe_3)_2PCl$ which features a Si-centered spiro[3.3]heptane-motif, into P–P bonds of 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 P_4 and $GaCl_3$. 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 $GaCl_3$ -induced rearrangement of **7** yielding the spiro-motif is slow compared to that of the subsequent phosphonium ion insertion.

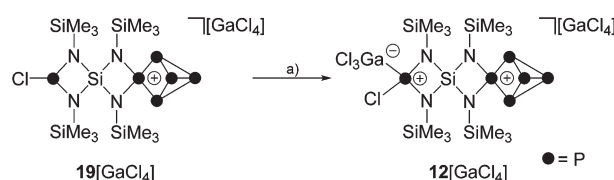
A tentative mechanism for the formation of such a Si-centered spiro[3.3]heptane-type species from **7** is illustrated in Scheme 5. While the reaction of **7** with one equivalent $GaCl_3$ gives the Lewis-acid/base adduct **11** (*vide supra*), an excess of $GaCl_3$ is assumed to initiate a chloride abstraction from the $SiCl_2$ -moiety. This is facilitated by the tendency of bicyclic compounds of type **7** to form a *seco*-heterocube-type structure.¹⁵ Thus, compound **7** might be in equilibrium with the related derivative **7¹**. Compound **7¹** features a hypervalent penta-coordinated Si-moiety which might favor the sequestering of a chloride anion. Thus, it is assumed that the reaction with $GaCl_3$ proceeds *via* chloride abstraction and formation of the cationic *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 *seco*-heterocube-type structure. Similar P–N bond ruptures were reported as decomposition pathways of diamino-*cyclo*-diphosphadiazanes.²⁶ Intermediate 16^+ features a diphosphadiazane $[NP]_2$ -ring which is assumed to react *via* a *cyclo*-reversion reaction to intermediate 17^+ . Cation 17^+ features an aminoiminophosphane moiety similar to **5** which is tethered to a four-membered SiN_2P -ring. Intramolecular nucleophilic attack of the imino-N atom on the chloro-substituted Si atom initiates a $GaCl_3$ -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 P_4 , chloride abstraction by $GaCl_3$ and subsequent insertion into a P–P bond of a second 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 $GaCl_3$ -molecule to the PCl-function. However, slow diffusion of *n*-hexane into the reaction mixture of 1 : 1 : 2 stoichiometry yielded compound **19** $[GaCl_4]$ in low yields (10%, Scheme 6). The $^{31}P\{^1H\}$ NMR spectrum of **19** $[GaCl_4]$ dissolved in CD_2Cl_2 shows an ABMX₂Y spin system which is in accordance with the C_s 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 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 ($\delta(P_Y) = 166.8$ ppm) in the typical range of silyl-substituted diamino-chlorophosphanes.^{13,30} A $^4J(PP)$ coupling between this P atom and the tetra-coordinated P atom of the P_5^+ -cage is not resolved. The 1H NMR spectrum of **19⁺** reveals three singlet resonances assigned to the chemically different Me_3Si -groups which integrate in a 2 : 1 : 1 ratio. The high-field resonance ($\delta(H) = 0.31$ ppm) exhibits the highest intensity and is assigned to the two Me_3Si -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**: $\delta(H) = 0.18$ ppm,¹³ **7**: $\delta(H) = 0.21$ ppm). Both resonances assigned to the Me_3Si -groups bonded to the N atoms adjacent to the



Scheme 5 Suggested $GaCl_3$ -induced rearrangement mechanism of **7** to phosphonium ion 18^+ featuring a Si-centered spiro[3.3]heptane-type motif; R denotes Me_3Si -substituents; for reasons of simplification the reactions of intermediates or products possessing a di-coordinated P atom with P_4 as well as retransfer of a chloride ion to a di-coordinated P atom are not considered.



Scheme 6 Reaction of **19** $[GaCl_4]$ with $GaCl_3$; (a) $+GaCl_3$, CD_2Cl_2 , r.t., 30 min.



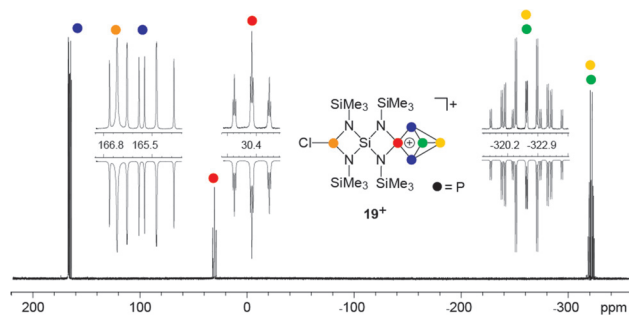


Fig. 3 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $19[\text{GaCl}_4]$ (CD_2Cl_2 , r.t.); insets show experimental (upwards) and fitted spectra (downwards); A_2MOX_2 spin system of 19^+ : $\delta(\text{P}_\text{A}) = -322.9$ ppm, $\delta(\text{P}_\text{B}) = -320.2$ ppm, $\delta(\text{P}_\text{M}) = 30.4$ ppm, $\delta(\text{P}_\text{X}) = 165.5$ ppm, $\delta(\text{P}_\text{Y}) = 166.8$ ppm, $^1J(\text{P}_\text{A}\text{P}_\text{B}) = -189.8$ Hz, $^1J(\text{P}_\text{A}\text{P}_\text{X}) = -143.4$ Hz, $^1J(\text{P}_\text{B}\text{P}_\text{X}) = -147.7$ Hz, $^1J(\text{P}_\text{M}\text{P}_\text{X}) = -245.1$ Hz, $^2J(\text{P}_\text{A}\text{P}_\text{M}) = 18.8$ Hz, $^2J(\text{P}_\text{B}\text{P}_\text{M}) = 18.0$ Hz.

P_5^+ -moiety exhibit a low field shift ($\delta(\text{H}) = 0.67$ ppm and 0.76 ppm) and are comparable to the corresponding resonance of 3^+ ($\delta(\text{H}) = 0.68$ ppm).^{10a} The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum exhibits a resonance at $\delta(\text{Si}) = -58.0$ ppm which is assigned to the Si spiro-atom. This resonance reveals a doublet of doublet splitting caused by $^2J(\text{SiP})$ -couplings to the tetra-coordinated P atom ($^2J(\text{SiP}_\text{M}) = 8.5$ Hz) and the chloro-substituted P atom ($^2J(\text{SiP}_\text{Y}) = 18.5$ Hz).

The molecular structure of 19^+ is depicted in Fig. 4 and the P–P bond lengths and angles in the P_5^+ -moiety are comparable to those of 3^+ .^{10a} Both 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: $89.79(9)^\circ$). 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 : $85.4(1)^\circ$, N3-Si3-N4 : $87.7(1)^\circ$) and two widened (N1-Si3-N3 : $122.9(1)^\circ$, N2-Si3-N4 : $118.8(1)^\circ$) 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^+ .^{9,10a} The Si–N bonds in the $[\text{SiN}_2\text{P}]$ -ring fused to the P_5^+ -cage (N1-Si3 : $1.755(3)$ Å, N2-Si3 : $1.751(3)$ Å) are of similar lengths as observed for 3^+ .^{10a} In contrast, the Si–N bonds in the second $[\text{SiN}_2\text{P}]$ -ring are shorter (N3-Si3 : $1.711(3)$ Å, N4-Si3 : $1.704(3)$ Å).

The addition of GaCl_3 to a solution of $19[\text{GaCl}_4]$ in CD_2Cl_2 yields the previously mentioned Lewis-acid base adduct 12^+ (Scheme 6). The A_2MOX_2 spin system observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 12^+ suggests a time averaged C_{2v} -symmetry of the molecule in solution which can be explained by a fluxional behavior of the coordinated GaCl_3 molecule (Fig. 5). The A_2MX_2 part of the A_2MOX_2 spin system corresponds to the P_5^+ -cage moiety and reveals comparable chemical shifts and coupling constants as observed for 3^+ .^{10a} The resonance corresponding to the O part of the spin system is very broad ($\delta(\text{P}_\text{O}) =$

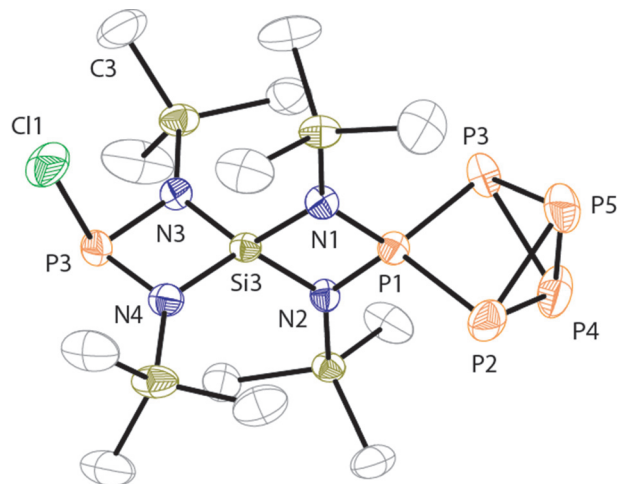


Fig. 4 Molecular structure of 19^+ in compound $19[\text{GaCl}_4]\cdot\text{C}_6\text{H}_5\text{F}$ (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected bond lengths [Å] and angles [$^\circ$]: N2-P1 $1.656(3)$, N1-P1 $1.661(3)$, N1-Si3 $1.755(3)$, N2-Si3 $1.751(3)$, N3-Si3 $1.711(3)$, N4-Si3 $1.704(3)$, N3-P6 $1.716(3)$, N4-P6 $1.711(3)$, Cl1-P6 $2.238(2)$, $\text{P1}\cdots\text{Si3}$ $2.445(1)$, $\text{P6}\cdots\text{Si3}$ $2.472(1)$, P1-P2 $2.167(1)$, P1-P3 $2.165(1)$, P2-P4 $2.249(2)$, P2-P5 $2.238(2)$, P3-P4 $2.251(2)$, P3-P5 $2.229(2)$, P4-P5 $2.169(2)$; N1-P1-N2 $91.5(1)$, P1-N1-Si3 $91.4(1)$, P1-N2-Si3 $91.7(1)$, N1-Si3-N2 $85.4(1)$, N3-Si3-N4 $87.7(1)$, N1-Si3-N3 $122.9(1)$, N2-Si3-N4 $118.8(1)$, N3-P6-N4 $87.2(1)$, N3-P6-Cl1 $102.2(1)$, N4-P6-Cl1 $101.7(1)$, P3-P1-P2 $91.15(5)$, P1-P2-P5 $83.95(5)$, P1-P2-P4 $82.53(5)$, P5-P2-P4 $57.82(5)$, P5-P4-P2 $60.83(5)$, P2-P5-P3 $87.67(5)$.

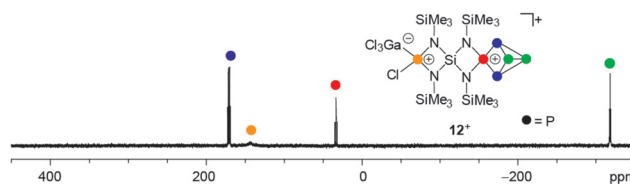
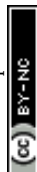


Fig. 5 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $12[\text{GaCl}_4]$ (CD_2Cl_2 , r.t.); A_2MOX_2 spin system of 12^+ : $\delta(\text{P}_\text{A}) = -318.3$ ppm, $\delta(\text{P}_\text{M}) = 33.4$ ppm, $\delta(\text{P}_\text{O}) = 144$ ppm ($\Delta\nu_{1/2} \sim 1200$ Hz), $\delta(\text{P}_\text{X}) = 170.8$ ppm, $^1J(\text{P}_\text{A}\text{P}_\text{X}) = -144.8$ Hz, $^1J(\text{P}_\text{M}\text{P}_\text{X}) = -248.6$ Hz, $^2J(\text{P}_\text{A}\text{P}_\text{M}) = 19.0$ Hz.

144 ppm, $\Delta\nu_{1/2} \sim 1200$ Hz) which is caused by the fluxional behavior of the coordinated GaCl_3 molecule and its quadrupole moment.

Dication 13^{2+} was isolated as a $[\text{Ga}_2\text{Cl}_7]^-$ salt from the reaction of **7**, **P**₄ and GaCl_3 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 $1,2\text{-C}_6\text{H}_4\text{F}_2$ yielded a suspension containing a yellow microcrystalline material of $13[\text{Ga}_2\text{Cl}_7]_2$. This compound was isolated by filtration in low yields (20%) in an approximate purity of 75%. Further purification by recrystallization from CH_2Cl_2 /*n*-hexane leads to significantly decreased yields (7% yield in >90% purity). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $13[\text{Ga}_2\text{Cl}_7]_2$ dissolved in CD_2Cl_2 shows an A_2MX_2 -spin system in accordance with the C_{2v} -symmetry of the molecule



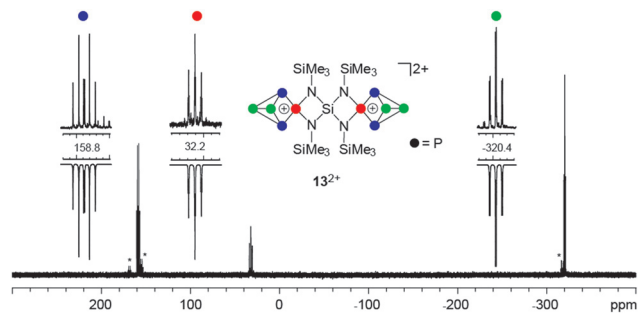


Fig. 6 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $13[\text{Ga}_2\text{Cl}_7]_2$ (CD_2Cl_2 , r.t.); unidentified side products are marked with asterisks; A_2MX_2 spin system of 13^{2+} : $\delta(\text{P}_\text{A}) = -320.4$ ppm, $\delta(\text{P}_\text{M}) = 32.2$ ppm, $\delta(\text{P}_\text{X}) = 158.8$ ppm, $^1J(\text{P}_\text{A}\text{P}_\text{X}) = -142.7$ Hz, $^1J(\text{P}_\text{M}\text{P}_\text{X}) = -259.1$ Hz, $^2J(\text{P}_\text{A}\text{P}_\text{M}) = 20.0$ Hz.

(Fig. 6). The C_2 -axis includes both tetra-coordinated P atoms and the spiro-Si atom and the mirror planes are defined by the four-membered $[\text{SiN}_2\text{P}]$ -rings. The resonances and coupling constants of 13^{2+} are similar to those observed for the related compounds 19^+ and 3^{10a} .

Single crystals of compound $13[\text{Ga}_2\text{Cl}_7]_2$ were obtained by diffusion of *n*-hexane in a CH_2Cl_2 solution of $13[\text{Ga}_2\text{Cl}_7]_2$ at -35°C . The compound crystallizes with two independent formula units in the asymmetric unit. Two of the four Ga_2Cl_7^- anions are highly disordered exhibiting unusually high thermal displacement parameters (see ESI† for details). Single crystals of $13[\text{Ga}_2\text{Cl}_7][\text{GaCl}_4]$ were obtained by layering the supernatant solution of the reaction mixture of the synthesis of $13[\text{Ga}_2\text{Cl}_7]_2$ with *n*-hexane at -35°C . The data obtained by X-ray single crystal structure determination was of higher quality and, thus, the molecular structure of $13[\text{Ga}_2\text{Cl}_7][\text{GaCl}_4]$ is discussed (Fig. 7). The P–P bond lengths and angles in the P_5^+ -moieties are comparable to those of related P_5^+ -cage compounds.^{9,10a} The P–N bonds in 13^{2+} are rather short (av. P–N: 1.666(8) Å) which is a typical feature of P–N bonds involving phosphonium moieties. The Si–N bond lengths in the four-membered rings are nearly identical (av. Si–N: 1.732(8) Å) and are between the two types of bond lengths observed for 19^+ (av. Si–N: 1.753(6) Å and Si–N: 1.7007(6) Å).

Conclusions

The bicyclic P–N–Si heterocycle **7** was targeted as source for the *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 **7** with GaCl_3 initially yields adduct **11**. This adduct is not stable and subsequently rearranges to give *in situ* spirocyclic, Si-centered compound $\text{ClP}(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}(\text{Cl})$. The latter species gives access to polyphosphorus cage cations $[\text{ClP}(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}_5]^+$ (19^+) and $[\text{P}_5(\text{NSiMe}_3)_2\text{Si}(\text{NSiMe}_3)_2\text{P}_5]^{2+}$ (13^{2+}) in the presence of GaCl_3 and P_4 . We are continuing to investigate the Lewis-acid mediated generation of phosphonium ions

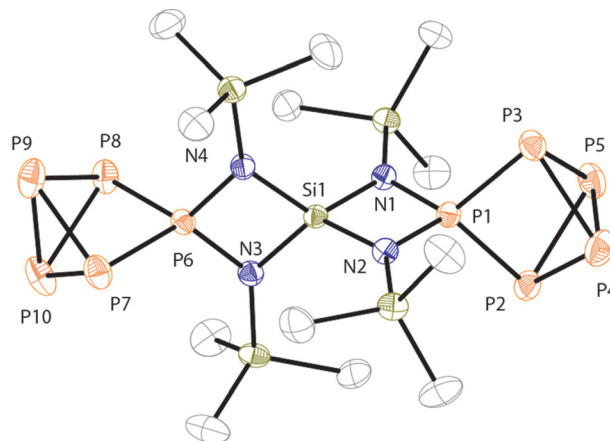


Fig. 7 Molecular structure of 13^{2+} in compound $13[\text{Ga}_2\text{Cl}_7][\text{GaCl}_4]$ (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected bond lengths [Å] and angles [$^\circ$]: N1–P1 1.667(2), N2–P1 1.671(2), N3–P6 1.663(2), N4–P6 1.665(2), Si1–N1 1.731(2), Si1–N2 1.732(2), Si1–N3 1.736(2), Si1–N4 1.728(2), P1...Si1 2.4452(8), P6...Si1 2.4277(8), P1–P2 2.1540(8), P1–P3 2.1499(8), P2–P4 2.245(1), P2–P5 2.245(1), P3–P4 2.246(1), P3–P5 2.2464(9), P4–P5 2.168(1), P6–P7 2.1511(8), P6–P8 2.1572(2), P7–P9 2.240(1), P7–P10 2.252(1), P8–P9 2.2415(9), P8–P10 2.242(1), P9–P10 2.172(1); N1–P1–N2 90.81(9), N3–P6–N4 90.99(9), N1–Si1–N2 86.73(9), N3–Si1–N4 86.49(9), P1–N1–Si1 91.26(9), P1–N2–Si1 91.12(9), P6–N3–Si1 91.14(9), P6–N4–Si1 91.34(9), P3–P1–P2 92.59(3), P1–P2–P5 81.73(3), P1–P2–P4 83.19(3), P5–P2–P4 57.69(3), P5–P4–P2 61.25(3), P2–P5–P3 87.60(3), P7–P6–P8 92.30(3), P6–P7–P10 82.39(3), P6–P7–P9 82.89(3), P10–P7–P9 57.83(3), P10–P9–P7 61.36(3), P7–P10–P8 87.48(3).

for P_4 activation from related phosphorus–nitrogen–element bicycles. 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

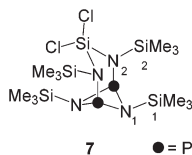
General information on materials and methods as well as $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of reaction mixtures are given in the ESI.†

Synthesis of $\text{Cl}_2\text{Si}(\text{NSiMe}_3)_2(\text{PNSiMe}_3)_2$ (**7**)

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 $\text{C}_6\text{H}_5\text{F}$ (5 mL) yielding a turbid suspension. The solvent was removed *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^{-3} mbar) which solidified shortly after distillation. **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_3SiCl on



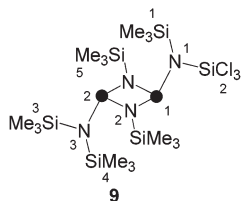
colder parts of the reaction vessel. After cooling to ambient temperature the reaction mixture remains a liquid. Isolation of **7** from this mixture proceeds as described in method A.



m.p.: 55.6–57.8 °C; **Raman** (300 mW, [cm⁻¹]): ν = 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]): ν = 2956 (w), 1408 (vw), 1249 (s), 1098 (vw), 973 (vw), 942 (w), 883 (w), 830 (vs), 776 (vw), 754 (vw), 713 (w), 682 (w), 643 (vw), 556 (s), 450 (m); **¹H NMR** (C₆D₆, [ppm]): δ = 0.21 (18H, s, H1), 0.39 (18H, s, H2); **¹³C{¹H} NMR** (C₆D₆, [ppm]): δ = -0.08 (6C, t, C1, ³*J*(CP) = 3.6 Hz), 2.7 (6C, *pseudo*-t, C2, ³*J*(CP) = 5.0 Hz); **²⁹Si{¹H} NMR** (C₆D₆, [ppm]): δ = -47.4 (1Si, s, Si3), 1.8 (2Si, t, Si1, ²*J*(SiP) = 11.7 Hz), 7.7 (2Si, *pseudo*-t, Si2, ²*J*(SiP) = 11.8 Hz); **¹⁵N NMR** (C₆D₆, [ppm]): δ = -397 (t, N1, ¹*J*(NP) = 55 Hz), -374 (d, N2, ¹*J*(NP) = 75 Hz); **³¹P{¹H} NMR** (C₆D₆, [ppm]): δ = 211.8 (s); **elemental analysis** for C₁₂H₃₆Cl₂N₄P₂Si₅: calcd: C 28.3, H 7.1, N 11.0; found: C 28.5, H 7.3, N 10.6; **MS-ESI-EM**: 473.0943 [M-Cl⁻], calcd: for C₁₂H₃₆Cl₁N₄P₂Si₅: 473.0945.

Synthesis of (SiMe₃)₂N(PNSiMe₃)₂N(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%).

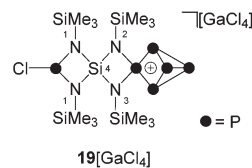


m.p.: 180.2–182.5 °C; **Raman** (300 mW, [cm⁻¹]): ν = 2957 (37), 2906 (100), 1410 (15), 686 (13), 651 (4), 641 (64), 586 (21), 488 (4), 436 (38), 351 (21), 206 (37), 107 (27), 78 (18); **IR** (ATR, [cm⁻¹]): ν = 3139 (vw), 3047 (m), 2958 (vw), 1406 (m), 1251 (s), 1060 (m), 923 (m), 834 (vs), 778 (vw), 755 (w), 712 (w), 677 (w), 572 (vw), 559 (m), 506 (w), 432 (vw); **¹H NMR** (C₆D₆, [ppm]): δ = 0.17 (18H, s, H5), 0.27 (9H, d, H3, ⁴*J*(HP) = 3.7 Hz), 0.52 (9H, s, H4), 0.64 (9H, s, H1); **¹³C{¹H} NMR** (C₆D₆, [ppm]): δ = 1.4 (6C, t, C5, ³*J*(CP) = 2.5 Hz), 4.7 (3C, d, C1, ³*J*(CP) = 10.5 Hz), 4.8 (3C, d, C3, ³*J*(CP) = 19.8 Hz), 5.0 (3C, d, C4, ³*J*(CP) = 8.0 Hz); **²⁹Si{¹H} NMR** (C₆D₆, [ppm]): δ = -27.3 (1Si, d, Si2, ²*J*(SiP) = 26.0 Hz), 0.2 (1Si, d, Si4, ²*J*(SiP) = 3.0 Hz), 1.5 (2Si, t, Si5, ²*J*(SiP) = 7.4 Hz), 4.5 (1Si, d, Si2, ²*J*(SiP) = 4.2 Hz), 7.6 (1Si, d, Si3, ²*J*(SiP) = 32.4 Hz); **¹⁵N NMR** (C₆D₆, [ppm]): δ = 67.1 (t, N2, ¹*J*(NP) = 50 Hz), 93.8 (d, N1, ¹*J*(NP_X) = 90 Hz), 113.9 (d, N3, ¹*J*(NP_A) = 90 Hz); **³¹P{¹H} NMR** (C₆D₆, [ppm]): AX spin system: δ (P_A) = 218.6 (d, P1, $\Delta\nu_{1/2}$ = 42 Hz, ²*J*(P_AP_X) = 12 Hz), δ (P_X) =

232.2 (d, P2, $\Delta\nu_{1/2}$ = 37 Hz, ²*J*(P_AP_X) = 12 Hz); **elemental analysis** for C₁₅H₄₅Cl₃N₄P₂Si₆: calcd: C 29.1, H 7.3, N 9.1; found: C 28.8, H 7.3, N 8.6.

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

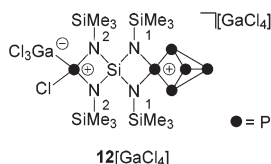
1 : 1 : 2: Compound **7** (256 mg, 0.50 mmol, 1.0 eq.) was added to a suspension of **P₄** (62 mg, 0.50 mmol, 1.0 eq.) in C₆H₅F (5 mL). A solution of GaCl₃ (176 mg, 1.00 mmol, 2.0 eq.) in C₆H₅F (2 mL) was added dropwise to the suspension giving a red colored reaction mixture which was stirred for 12 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 washed with 1,2-C₆H₄F₂/*n*-hexane (1 : 1 mixture, 2 × 2 mL). The obtained yellow powder consisting of **13**[Ga₂Cl₇]₂ 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]-[GaCl₄] were obtained by layering the diluted supernatant of the reaction mixture with *n*-hexane at -35 °C.



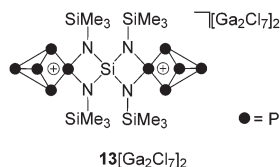
m.p.: 115.0–116.9 °C; **Raman** (300 mW, [cm⁻¹]): ν = 2961 (37), 2998 (100), 1412 (24), 636 (37), 552 (63), 442 (22), 398 (24), 376 (14), 344 (43), 152 (44), 121 (13); **IR** (ATR, [cm⁻¹]):



$\nu = 2956$ (vw), 2897 (vw), 1411 (vw), 1254 (m), 1123 (vw), 993 (s), 905 (s), 822 (vs), 756 (vw), 724 (s), 690 (w), 639 (w), 548 (vw), 509 (w), 462 (m); $^1\text{H NMR}$ (CD_2Cl_2 , [ppm]): $\delta = 0.31$ (18H, s, H1), 0.67 (9H, s, H2), 0.76 (9H, s, H3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): $\delta = 1.4$ (6C, d, C1, $^3J(\text{CP}) = 3.1$ Hz), 2.2 (3C, m, C2), 3.1 (3C, m, C3); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): $\delta = -58.0$ (dd, Si4, $^2J(\text{SiP}_Y) = 18.5$ Hz, $^2J(\text{SiP}_M) = 8.5$ Hz), 7.4 (d, Si1, $^2J(\text{SiP}) = 8.4$ Hz), 10.9 (s, Si2), 11.7 (s, Si3); ^{15}N NMR (CD_2Cl_2 , [ppm]): $\delta = 96$ (s, N1), 115 (s, N2), 125 (s(br), N3); $^{71}\text{Ga}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): $\delta = 249.6$ (s); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): ABMX₂Y spin system: $\delta(\text{P}_A) = -322.9$, $\delta(\text{P}_B) = -320.2$, $\delta(\text{P}_M) = 30.4$, $\delta(\text{P}_X) = 165.5$, $\delta(\text{P}_Y) = 166.8$, $^1J(\text{P}_A\text{P}_B) = -189.8$ Hz, $^1J(\text{P}_A\text{P}_X) = -143.4$ Hz, $^1J(\text{P}_B\text{P}_X) = -147.7$ Hz, $^1J(\text{P}_M\text{P}_X) = -245.1$ Hz, $^2J(\text{P}_A\text{P}_M) = 18.8$ Hz, $^2J(\text{P}_B\text{P}_M) = 18.0$ Hz; **elemental analysis** for $\text{C}_{12}\text{H}_{36}\text{GaCl}_5\text{P}_6\text{N}_4\text{Si}_5$: calcd: C 17.8, H 4.5, N 6.9; found: C 17.1, H 4.4, N 5.5.



$^1\text{H NMR}$ (CD_2Cl_2 , [ppm]): $\delta = 0.37$ (18H, s, H2), 0.75 (18H, s, H1); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): ABMOX₂ spin system: $\delta(\text{P}_A) = -318.3$, $\delta(\text{P}_M) = 33.4$, $\delta(\text{P}_O) = 144$ ($\Delta\nu_{1/2} = \sim 1200$ Hz), $\delta(\text{P}_X) = 170.8$, $^1J(\text{P}_A\text{P}_X) = -144.8$ Hz, $^1J(\text{P}_M\text{P}_X) = -248.6$ Hz, $^2J(\text{P}_A\text{P}_M) = 19.0$ 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 CD_2Cl_2 (1 mL). The obtained colorless solution was stirred for 30 min at ambient temperature and subsequently investigated by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.



m.p.: 164.5–167.5 °C (decomposition); **Raman** (250 mW, [cm⁻¹]): $\nu = 2962$ (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]): $\nu = 2956$ (vw), 2898 (vw), 1409 (w), 1257 (s), 994 (vs), 899 (m), 814 (vs), 759 (vw), 729 (w), 692 (vw), 637 (w), 544 (w), 490 (w), 441 (vw), 409 (w); $^1\text{H NMR}$ (CD_2Cl_2 , [ppm]): $\delta = 0.72$ (36H, s, CH₃); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): $\delta = 2.7$ (12C, s, CH₃); $^{29}\text{Si}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): $\delta = 13.7$ (s, Si(CH₃)₃), the Si atom of the SiN₄-moiety was not detected; ^{15}N NMR (CD_2Cl_2 , [ppm]): $\delta = 115$ (s); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , [ppm]): A₂MX₂ spin system: $\delta(\text{P}_A) = -320.4$, $\delta(\text{P}_M) = 32.2$, $\delta(\text{P}_X) = 158.8$, $^1J(\text{P}_A\text{P}_X) = -142.7$ Hz, $^1J(\text{P}_M\text{P}_X) = -259.1$ Hz, $^2J(\text{P}_A\text{P}_M) = 20.0$ Hz; **elemental analysis** for $\text{C}_{12}\text{H}_{36}\text{Ga}_4\text{Cl}_{14}\text{P}_{10}\text{N}_4\text{Si}_5$: calcd: C 10.8, H 2.5, N 3.8; found: C 10.9, H 2.5, N 4.0.

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Notes and references

- 1 M. H. Holthausen and J. J. Weigand, *Chem. Soc. Rev.*, 2014, **43**, 6639.
- 2 C. A. Dyker and N. Burford, *Chem. – Asian J.*, 2008, **3**, 28.
- 3 P-rich cations R_nP_m ($n < m$) were also prepared from P_1 -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. Bodensteiner and J. J. Weigand, *Chem. – Eur. J.*, 2014, **20**, 17306.
- 4 (a) Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull and C. E. Hughes, *Angew. Chem., Int. Ed.*, 2004, **43**, 3443; (b) G. Prabusankar, A. Doddi, C. Gemel, M. Winter and R. A. Fischer, *Inorg. Chem.*, 2010, **49**, 7976; (c) W. Uhl and M. Benter, *Chem. Commun.*, 1999, 771; (d) Y. Xiong, S. Yao, M. Brym and M. Driess, *Angew. Chem., Int. Ed.*, 2007, **46**, 4511; (e) S. Khan, R. Michel, S. S. Sen, H.-W. Roesky and D. Stalke, *Angew. Chem., Int. Ed.*, 2011, **50**, 11786; (f) S. Khan, R. Michel, J. M. Dieterich, R. A. Mata, H. W. Roesky, J.-P. Demers, A. Lange and D. Stalke, *J. Am. Chem. Soc.*, 2011, **133**, 17889; (g) C. D. Martin, C. M. Weinstein, C. E. Moore, A. L. Rheingold and G. Bertrand, *Chem. Commun.*, 2013, **49**, 4486; For overviews of P_4 activation by nucleophiles, electrophiles and predominantly nucleophilic ambiphiles see: (h) M. Scheer, G. Balázs and A. Seitz, *Chem. Rev.*, 2010, **110**, 4236; (i) N. A. Giffin and J. D. Masuda, *Coord. Chem. Rev.*, 2011, **255**, 1342; (j) S. Khan, S. S. Sen and H. W. Roesky, *Chem. Commun.*, 2012, **48**, 2169.
- 5 I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2001, **40**, 4406; For insertion of a related NO^+ species into a P–P bond of P_4 see: (a) T. Köchner, S. Riedel, A. J. Lehner, H. Scherer, I. Raabe, T. A. Engesser, F. W. Scholz, U. Gellrich, P. Eiden, R. A. Paz Schmidt, D. A. Plattner and I. Krossing, *Angew. Chem., Int. Ed.*, 2010, **49**, 8139; (b) T. Köchner, T. A. Engesser, H. Scherer, D. A. Plattner, A. Steffani and I. Krossing, *Angew. Chem., Int. Ed.*, 2012, **51**, 6529.
- 6 (a) M. Gonsior, I. Krossing, L. Müller, I. Raabe, M. Jansen and L. van Wüllen, *Chem. – Eur. J.*, 2002, **8**, 4475; (b) I. Krossing, *J. Chem. Soc., Dalton Trans.*, 2002, 500.
- 7 (a) M. H. Holthausen, K.-O. Feldmann, S. Schulz, A. Hepp and J. J. Weigand, *Inorg. Chem.*, 2012, **51**, 3374; (b) M. H. Holthausen and J. J. Weigand, *Z. Anorg. Allg. Chem.*, 2012, **638**, 1103; (c) M. H. Holthausen, A. Hepp and J. J. Weigand, *Chem. – Eur. J.*, 2013, **19**, 9895.



- 8 J. J. Weigand, M. H. Holthausen and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2009, **48**, 295.
- 9 M. H. Holthausen and J. J. Weigand, *J. Am. Chem. Soc.*, 2009, **131**, 14210.
- 10 (a) M. H. Holthausen, C. Richter, A. Hepp and J. J. Weigand, *Chem. Commun.*, 2010, **46**, 6921; (b) J. W. Dube, C. M. E. Graham, C. L. B. Macdonald, Z. D. Brown, P. P. Power and P. J. Ragona, *Chem. – Eur. J.*, 2014, **20**, 6739.
- 11 M. H. Holthausen, S. K. Surmiak, P. Jerabek, G. Frenking and J. J. Weigand, *Angew. Chem., Int. Ed.*, 2013, **52**, 11078.
- 12 E. Niecke and R. Kröher, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 692.
- 13 E. Niecke and W. Bitter, *Chem. Ber.*, 1976, **109**, 415; performing the reaction in 2 : 1 stoichiometry of **5** and SiCl₄ gave **6** and **7** in similar ratios.
- 14 Ref. 13 reports that after removal of **6** the residue consists mainly of polymeric material of unknown constitution and minor amounts of spirocyclic compound ClP(NSiMe₃)₂Si(NSiMe₃)₂PdCl. Investigation of the residue by ³¹P{¹H} NMR (C₆H₅F solvent), however, revealed **7** is the main compound (~60%) next to several minor species, see ESI† for more information.
- 15 L. Stahl, *Coord. Chem. Rev.*, 2000, **210**, 203.
- 16 (a) N. Burford and D. J. LeBlanc, *Inorg. Chem.*, 1999, **38**, 2248; (b) I. Schranz, L. P. Grocholl and L. Stahl, *Inorg. Chem.*, 2000, **39**, 3037.
- 17 E. Niecke, W. Flick and S. Pohl, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 309.
- 18 J. Heinicke, S. Mantey, A. Oprea, M. K. Kindermann and P. G. Jones, *Heteroat. Chem.*, 1999, **10**, 605.
- 19 Next to main species **7**, also minor amounts of compounds **8**, **9** and **9'** were observed in the ¹H and ³¹P{¹H} NMR spectra of the residue described in ref. 14, see ESI† for more information.
- 20 P. Paetzgold, C. von Plotho, E. Niecke and R. Rüger, *Chem. Ber.*, 1983, **116**, 1678.
- 21 M. L. Filleus-Blanchard, *Org. Mag. Res.*, 1979, **12**, 12.
- 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 diphosphadiazanes (e.g. **8**: Δ*G* > 27 kcal mol^{−1}, ref. 17).
- 23 Several isomerization pathways are conceivable: (a) L. Horner and H. Winkler, *Tetrahedron Lett.*, 1964, 461; (b) A. Rauk, L. C. Allen and K. Miskow, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 400; (c) J. Silaghi-Dumitrescu, F. Lara-Ochoa and I. Haiduc, *Main Group Chem.*, 1998, **2**, 309; (d) I. Schranz, D. F. Moser, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1999, **38**, 5814; (e) U. Wirringa, H. Voelker, H. W. Roesky, Y. Shermolovich, L. Markovski, I. Uson, M. Noltemeyer and H.-G. Schmidt, *J. Chem. Soc., Dalton Trans.*, 1995, 1951; (f) H.-J. Chen, R. C. Haltiwanger, T. G. Hill, M. L. Thompson, D. E. Coons and A. D. Norman, *Inorg. Chem.*, 1985, **24**, 4725.
- 24 Next to **7** (25%), compounds **5** (33%) and **6** (42%) are main products of this reaction. It is assumed, that **5** and Me₃SiN=PN(SiCl₃)(SiMe₃) form upon *cyclo*-reversion of **9**. Compound Me₃SiN=PN(SiCl₃)(SiMe₃) is assumed to eliminate Me₃SiCl yielding four-membered heterocycle **6**.
- 25 A. Villinger, P. Mayer and A. Schulz, *Chem. Commun.*, 2006, 1236.
- 26 A. Villinger, A. Westenkirchner, R. Wustrack and A. Schulz, *Inorg. Chem.*, 2008, **47**, 9140.
- 27 (a) B. Luo, V. G. Young and W. L. Gladfelter, *J. Organomet. Chem.*, 2002, 268; (b) H. Schmidtbauer and W. Findeiss, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 696.
- 28 M. Rastätter, P. W. Roesky, D. Gudat, G. B. Deacon and P. C. Junk, *Chem. – Eur. J.*, 2007, **13**, 7410.
- 29 (a) R. W. Shaw, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1978, **4**, 101; (b) S. S. Krishnamurthy, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1994, **87**, 101.
- 30 A. H. Cowley, M. Lattman and J. C. Wilburn, *Inorg. Chem.*, 1981, **20**, 2916.

