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Formation of the spirocyclic, Si-centered cage cations $[ClP(NSiMe_3)_2Si(NSiMe_3)_2P_5]^+$ and $[P_5(NSiMe_3)_2Si(NSiMe_3)_2P_5]^{2+}$†

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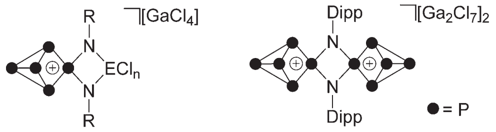
On account of our interest in P_4 activation by phosphenium ion insertion into P–P bonds we have developed synthetic routes to bicyclic N–P–Si-heterocycle **7** and probed its reactivity towards $GaCl_3$ and P_4. A $GaCl_3$-induced rearrangement of **7** leads to the *in situ* formation of spirocyclic, Si-centered phosphenium ions. Their insertion into P–P bonds of one or two P_4 tetrahedra yields polyphosphorus cages $[ClP(NSiMe_3)_2Si(NSiMe_3)_2P_5]^+$ (**19**$^+$) and $[P_5(NSiMe_3)_2Si(NSiMe_3)_2P_5]^{2+}$ (**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 phosphenium 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 (X = Cl, Br, I).[5,6] We expanded this methodology and prepared a series of symmetrically and unsymmetrically-substituted $R_2P_5^+$- and RP_5Cl^+-cations (R = aryl, alkyl, R_2N).[7] The additional stability added by organo-substituents allowed for the stepwise insertion of up to three $[Ph_2P]^+$ phosphenium ions into P–P bonds of one P_4 molecule yielding mono- to tri-cationic $[Ph_2P_5]^+$-, $[Ph_4P_6]^{2+}$- and $[Ph_6P_7]^{3+}$-cages.[8] A complementary study exploited 1,3-dichloro-*cyclo*-1,3-diphosphadiazane $ClP(NDipp)_2PCl$ (Dipp = 2,6-di*iso*propylphenyl), as a twofold phosphenium ion source for the stepwise activation of two P_4 tetrahedra which yielded the mono- and dicationic species $[ClP(NDipp)_2P_5]^+$ (1^+) and $[P_5(NDipp)_2P_5]^{2+}$ (2^{2+}, Fig. 1).[9] The related P_5^+-species $3[GaCl_4]$ was obtained by the reaction of P_4 with the four-membered heterocycle $Cl_2Si(NSiMe_3)_2PCl$ and $GaCl_3$ while the isolobale Al-species **4** is the result of the reaction of phosphenium zwitterion $Cl_2Al(NSiMe_3)_2P$ with P_4.[10]



1$[GaCl_4]$ (R = Dipp, E = P, n = 1)
3$[GaCl_4]$ (R = $SiMe_3$, E = Si, n = 2)
4 (R = $SiMe_3$, E = Al, n = 2)

2$[Ga_2Cl_7]_2$

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

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 phosphenium ion insertion.[10b]

With the intention to further expand the range of methods for the *in situ* generation of phosphenium 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 $ClP(NSiMe_3)_2Si(NSiMe_3)_2PCl$. Chloride abstraction by $GaCl_3$ and insertion of the respective phosphenium ion in P–P bonds of one or two P_4 molecules yields the Si-centered polyphosphorus cages $[ClP(NSiMe_3)_2Si(NSiMe_3)_2P_5]^+$ (**19**$^+$) and $[P_5(NSiMe_3)_2Si(NSiMe_3)_2P_5]^{2+}$ (**13**$^{2+}$).

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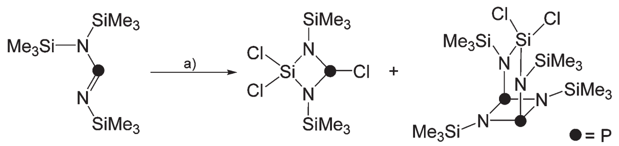
Results and discussion

Synthetic routes towards and characterization of 7

As part of our ongoing interest in four-membered phosphorus–nitrogen-element heterocycles as precursors for phosphenium ions[12] 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 rare[16] and contrasts other known diamido-cyclodiphosphazane compounds 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, 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]



5 **6** (41 %) **7** (18 %)

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

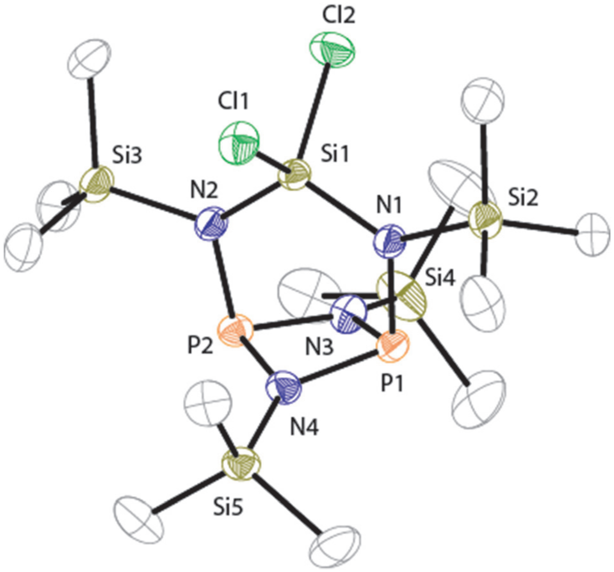
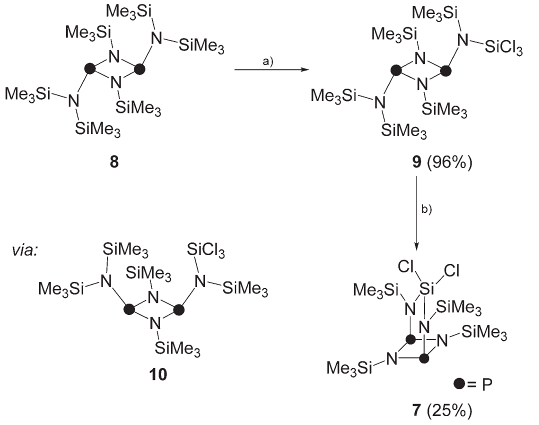


Fig. 2 Molecular structure of **7** (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected bond lengths [Å] and angles [°]: N1–P1 1.734(1), N3–P1 1.721(1), N4–P1 1.719(4), N2–P2 1.738(1), N3–P2 1.724(1), N4–P2 1.720(1), P1···P2 2.5235(6), N1–Si1 1.708(1), 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).

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



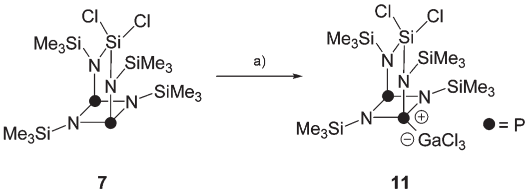
Scheme 2 Synthesis of **9** *via* reaction of **8** and $SiCl_4$; (a) $+SiCl_4$, $-Me_3SiCl$, rt, 12 h, 96%; and subsequent transformation to **7**; (b) neat, 185 °C, 10 min, 25%.

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 $^4J(PH)$ 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 ($\delta(Si) = -27.3$ ppm)[21] with a remarkably large coupling constant of $^2J(SiP_X) = 26.0$ Hz. A coupling constant of similar magnitude is observed for the Me_3Si-group pointing away from the four-membered ring ($\delta(Si) = 7.8$ ppm, $^2J(SiP_A) = 32.4$ 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; $^2J(SiP) = 4.2$ and 3.0 Hz). Similarly the $^{13}C\{^1H\}$ NMR spectrum reveals rather small coupling constants for the latter Me_3Si-groups ($^3J(CP) = 8.0$ and 10.5 Hz) and a large coupling constant for the Me_3Si-group pointing away from the $[NP]_2$-ring plane ($^3J(CP_A) = 19.8$ Hz).

It is assumed, that **7** is obtained from **9** *via* an intermediate of type **10** which forms upon rotation[22] of the P–N bond involving the $SiCl_3$-substituted N atom and inversion[23] 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

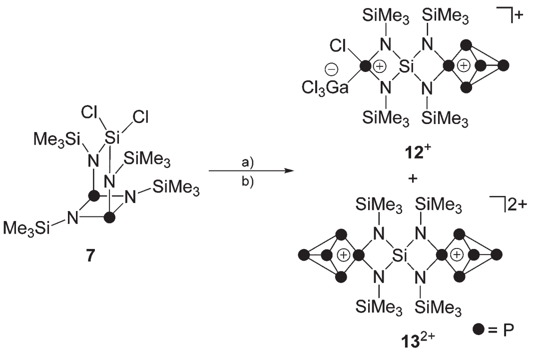
Diphosphadiazanes and related compounds bearing chloro- and Me_3Si-substituents are known to undergo a variety of distinct reactions with Lewis acids. Next to halide abstraction,[10] also elimination of Me_3SiCl,[25] migration of Me_3Si-,[26] chloro- or methyl-substituents[27] and P–N bond cleavage reactions are reported.[28] Especially the latter reaction is of interest, since it is assumed to proceed *via* phosphenium ion intermediates. Thus, bicyclic compound **7** is a promising substrate for the generation of phosphenium 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) $+GaCl_3$, C_6H_5F, 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 C_6H_5F gave a reddish colored reaction mixture which was investigated by means of $^{31}P\{^1H\}$ 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 ($\delta(P_A) = 115$ ppm, $\Delta\nu_{1/2} = 1200$ Hz; $\delta(P_X) = 179.6$ 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 $GaCl_3$.

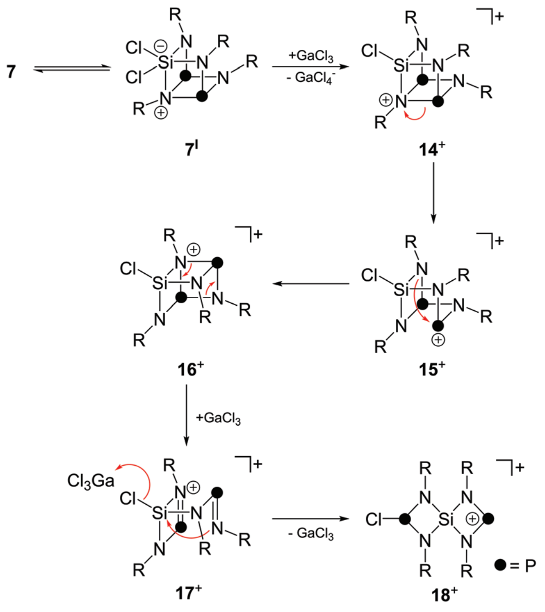
Interestingly, P_4 does not react with **11** which indicates that the latter is not a suitable phosphenium ion source. Adding two equivalents of $GaCl_3$ to a solution of **7** in C_6H_5F, however, results in the rapid consumption of *in situ* generated **11**. This reaction yields a complex mixture 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 $^{31}P\{^1H\}$ NMR spectroscopy revealed the formation of P_5^+ cage cation $\mathbf{12}^+$ and bridged *bis*(P_5^+)-cage dication $\mathbf{13}^{2+}$ 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) $+P_4$, +2, $GaCl_3$, C_6H_5F, r.t., 24 h; (b) +2, P_4, +4, $GaCl_3$, r.t., C_6H_5F, 24 h; the equation depicts the major products and is not balanced; anions of the products are not depicted.

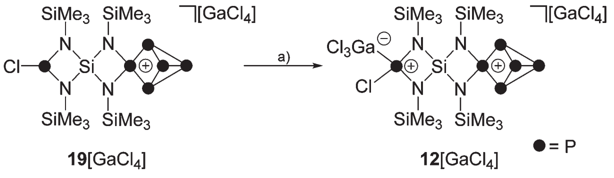
In addition, both spectra reveal significant amounts of P_4 but neither remaining **7** nor the corresponding adduct **11** were observed which is attributed to unidentified side reactions. The products $\mathbf{12}^+$ and $\mathbf{13}^{2+}$ are formally obtained by the insertion of phosphenium ions 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 $\mathbf{12}^+$ and $\mathbf{13}^{2+}$ 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 $\mathbf{13}^{2+}$ in the presence of excess P_4 and $GaCl_3$. In addition, the formation of large quantities of $\mathbf{13}^{2+}$ 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 phosphenium 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 $\mathbf{7}^\mathbf{I}$. Compound $\mathbf{7}^\mathbf{I}$ 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 $\mathbf{14}^+$ featuring a tetra-coordinated N atom. The next two steps constitute P–N bond cleavage and formation reactions yielding intermediates $\mathbf{15}^+$ and $\mathbf{16}^+$ *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 $\mathbf{16}^+$ features a diphosphadiazane $[NP]_2$-ring which is assumed to react *via* a *cyclo*-reversion reaction to intermediate $\mathbf{17}^+$. Cation $\mathbf{17}^+$ 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 phosphenium ion $\mathbf{18}^+$. Cation $\mathbf{18}^+$ features the Si-centered spiro[3.3]heptane-motif and, thus, is assumed to be accountable for the formation of cages cations $\mathbf{12}^+$ and $\mathbf{13}^{2+}$ *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.



Scheme 5 Suggested $GaCl_3$-induced rearrangement mechanism of **7** to phosphenium ion $\mathbf{18}^+$ 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.

Attempts to isolate a gallate salt of $\mathbf{12}^+$ 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 $ABMX_2Y$ 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 $\mathbf{3}^+$.[10a] The chloro-substituted P atom in $\mathbf{19}^+$ 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 $\mathbf{19}^+$ 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 6 Reaction of **19**$[GaCl_4]$ with $GaCl_3$; (a) $+GaCl_3$, CD_2Cl_2, r.t., 30 min.

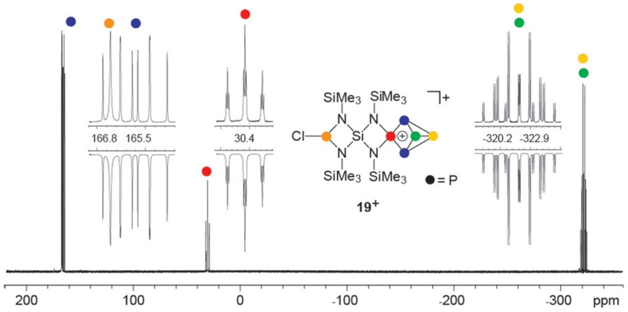


Fig. 3 $^{31}P\{^1H\}$ NMR spectrum of **19**[GaCl$_4$] (CD$_2$Cl$_2$, r.t.); insets show experimental (upwards) and fitted spectra (downwards); ABMX$_2$Y spin system of **19**$^+$: $\delta(P_A) = -322.9$ ppm, $\delta(P_B) = -320.2$ ppm, $\delta(P_M) = 30.4$ ppm, $\delta(P_X) = 165.5$ ppm, $\delta(P_Y) = 166.8$ ppm, $^1J(P_AP_B) = -189.8$ Hz, $^1J(P_AP_X) = -143.4$ Hz, $^1J(P_BP_X) = -147.7$ Hz, $^1J(P_MP_X) = -245.1$ Hz, $^2J(P_AP_M) = 18.8$ Hz, $^2J(P_BP_M) = 18.0$ Hz.

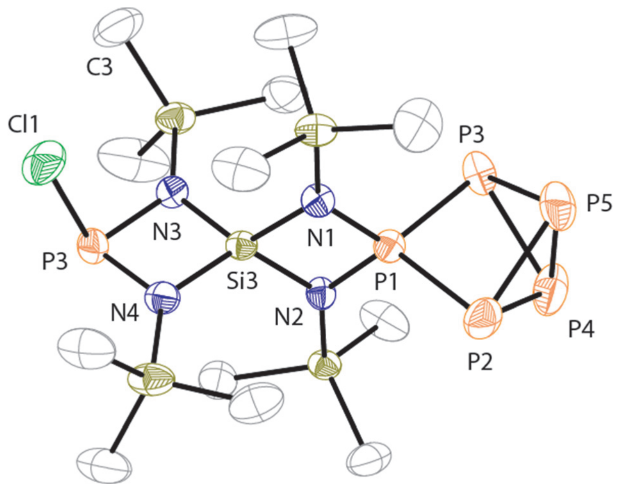


Fig. 4 Molecular structure of **19**$^+$ in compound **19**[GaCl$_4$]·C$_6$H$_5$F (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected bond lengths [Å] and angles [°]: N2–P1 1.656(3), N1–P1 1.661(3), N1–Si3 1.755(3), N2–Si3 1.751(3), N3–Si3 1.711(3), N4–Si3 1.704(3), N3–P6 1.716(3), N4–P6 1.711(3), Cl1–P6 2.238(2), P1⋯Si3 2.445(1), P6⋯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).

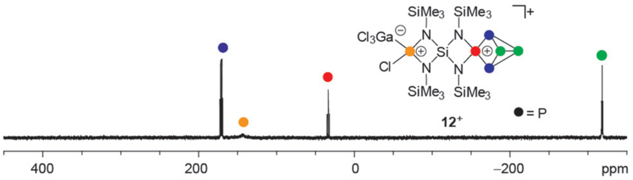


Fig. 5 $^{31}P\{^1H\}$ NMR spectrum of **12**[GaCl$_4$] (CD$_2$Cl$_2$, r.t.); A$_2$MOX$_2$ spin system of **12**$^+$: $\delta(P_A) = -318.3$ ppm, $\delta(P_M) = 33.4$ ppm, $\delta(P_O) = 144$ ppm ($\Delta\nu_{1/2} = {\sim}1200$ Hz), $\delta(P_X) = 170.8$ ppm, $^1J(P_AP_X) = -144.8$ Hz, $^1J(P_MP_X) = -248.6$ Hz, $^2J(P_AP_M) = 19.0$ Hz.

P_5^+-moiety exhibit a low field shift (δ(H) = 0.67 ppm and 0.76 ppm) and are comparable to the corresponding resonance of **3**$^+$ (δ(H) = 0.68 ppm).[10a] The $^{29}Si\{^1H\}$ NMR spectrum exhibits a resonance at δ(Si) = −58.0 ppm which is assigned to the Si spiro-atom. This resonance reveals a doublet of doublet splitting caused by ^2J(SiP)-couplings to the tetra-coordinated P atom ($^2J(SiP_M) = 8.5$ Hz) and the chloro-substituted P atom ($^2J(SiP_Y) = 18.5$ 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)°). 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**$^+$.[9,10a] The Si–N bonds in the [SiN$_2$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 [SiN2P]-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**[GaCl$_4$] in CD$_2$Cl$_2$ yields the previously mentioned Lewis-acid base adduct **12**$^+$ (Scheme 6). The A$_2$MOX$_2$ spin system observed in the $^{31}P\{^1H\}$ 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$_2$MX$_2$ part of the A$_2$MOX$_2$ 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 ($\delta(P_O)$ = 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 [Ga$_2$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-C$_6$H$_4$F$_2$ yielded a suspension containing a yellow microcrystalline material of **13**[Ga$_2$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$_2$Cl$_2$/*n*-hexane leads to significantly decreased yields (7% yield in >90% purity). The $^{31}P\{^1H\}$ NMR spectrum of **13**[Ga$_2$Cl$_7$]$_2$ dissolved in CD$_2$Cl$_2$ shows an A$_2$MX$_2$-spin system in accordance with the C_{2v}-symmetry of the molecule

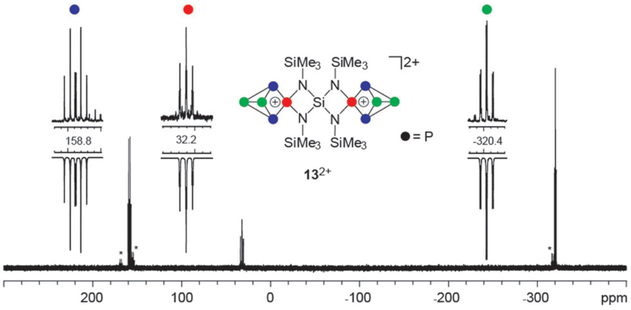


Fig. 6 $^{31}P\{^1H\}$ NMR spectrum of **13**$[Ga_2Cl_7]_2$ (CD_2Cl_2, r.t.); unidentified side products are marked with asterisks; A_2MX_2 spin system of $\mathbf{13}^{2+}$: $\delta(P_A)$ = −320.4 ppm, $\delta(P_M)$ = 32.2 ppm, $\delta(P_X)$ = 158.8 ppm, $^1J(P_AP_X)$ = −142.7 Hz, $^1J(P_MP_X)$ = −259.1 Hz, $^2J(P_AP_M)$ = 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 $[SiN_2P]$-rings. The resonances and coupling constants of $\mathbf{13}^{2+}$ are similar to those observed for the related compounds $\mathbf{19}^+$ and $\mathbf{3}^+$.[10a]

Single crystals of compound **13**$[Ga_2Cl_7]_2$ were obtained by diffusion of *n*-hexane in a CH_2Cl_2 solution of **13**$[Ga_2Cl_7]_2$ 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**$[Ga_2Cl_7][GaCl_4]$ were obtained by layering the supernatant solution of the reaction mixture of the synthesis of **13**$[Ga_2Cl_7]_2$ 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**$[Ga_2Cl_7]$-$[GaCl_4]$ 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 $\mathbf{13}^{2+}$ 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 $\mathbf{19}^+$ (*av.* Si–N: 1.753(6) Å and Si–N: 1.7007(6) Å).

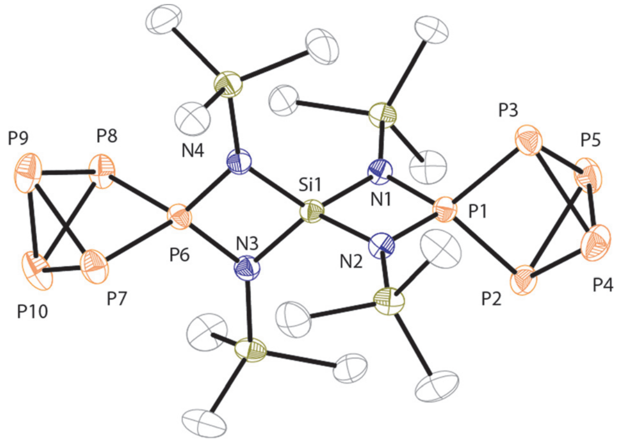


Fig. 7 Molecular structure of $\mathbf{13}^{2+}$ in compound **13**$[Ga_2Cl_7][GaCl_4]$ (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected bond lengths [Å] and angles [°]: N1–P1 1.667(2), N2–P1 1.671(2), N3–P6 1.663(2), N4–P6 1.665(2), Si1–N1 1.731(2), Si1–N2 1.732(2), S1–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).

Conclusions

The bicyclic P–N–Si heterocycle **7** was targeted as source for the *in situ* generation of phosphenium 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 $ClP(NSiMe_3)_2Si(NSiMe_3)_2PCl$. The latter species gives access to polyphosphorus cage cations $[ClP(NSiMe_3)_2Si(NSiMe_3)_2P_5]^+$ ($\mathbf{19}^+$) and $[P_5(NSiMe_3)_2Si(NSiMe_3)_2P_5]^{2+}$ ($\mathbf{13}^{2+}$) in the presence of $GaCl_3$ and P_4. We are continuing to investigate the Lewis-acid mediated generation of phosphenium ions for P_4 activation from related phosphorus–nitrogen-element bicycles. Furthermore, studies directed towards the utilization of $\mathbf{12}^+$, $\mathbf{19}^+$ and $\mathbf{13}^{2+}$ as synthetic building blocks will be the target of future efforts.

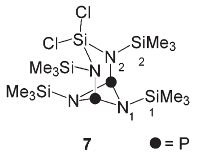
Experimental

General

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

Synthesis of $Cl_2Si(NSiMe_3)_2(PNSiMe_3)_2$ (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 C_6H_5F (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.

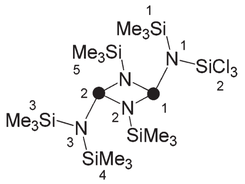


7

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); **^{1}H NMR (C_6D_6, [ppm]):** δ = 0.21 (18H, s, H1), 0.39 (18H, s, H2); **^{13}C{^{1}H} NMR (C_6D_6, [ppm]):** δ = −0.08 (6C, t, C1, ^3J(CP) = 3.6 Hz), 2.7 (6C, *pseudo*-t, C2, ^3J(CP) = 5.0 Hz); **^{29}Si{^{1}H} NMR (C_6D_6, [ppm]):** δ = −47.4 (1Si, s, Si3), 1.8 (2Si, t, Si1, ^2J(SiP) = 11.7 Hz), 7.7 (2Si, *pseudo*-t, Si2, ^2J(SiP) = 11.8 Hz); **^{15}N NMR (C_6D_6, [ppm]):** δ = −397 (t, N1, ^1J(NP) = 55 Hz), −374 (d, N2, ^1J(NP) = 75 Hz); **^{31}P{^{1}H} NMR (C_6D_6, [ppm]):** δ = 211.8 (s); **elemental analysis for $C_{12}H_{36}Cl_2N_4P_2Si_5$:** 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 $C_{12}H_{36}Cl_1N_4P_2Si_5$: 473.0945.

Synthesis of $(SiMe_3)_2N(PNSiMe_3)_2N(SiMe_3)(SiCl_3)$ (9)

Compound **8** (1.114 g, 2.00 mmol, 1.0 eq.) was suspended in $SiCl_4$ (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%).

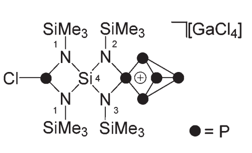


9

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); **^{1}H NMR (C_6D_6, [ppm]):** δ = 0.17 (18H, s, H5), 0.27 (9H, d, H3, ^4J(HP) = 3.7 Hz), 0.52 (9H, s, H4), 0.64 (9H, s, H1); **^{13}C{^{1}H} NMR (C_6D_6, [ppm]):** δ = 1.4 (6C, t, C5, ^3J(CP) = 2.5 Hz), 4.7 (3C, d, C1, ^3J(CP) = 10.5 Hz), 4.8 (3C, d, C3, ^3J(CP) = 19.8 Hz), 5.0 (3C, d, C4, ^3J(CP) = 8.0 Hz); **^{29}Si{^{1}H} NMR (C_6D_6, [ppm]):** δ = −27.3 (1Si, d, Si2, ^2J(SiP) = 26.0 Hz), 0.2 (1Si, d, Si4, ^2J(SiP) = 3.0 Hz), 1.5 (2Si, t, Si5, ^2J(SiP) = 7.4 Hz), 4.5 (1Si, d, Si2, ^2J(SiP) = 4.2 Hz), 7.6 (1Si, d, Si3, ^2J(SiP) = 32.4 Hz); **^{15}N NMR (C_6D_6, [ppm]):** δ = 67.1 (t, N2, ^1J(NP) = 50 Hz), 93.8 (d, N1, ^1J(NP$_X$) = 90 Hz), 113.9 (d, N3, ^1J(NP$_A$) = 90 Hz); **^{31}P{^{1}H} NMR (C_6D_6, [ppm]):** AX spin system: $\delta(P_A)$ = 218.6 (d, P1, $\Delta\nu_{1/2}$ = 42 Hz, $^2J(P_AP_X)$ = 12 Hz), $\delta(P_X)$ = 232.2 (d, P2, $\Delta\nu_{1/2}$ = 37 Hz, $^2J(P_AP_X)$ = 12 Hz); **elemental analysis for $C_{15}H_{45}Cl_3N_4P_2Si_6$:** calcd: C 29.1, H 7.3, N 9.1; found: C 28.8, H 7.3, N 8.6.

Reaction of 7, P_4 and $GaCl_3$ in 1 : 1 : 2 and 1 : 2 : 4 stoichiometries

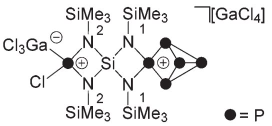
1 : 1 : 2: Compound **7** (256 mg, 0.50 mmol, 1.0 eq.) was added to a suspension of P_4 (62 mg, 0.50 mmol, 1.0 eq.) in C_6H_5F (5 mL). A solution of $GaCl_3$ (176 mg, 1.00 mmol, 2.0 eq.) in C_6H_5F (2 mL) was added dropwise to the suspension giving a red colored reaction mixture which was stirred for 12 h at ambient temperature. In the course of the reaction the color of the reaction mixture changed to yellow and the dissolving of P_4 was observed. The reaction mixture was investigated by means of ^{31}P{^{1}H} NMR spectroscopy (see ESI†). *1 : 2 : 4:* Compound **7** (256 mg, 0.50 mmol, 1.0 eq.) was added to a suspension of P_4 (124 mg, 1.00 mmol, 2.0 eq.) in C_6H_5F (5 mL). A solution of $GaCl_3$ (352 mg, 2.00 mmol, 4 eq.) in C_6H_5F (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 P_4 was observed. The reaction mixture was investigated by means of ^{31}P{^{1}H} NMR spectroscopy (see ESI†). *n*-Hexane (2 mL) was added leading to the formation of a brown oil. The supernatant was removed, diluted with C_6H_5F (6 mL) and layered with *n*-hexane (3 mL) at −35 °C. Small amounts of crystalline material of **19**[$GaCl_4$] (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-$C_6H_4F_2$ (2 mL) leading to the formation of a yellow, microcrystalline solid. The supernatant was removed and the yellow powder was washed with 1,2-$C_6H_4F_2$/*n*-hexane (1 : 1 mixture, 2 × 2 mL). The obtained yellow powder consisting of **13**[Ga_2Cl_7]$_2$ in an approximate purity of 75% (determined by ^{31}P{^{1}H} NMR spectroscopy, 20% yield, 145 mg) was isolated by filtration and dried *in vacuo.* Recrystallization from a CH_2Cl_2 solution by slow diffusion of *n*-hexane yielded crystalline material of **19** [Ga_2Cl_7]$_2$ (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**[Ga_2Cl_7]-[$GaCl_4$] were obtained by layering the diluted supernatant of the reaction mixture with *n*-hexane at −35 °C.



19[$GaCl_4$]

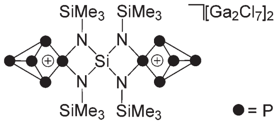
m.p.: 115.0–116.9 °C; **Raman (300 mW, [cm^{-1}]):** ν = 2961 (37), 2998 (100), 1412 (24), 636 (37), 552 (63), 442 (22), 398 (24), 376 (14), 344 (43), 152 (44), 121 (13); **IR (ATR, [cm^{-1}]):**

ν = 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}H NMR (CD_2Cl_2, [ppm]):** δ = 0.31 (18H, s, H1), 0.67 (9H, s, H2), 0.76 (9H, s, H3); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 1.4 (6C, d, C1, ^3J(CP) = 3.1 Hz), 2.2 (3C, m, C2), 3.1 (3C, m, C3); **^{29}Si{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = −58.0 (dd, Si4, $^2J(\mathrm{SiP_Y})$ = 18.5 Hz, $^2J(\mathrm{SiP_M})$ = 8.5 Hz), 7.4 (d, Si1, ^2J(SiP) = 8.4 Hz), 10.9 (s, Si2), 11.7 (s, Si3); **^{15}N NMR (CD_2Cl_2, [ppm]):** δ = 96 (s, N1), 115 (s, N2), 125 (s(br), N3); **^{71}Ga{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 249.6 (s); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** $ABMX_2Y$ spin system: $\delta(P_A)$ = −322.9, $\delta(P_B)$ = −320.2, $\delta(P_M)$ = 30.4, $\delta(P_X)$ = 165.5, $\delta(P_Y)$ = 166.8, $^1J(P_AP_B)$ = −189.8 Hz, $^1J(P_AP_X)$ = −143.4 Hz, $^1J(P_BP_X)$ = −147.7 Hz, $^1J(P_MP_X)$ = −245.1 Hz, $^2J(P_AP_M)$ = 18.8 Hz, $^2J(P_BP_M)$ = 18.0 Hz; **elemental analysis for $C_{12}H_{36}GaCl_5P_6N_4Si_5$:** calcd: C 17.8, H 4.5, N 6.9; found: C 17.1, H 4.4, N 5.5.



12[GaCl$_4$]

^{1}H NMR (CD_2Cl_2, [ppm]): δ = 0.37 (18H, s, H2), 0.75 (18H, s, H1); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** $ABMOX_2$ spin system: $\delta(P_A)$ = −318.3, $\delta(P_M)$ = 33.4, $\delta(P_O)$ = 144 ($\Delta\nu_{1/2}$ = ∼1200 Hz), $\delta(P_X)$ = 170.8, $^1J(P_AP_X)$ = −144.8 Hz, $^1J(P_MP_X)$ = −248.6 Hz, $^2J(P_AP_M)$ = 19.0 Hz. Compound **12**[GaCl$_4$] was independently synthesized by addition of $GaCl_3$ (18 mg, 0.10 mmol, 1.0 eq.) to a solution of **19**[GaCl$_4$] (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 ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.



13[Ga$_2$Cl$_7$]$_2$

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 (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}H NMR (CD_2Cl_2, [ppm]):** δ = 0.72 (36H, s, CH_3); **^{13}C{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 2.7 (12C, s, CH_3); **^{29}Si{^{1}H} NMR (CD_2Cl_2, [ppm]):** δ = 13.7 (s, $Si(CH_3)_3$), the Si atom of the SiN_4-moiety was not detected; **^{15}N NMR (CD_2Cl_2, [ppm]):** δ = 115 (s); **^{31}P{^{1}H} NMR (CD_2Cl_2, [ppm]):** A_2MX_2 spin system: $\delta(P_A)$ = −320.4, $\delta(P_M)$ = 32.2, $\delta(P_X)$ = 158.8, $^1J(P_AP_X)$ = −142.7 Hz, $^1J(P_MP_X)$ = −259.1 Hz, $^2J(P_AP_M)$ = 20.0 Hz; **elemental analysis for $C_{12}H_{36}Ga_4Cl_{14}P_{10}N_4Si_5$:** calcd: C 10.8, H 2.5, N 3.8; found: C 10.9, H 2.5, N 4.0.

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