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Phosphorus Azides

Low-Temperature Isolation of An Azidophosphenium Cation[**]

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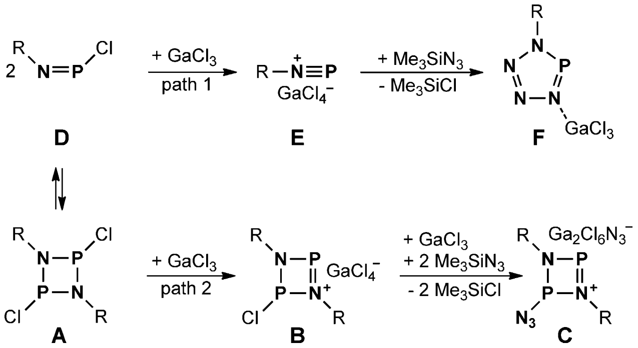
Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday

The first two-coordinate phosphorus cations, observed in so-called phosphamethine cyanines, were reported by Dimroth and Hoffmann in 1964.[1] The term phosphenium ion has been introduced to imply a high degree of positive charge accumulation at the two-coordinate phosphorus center with a formally vacant 3p orbital.[2] Phosphenium ions have some resemblance to carbenes of the type X−C−Y except that P^+ replaces the central carbon atom.[3] As is well-known, carbenes are stabilized best when X and Y are atoms or groups such as NR_2, which can serve as π-electron donors to the carbon atom. Parry et al. reported the first examples of acyclic phosphenium ions $[(Me_2N)_2P]^+$ and $[(Me_2N)(Cl)P]^+$, which were obtained by chloride abstraction from the corresponding aminochlorophosphanes by employing Lewis acids, such as ECl_3 (E = Fe, Al, Ga).[4] Structural data of acyclic aminophosphenium ions are still limited to only a few examples substituted by an amino group: $[(iPr_2N)_2P]X$ (X = $AlCl_4^-$, $GaCl_4^-$, BPh_4^-).[5,6] To the best of our knowledge, halogen- or pseudohalogen-substituted phosphenium ions of the type $[R_2N{-}P{-}X]^+$ (X = halogen or pseudohalogen) have not been isolated and structurally characterized.

Cyclo-diphosphadiazenium salts can also be regarded as phosphenium ions (Scheme 1, species **B**). Upon addition of a Lewis acid to the *cyclo*-diphosphadiazanes **A**, the corresponding cyclic cation **B** is formed, which can be regarded as binary P^{III}/N four-membered heterocyclic cation with two- and three-coordinate phosphorus atoms and a delocalized π bond within the $NP^{(+)}N$ unit. Only recently, the synthesis and full characterization of a 1-azido-*cyclo*-1,3-diphospha-2,4-diazenium salt was reported (Scheme 1, species **C**).[7] As illustrated in Scheme 1, an equilibrium between a *cyclo*-diphosphadiazane and its monomer, the corresponding iminophosphane, might be observed depending on the sterical strain of the bulky substituent R. For example, for R = terphenyl (Ter), only a stable dimer is found in the solid state and in solution but no monomeric iminophosphane R−N=P−Cl.[7b] Addition of $GaCl_3$ results in the formation of *cyclo*-diphosphadiazenium salt **B**, and in the presence of Me_3SiN_3, species **C** can be isolated. In contrast, if the bulky substituent R = supermesityl (Mes*), the monomeric species **D** is favored; thus upon addition of $GaCl_3$, an iminophosphenium ion is formed, which reacts as dipolarophile in the presence of the 1,3-dipole molecule Me_3SiN_3 to the corresponding tetrazaphosphole (Scheme 1, species **F**) in a formal [3+2] cyclization. However, no isomeric species **C** is observed.[8,9] Recently, it was shown that disguised dipolarophiles, that is, the amino-substituted dichlorophosphane $Ter(Me_3Si)N{-}PCl_2$ can also be used, which releases Me_3SiCl, forming the necessary highly reactive, bare dipolarophile Ter−N=P−Cl in situ. Again, addition of the 1,3-dipole Me_3SiN_3 in the presence of a Lewis acid yields the tetrazaphospole **F**.



Scheme 1. Different reaction paths observed for *cyclo*-diphosphadiazanes (species **A**) depending on the sterical strain: path 1 for R = Mes*, path 2 for R = Ter.

These synthetic concepts can also be applied to the heavier analogues, but although the isolation and comprehensive characterization of tetrazapnictoles of the type $R{-}NE_4$ (E = N, P, As, Sb) were achieved, there are still open questions with respect to the reaction mechanism. Theoretical studies, carried out to determine the mechanism,[10] indicate that pnictenium ions are intermediates on the reaction path.[7b] Following our interest in the chemistry of compounds bearing binary NPn fragments (Pn = P,[7,8,10] As,[9] Sb,[11] and Bi[12]), we studied the reaction of the disguised dipolarophile $(Me_3Si)_2N{-}PCl_2$ (**1**) with the Lewis acid $GaCl_3$ by means of low-temperature techniques.[13]

We report herein on the synthesis and full characterization of the hitherto unknown, highly labile amino(azido)phosphenium salt $[(Me_3Si)_2N{=}P{-}N_3][GaCl_4]$ (**4**) utilizing a pseudohalogen/chlorine exchange reaction in aminochlorophosphenium ion $[(Me_3Si)_2N{-}PCl]^+$ (**2a**, Scheme 2).[14] The cation in the azide-substituted phosphenium salt **4** can formally be regarded as the first known phosphapentacenium ion $[R_2NPNNN]^+$; the parent pentacenium ion N_5^+ was described by Christe et al. in 1999.[15]

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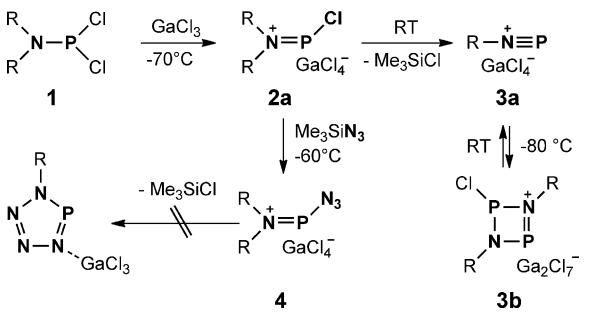

Scheme 2. Synthesis of different aminophosphenium, iminophosphenium, and *cyclo*-diphosphadiazenium salts (R = Me$_3$Si).

As illustrated in Scheme 2, addition of GaCl$_3$ to a solution of (Me$_3$Si)$_2$N−PCl$_2$ (**1**) at −70 °C resulted (according to X-ray crystallography) in the formation of a highly labile amino-chlorophosphenium ion in [(Me$_3$Si)$_2$N=P−Cl][GaCl$_4$] (**2a**), which could be isolated as colorless crystals at −50 °C (Figure 1, right).[4] Furthermore, the synthetic approach was modified and two equivalents of GaCl$_3$ were used, resulting in the formation of the [(Me$_3$Si)$_2$N=P−Cl][Ga$_2$Cl$_7$] (**2b**).[14] With AlCl$_3$ as Lewis acid, the isolation of [(Me$_3$Si)$_2$N=P−Cl][AlCl$_4$] (**2c**) was achieved at temperatures below −50 °C. However, the bare cation of **2a–c** could not be detected in solution. This quite astonishing observation prompted us to study the temperature-dependent equilibrium chemistry of the system (Me$_3$Si)$_2$N−PCl$_2$/GaCl$_3$ by means of variable-temperature ^{31}P NMR spectroscopy (Figure 2).

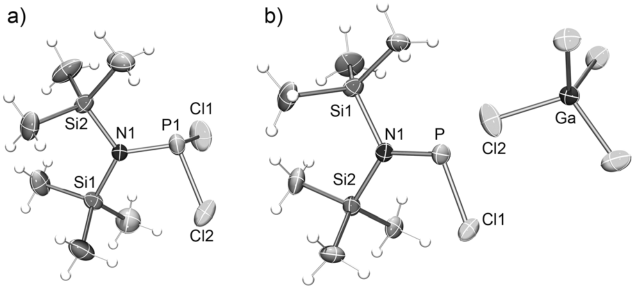

Figure 1. ORTEP view of the molecular structure of **1** (a) and **2a** (b) from signgle-crystal X-ray diffraction at 173 K. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: **1**: P–N 1.6468(8), P–Cl2 2.0834(5), P–Cl1 2.1074(5), N–Si1 1.7940(9), N–Si2 1.7961(9); N-P-Cl2 104.37(4), N-P-Cl1 104.86(3), Cl2-P-Cl1 96.76(2), P-N-Si1 126.80(5), P-N-Si2 112.39(5), Si1-N-Si2 120.81(5). **2a**: P1A–N 1.595(2), P1B–N 1.584 (3), P–Cl1 2.019(4), Si1–N 1.847(2), Si2–N 1.841(2), P1A–Cl2A 2.871(4), P1B–Cl2B 2.811(11), Ga–Cl2 2.198(5), Ga–Cl4 2.201(8); N-P-Cl1 107.6(1), P-N-Si2 111.3 (1), P-N-Si1 126.8(1), Si2-N-Si1 121.8(1), Cl1-P-N-Si2 175.6(1).

If an equimolar mixture of GaCl$_3$ and **1** is allowed to warm to ambient temperature, while monitoring the process with ^{31}P NMR spectroscopy, at −80 °C only the ^{31}P NMR signal of the GaCl$_3$ adduct of starting material **1** (broad singlet at $\delta = 188$ ppm) is observed. Between −80 °C and −15 °C a temperature-dependent downfield shift of the resonance of **1**·GaCl$_3$ from 188 ($\Delta\nu_{1/2} = 4000$ Hz) to 285 ppm ($\Delta\nu_{1/2} = 370$ Hz) is observed, while at the same time the signal becomes sharper, indicating the transition to salt formation, [(Me$_3$Si)$_2$N(Cl)P−Cl···GaCl$_3$], upon chloride abstraction by GaCl$_3$ (Figure 2). However, the most downfield-shifted signal at $\delta = 285$ ppm (−15 °C) is still far away from the expected range for the cation of **2a** (cf. $\delta = 330$ ppm in [(Me$_2$N)(Cl)P]$^+$;[4b] computed shift for **2a**: $\delta = 393$ ppm).[14b] Obviously, species **2a** containing the amino(chloro)phosphenium ion is formed only upon crystallization, and is only stable in the solid state at temperatures below −50 °C. At −5 °C the signal for the simple adduct **1**·GaCl$_3$, [(Me$_3$Si)$_2$N(Cl)P−Cl···GaCl$_3$], has completely disappeared, while a new signal at $\delta = 89$ ppm and an adduct of starting material **1** and the chlorophosphenium ion in **2a**, [R$_2$NP(Cl)·(Cl$_2$)PNR$_2$][GaCl$_4$] (R = SiMe$_3$; $^1J_{\mathrm{P,P}} = 669$ Hz), are observed. This large $^1J_{\mathrm{P,P}}$ coupling constant is in good agreement with donor–acceptor adducts bearing a direct P−P linkage.[16] At room temperature, only one signal in the ^{31}P NMR spectrum remains at 89 ppm, which can be assigned to the *N*-(trimethylsilyl)iminophosphenium tetrachlorogallate, [Me$_3$Si−N≡P][GaCl$_4$] (Scheme 2, species **3a**),[17] a yellow, viscous compound that is an ionic liquid at room temperature. If **3a** is then cooled down again (Supporting Information, Figure S2), at −80 °C compound **3a** is in an equilibrium with its cyclic dimer, a chloro-*cyclo*-diphosphadiazenium salt (**3b**), which has characteristic NMR signals for its two- and three-coordinate phosphorus centers (Scheme 2).[7a,18]

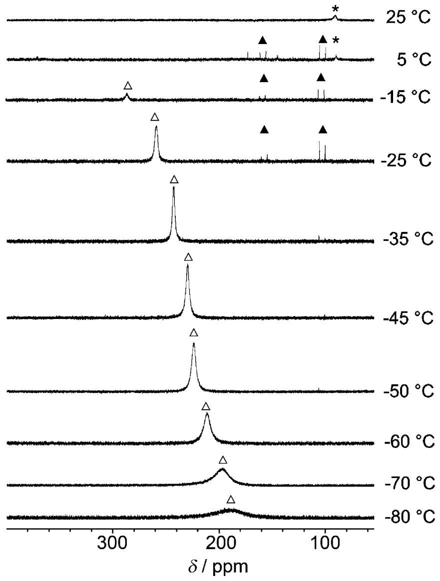

Figure 2. Temperature-dependent ^{31}P NMR study of an equimolar mixture of **1** and GaCl$_3$ between −80 °C and 25 °C. The observed species are indicated as follows: ▲ = **1**·GaCl$_3$→**2a**, △ = [R$_2$N**P**(Cl)·(Cl$_2$)**P**NR$_2$][GaCl$_4$], ⋆ = **3a**.[14]

In another series of experiments, we studied the reaction of amino(chloro)phosphenium salt **2a** with 1,3-dipole molecules such as Me$_3$SiN$_3$, which can be regarded as a trimethylsilylpseudohalide.[19] Astonishingly, when a solution of Me$_3$SiN$_3$ in CH$_2$Cl$_2$ is added to **2a** at −50 °C, colorless crystals precipitate from the reaction mixture that were unequivocally identified as the highly labile amino(azido)phosphenium salt [(Me$_3$Si)$_2$N=P−N$_3$][GaCl$_4$] (**4**) by low-temperature single-crystal X-ray analysis and ^{31}P NMR studies at −70 °C (cf.

$\delta_{exp} = 367$ vs. $\delta_{calc} = 354$ ppm).[14b] Compound **4** contains the first cation with an azide group attached to a two-coordinate phosphorus atom and might be regarded as constitutional isomer of a tetrazaphospholium ion with a cyclic $R_2PN_4^+$ moiety.[20] Compound **4** is a colorless crystalline solid and can be stored for at least one year under an argon atmosphere at temperatures below −30 °C, which is remarkable, because phosphorus azides are well-known for a facile release of molecular nitrogen. In contrast, **4** is stable in solution only at temperatures below −40 °C, and slowly decomposes upon further warming, releasing N_2 in a Staudinger reaction. This Staudinger reaction was studied by means of ^{31}P NMR experiments yielding a mixture of oligomeric decomposition products of the type $[R_2NP{=}NP(X)NR_2]^{2+}$ ($R = Me_3Si$; $X = Cl$, N_3), that could not be isolated. No indications for the formation of a tetrazaphosphole were observed. The intermediate formation of azidophosphenium ions bearing an azido substituent directly on the two-coordinate phosphorus atom has been discussed before solely on the basis of ^{31}P NMR data in the reaction of $i\mathrm{Pr}_2\mathrm{N{-}PCl_2}$ with Me_3SiN_3 in the presence of $AlCl_3$.[21] Usually, the reaction of phosphenium ions with azides is an interesting extension of the Staudinger reaction, and so far it was impossible to isolate the azidophosphenium species. For example, it was found that only bis(dialkylamino)phosphenium ions $[(R_2N)_2P]^+$ react with azides to afford the corresponding bis(dialkylamino)-iminophosphonium ions $[(R_2N)_2P{=}NR]^+$.[22]

Aminodichlorophosphane **1** and the chlorophosphenium salts **2a**, **2b**, and **2c** crystallize in the monoclinic space group $P2_1/c$ with four formula units per cell, whereas azidophosphenium salt **4** crystallizes in the monoclinic space group $P2_1/m$ with two formula units per cell (Figure 3). A striking feature of all structures is the almost planar environment of the amino nitrogen atom (∡Si1-Si2-N-P in **1** 179.8, **2a** 176.2, **2b** 178.1, **2c** 178.1, **4** 180.0°). Thus, as shown by NBO analyses (NBO = natural bond orbital),[23] the one lone pair on the amino nitrogen atom is localized in a pure p-type atomic orbital. As expected, the three-coordinate P atom in **1** (Figure 1, left) adopts a trigonal pyramidal geometry, and a rather short $P{-}N_{amino}$ bond length of 1.6468(8) Å is found (cf. $\Sigma r_{cov}(P{-}N) = 1.82$, $\Sigma r_{cov}(P{=}N) = 1.62$ Å),[24] indicating partial double bond character owing to hyperconjugative effects of the lone pair (LP) of the amino nitrogen atom with the antibonding σ*(P−Cl) bond orbital. This p-LP(N)→σ*(P−Cl) donor–acceptor interaction accounts also for the slightly elongated P−Cl1 bond (2.1074(5) Å, cf. $\Sigma r_{cov}(P{-}Cl) = 2.04$ Å)[24] in **1**. Similar structural features with short P−N distances (1.67 ± 3 Å) have already been observed in a series of amino–iminophosphanes ($R_2N{-}P{=}N{-}R'$).[25] Even shorter $P{-}N_{amino}$ distances, ranging from 1.59 to 1.60 Å, are observed in the cations of **2a–c** and **4** (**2a** 1.595(2),[26] **2b** 1.580(2), **2c** 1.601(2), and **4** 1.597(2) Å) in accord with a typical P−N double bond (cf. $\Sigma r_{cov}(P{-}N) = 1.82$, $\Sigma r_{cov}(P{=}N) = 1.62$ Å;[24] 1.59(1) and 1.60(1) Å in $[(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{P}][\mathrm{GaCl_4}]$).[6] In contrast to **1**, for **2a–c** and **4** NBO analyses display a localized N−P $p_\pi p_\pi$ double bond as expected for phosphenium ions of the type $[R_2N{=}P{-}X]^+$ ($X = Cl$, N_3).

As shown on numerous occasions, covalently bound azide groups display a *trans*-bent configuration (regarding the P atom, P-N1-N2-N3 180.0) with a N1-N2-N3 angle of 172.2 (2)° and a formally sp^2-hybridized N_α atom (N2-N1-P 121.1(1)°). It is interesting to note that the whole NPNNN chain, including both silicon atoms, lies in-plane (N1-P-N4-Si2 180.0°), which is obviously energetically favored. As the entire Si_2N_4P skeleton in the azido-substituted cation **4** is planar, strong in-plane and out-of-plane delocalization of π electrons is found in the MO and NBO depiction (Figure 4, top), respectively, leading among other things to a fairly short P−NNN distance of 1.673(2) Å, in accord with partial double-bond character. For comparison, the P−NNN distance in 1-azido-*cyclo*-1,3-diphospha-2,4-diazenium with 1.706(3) Å is a typical single bond (Scheme 1, species **C**).[7a]

The NBO Lewis depiction[23] of **4** shows two σ P−N bonds and one $P{-}N_{amino}$ double bond according to Lewis representation **I** in Figure 4 (bottom). However, both lone pairs localized at the N_{azide} atom are strongly delocalized, for example, into the $\pi^*(P{-}N_{amino})$ with a hyperconjugative energy of $\Delta E^{(2)} = 39$ kcal mol^{-1} corresponding to a covalent $\pi(P{-}N_{azide})$ MO bond order of 0.16 (cf. 0.46 for $\pi(P{-}N_{amino})$).

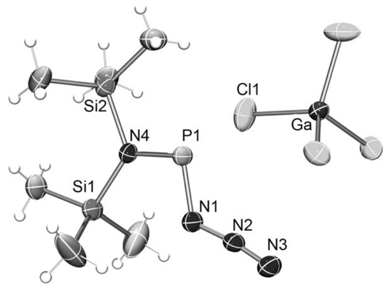

Figure 3. ORTEP view of the molecular structure of **4** from signgle-crystal X-ray diffraction at 173 K. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: P1–N4 1.597(2), P–N1 1.673(2), N1–N2 1.254(2), N2–N3 1.113(3), N4–Si2 1.839(2), N4–Si1 1.851(2), Ga1–Cl3 2.1597(7), Ga1–Cl2 2.1688(4), Ga1–Cl1 2.1825(7), Ga–Cl4 2.1825(7), P1–Cl1 3.3923(6), P1–Cl2 3.7491(3); N4-P1-N1 101.03(9), N2-N1-P1 121.1(1), N3-N2-N1 172.2 (2), N1-P-N4-Si2 180.0, P-N1-N2-N3 180.0.

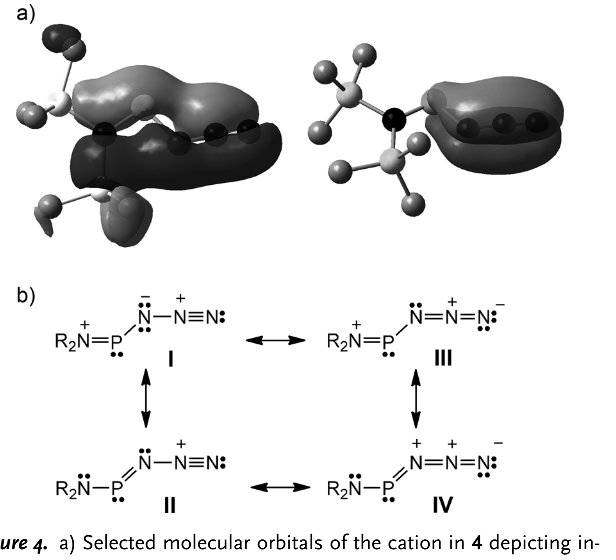

Figure 4. a) Selected molecular orbitals of the cation in **4** depicting in-plane (left) and out-of-plane π bonding (right) along the NPN_3 moiety. b) Lewis representations showing the π bonding along the NPN_3 unit.

Thus, in the VB picture the π bonding can be best described by at least four resonance structures (Figure 4, bottom). This considerable π bonding along the NPNNN unit might be one of the reasons why the Staudinger reaction occurs only at higher temperatures in solution then triggering the decomposition process. Both the σ and π P–N bonds are highly polarized (Table 1).[10] For example, only 24 % of the P=N_{amino} double bond in **4** is localized at the phosphorus atom. Similar values (23–24 %) are found for the σ bonds in **1**, **2a–c**, and **4**.

Table 1: Calculated partial charges [e] and charge transfer Q_{CT}^{tot} [e] in an isolated ion pair of **1**, **2a–c**, and **4**[14b] along with partial charges of the $[(Me_3Si)_2N{=}P{-}X]^+$ ion.[a]

	1	2a	2b	2c	4
$q(P_{salt})$	1.05	1.19	1.21	1.19	1.41
$q(N_{amino,\,salt})$	−1.65	−1.54	−1.51	−1.52	−1.51
$q(X_{salt})$[a]	−0.31	−0.21	−0.20	−0.17	−0.33
$q(P_{cat})$	1.24	1.26	1.20	1.20	1.37
$q(N_{amino,\,cat})$	−1.49	−1.52	−1.46	−1.46	−1.47
$q(X_{cat})$[a]	−0.18	−0.18	−0.18	−0.17	−0.31[e]
Q_{ct}^{tot}[b]	**1**	**2a**	**2b**	**2c**	**4**

[a] Compound **1** was formally considered as the salt $[(Me_3Si)_2N{=}P{-}Cl]^+[Cl]^-$. **1** and **2a–c** X = Cl, **4** X = N_3. [b] Q_{ct}^{tot} = charge transfer with respect to the $[(Me_3Si)_2N{=}P{-}X]^{n+}$ ion (X = Cl for **1**, **2a–c** and X = N_3 for **4**), thus $Q_{cation} = 1 - Q_{CT}^{tot}$. [c] $Q_{CT}^{tot} = q(Cl^-)$. [d] $Q_{CT}^{tot} = 1 + \Sigma q(A_i)$ with the A_i atom of the anion. [e] $q(N_{azide,\,salt}) = -0.72$ versus $q(N_{azide,\,cat}) = -0.70$.

Interestingly, significant cation–anion interactions are detected in the salts **2a–c** but are only very weak in azido species **4**. The localized nonbonding electron pairs available on the $GaCl_4^-$ ion ($Ga_2Cl_7^-$ or $AlCl_4^-$) offer sites for effective electrostatic interaction with the cation and allow ion pairing, which inhibits the reactivity of the phosphenium center. The shortest P···$ClGaCl_3$ distances in **2a** amount to 2.870 and 3.021 Å, which is considerably shorter than the sum of the van der Waals radii (cf. $\Sigma r_{vdw}(P{-}Cl) = 3.70$ and $\Sigma r_{cov}(P{-}Cl) = 2.04$ Å;[24] 3.867(6), 3.976(6) and 4.020(6) Å in $[(iPr_2N)_2P][GaCl_4]$), indicating strong van der Waals interactions.[6] Similarly close contacts are found in **2b** and **2c** (2.8–3.1 Å), whereas only very weak van der Waals interactions between the ions can be assumed for **4**, with four P···Cl distances between 3.392–3.749 Å. Nevertheless, the existence of such weak cation–anion interactions is supported by a small but noticeable charge transfer from the anion to the cation (Table 1). Compound **1** can also be included into these considerations, as **1** can formally be regarded as $[(Me_3Si)_2N{=}P{-}Cl][Cl]$. The largest charge transfer is computed for **1** ($Q_{CT}^{tot} = 0.66\,e$) and decreases for **2a** (0.19 e) and **4** (0.07 e). Thus the azidophosphenium ion in **4** can be considered as an almost bare $[(Me_3Si)_2N{=}P{-}N_3]^+$ ion.

In summary, from the mixture of $(Me_3Si)_2NPCl_2$ and $GaCl_3$ at low-temperatures, for the first time an amino(chloro)phosphenium ion has been isolated in **2a**, **2b**, and **2c** and structurally characterized; however, it decomposes under release of Me_3SiCl at ambient temperatures, forming an unusual hitherto unknown ionic liquid of the type $[Me_3Si{-}N{\equiv}P][GaCl_4]$ that is stable at room temperature. Reaction of **2a** with Me_3SiN_3 affords **4** bearing an highly reactive and labile azidophosphenium ion $[(Me_3Si)_2N{=}P{-}N_3]^+$, which is the first compound with an azide group attached to a two-coordinate phosphorus center. The $[(Me_3Si)_2N{=}P{-}N_3]^+$ ion can formally be regarded as phosphapentacenium ion with a planar molecule skeleton, indicating strong delocalization of π electron density. This cation is only stable at temperatures below −40 °C. Upon a temperature increase, it does not cyclize to give a tetrazaphosphole but decomposes in a Staudinger reaction, yielding oligomeric PN compounds. It can be assumed that kinetic protection is needed to support cyclization in preference to a Staudinger reaction.

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[14] The Supporting Information includes: a) Experimental details, properties, and structural data; b) a summary of the NBO and MO study; applied level of theory is pbe1pbe/aug-cc-pVDZ.

CCDC 878830 (**1**), CCDC 878831 (**2a**), and CCDC 878834 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[26] The positions of the cation and the anion in **2a** and **2c** were found to be disordered, as is the position of one cation in **2b**. For details, see the Supporting Information.