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P/N Cations

A Cationic Cyclic Phosphorus(III) Azide**

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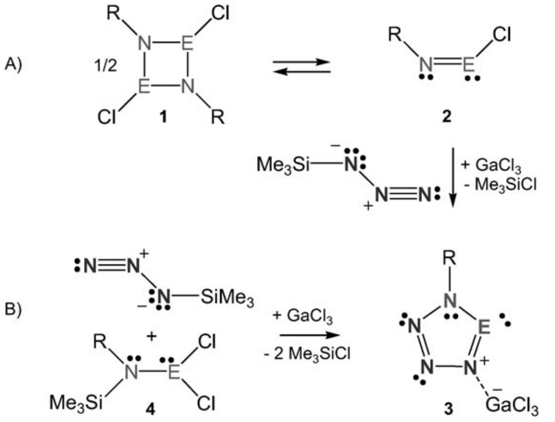
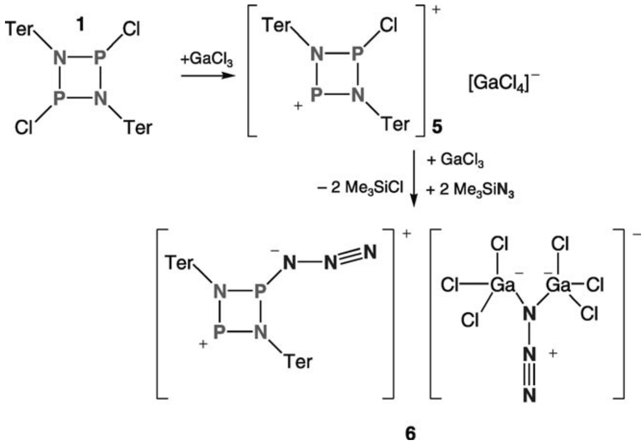
Recently we have become interested in $GaCl_3$-assisted [3+2] cycloaddition,[1] which led to the isolation of the first binary phosphorus/nitrogen five-membered heterocycles (e.g. tetrazaphospholes[2] and triazadiphospholes[3]) and arsenic/nitrogen five-membered heterocycles (e.g. tetrazarsole[4]). Access to tetrazaphospholes and -arsoles was gained by two different synthetic approaches, both triggered by the Lewis acid $GaCl_3$ (Scheme 1): A) The reaction of *cyclo*-1,3-dipnicta-2,4-diazane **1** with Me_3SiN_3 in the presence of $GaCl_3$ (Scheme 1, synthetic route A with pnictogen E = As, P and R = Mes* = 2,4,6-$tBu_3C_6H_2$) led to tetrazaphospholes and -arsoles **3** via monomeric iminopnictogen species **2**. B) The same pnictogen heterocycle **3** is obtained in the reaction of Me_3SiN_3 and $Mes^*N(SiMe_3)ECl_2$[5] when $GaCl_3$ is added. In this case, the reactive species **2** is generated in situ by $GaCl_3$-assisted elimination of Me_3SiCl.[4]



Scheme 1. Synthetic routes to binary Group 15 heterocycles (E = As, P; R = bulky groups such as terphenyl = 2,6-$Mes_2C_6H_3$ or Mes* = 2,4,6-$tBu_3C_6H_2$).

To study the effect of the bulky group on both synthetic routes according to Scheme 1, the supermesityl group (Mes*) was replaced with the terphenyl group[6] (terphenyl = Ter = 2,6-$Mes_2C_6H_3$, Mes = 2,4,6-$Me_3C_6H_2$) for kinetic stabilization of the iminophosphane (RN=PCl). For route A this substitution led to an astonishingly different reaction channel but not for route B. We report herein 1) the first structural characterization of a 1-chloro-*cyclo*-1,3-diphospha-2,4-diazenium cation **5**, 2) the unexpected formation of the intriguing energetic 1-azido-*cyclo*-1,3-diphospha-2,4-diazenium-μ-azido-hexachloridodigallate **6** (Scheme 2) when synthetic route A is applied, and 3) the formation of a tetrazaphosphole **3** according to synthetic route B (Scheme 1).



Scheme 2. Synthesis of **5** and **6**.

Burford et al. assumed that depending on the steric strain of residues R and R′ in derivatives of $[RPNR']_2$, either the dimer or the monomer can be observed.[7] For instance, Mes*NPCl is observed as an iminophosphane monomer in the solid state,[8] while slightly smaller substituents such as 2,6-diisopropylphenyl allow dimerization. In the case of monomeric Mes*NPCl, addition of $GaCl_3$ results in $[Mes^*NP]^+$-$[GaCl_4]^-$,[7b] while trimers and oligomers are formed when $GaCl_3$ is added to dimers with smaller substituents.[7c] These results have prompted us to utilize larger, more sterically hindered groups that are based upon the terphenyl substituent, which has been used to stabilize a variety of low-coordinate main-group-element species.[6]

Compound **1** (Scheme 2) is stable as a dimer in dichloromethane at ambient temperature for several days, as shown by ^{31}P NMR studies ($\delta(^{31}P) = 226.8$ (*cis*), 263.5 ppm (*trans* isomer)).[9] However, after adding a solution of $GaCl_3$ in dichloromethane, the ^{31}P NMR spectra indicated rapid, quantitative formation of the new phosphorus species **5** within ten minutes at −40 °C (Scheme 2).[10] Furthermore, the

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initially colorless solution turned dark red. Two new phosphorus resonances belonging to only one species were observed in the typical range for tricoordinated and dicoordinated phosphorus(III) compounds (doublets at $\delta = 203.6$ (P1) and 366.6 ppm (P2), $^{2}J(^{31}P^{31}P) = 53.0$ Hz; cf. $\delta = 176.6$ and 365.7 ppm, $^{2}J(^{31}P^{31}P) = 73.2$ Hz in 1-chloro-2,4-bis-*tert*-butyl-*cyclo*-1,3-diphospha-2,4-diazeniumtetrachloridoaluminate[11]). The solvent volume was then reduced in vacuo to incipient crystallization, and the solution was stored at −25 °C for ten hours, resulting in the deposition of red crystals of **5** (yield: 96 %). Single crystal X-ray studies revealed a 1-chloro-2,4-bis(terphenyl)-*cyclo*-1,3-diphospha-2,4-diazeniumtetrachloridogallate salt (Figure 1), the first fully characterized 1-chloro-*cyclo*-1,3-diphospha-2,4-diazenium salt that is not stabilized by any Lewis base.[9,12] Interestingly, upon addition of $GaCl_3$, neither monomerization nor any transformation to trimeric or oligomeric species was observed.

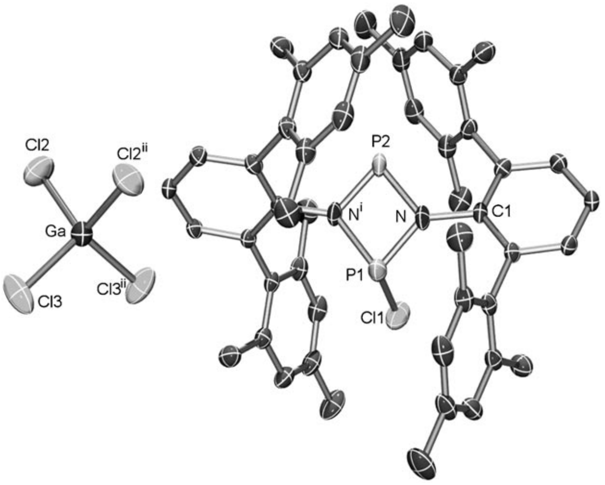


Figure 1. ORTEP drawing of the molecular structure of **5**. Thermal ellipsoids are set at the 50 % probability level (at 173 K); hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–N 1.664(2), P1–N^{i} 1.813(2), P2–N^{i} 1.614(2), P2–N 1.736(2), P1–Cl1 1.986(2), N–C1 1.435(2), Ga–Cl3 2.1507(8), Ga–Cl2 2.1834(9), P1–P2 2.555(2); C1-N-P1 136.9(2), C1-N-P2 124.7(2), P1-N-P2 97.4(1), N-P1-Cl1 101.2(1). Symmetry codes: (i) $-x, y, -z+1/2$; (ii) $-x, y, -z+3/2$.[10]

The first observation of a monochlorodiphosphadiazenium cation ($R_2N_2P_2Cl^+$, R = *t*Bu) in a detailed ^{31}P NMR study was reported by Cowley et al. in the reaction of the corresponding *cyclo*-diphosphadiazane with $AlCl_3$, independent of reaction stoichiometry.[11] Later, Burford et al. assumed 1-halo-2,4-di(aryl)-*cyclo*-1,3-dipnicta-2,4-diazenium cations as intermediate species in the reaction of $[RNPX]_2$ (R = 2,6-dimethylphenyl, 2,6-diisopropylphenyl; X = Cl, Br) with GaX_3, which led to trimeric species $[RNPX]_3$ by GaX_3-induced heterocycle expansion.[7a,b]

Despite the surprising formation of **5**, we tried the $GaCl_3$-assisted [3+2] cycloaddition and added Me_3SiN_3 (2 equiv) and another equivalent of $GaCl_3$ (Scheme 2). Again a clean reaction with only one final product (**6**) was observed ($\delta(^{31}P) = 197.0$, 349.3 ppm). Removal of the solvent and the by-product Me_3SiCl resulted in a red crystalline solid (yield 93 %). X-ray quality crystals were obtained from a saturated CH_2Cl_2 solution of **6**, and the single crystal X-ray study revealed an intriguing 1-azido-*cyclo*-1,3-diphospha-2,4-diazenium-μ-azidohexachlorido-digallate, the first fully characterized cyclic phosphorus(III) azide cation.[13] Also, the μ-azidohexachloridodigallate(−1) anion has not been described to date.

Both **5** and **6** are air- and moisture-sensitive but stable in argon over a long period as solids and in CH_2Cl_2. Azide **6** is neither heat- nor shock-sensitive. The dark red color of **5** and **6** vanishes rapidly when traces of H_2O are present. Compounds **5** and **6** are easily prepared in bulk and are infinitely stable when stored in a sealed tube and kept at −25 °C in the dark.[10e] Compound **5** is thermally stable to over 210 °C, while **6** can be heated up to 140 °C, which is quite astonishing for a phosphorus azide. Decomposition starts at these temperatures.

X-ray studies of crystals from the reaction sequences illustrated in Scheme 2 revealed salts **5** and **6** with a *cyclo*-1,3-diphospha-2,4-diazenium cation kinetically protected in the pocket formed by the terphenyl groups (Figures 1 and 2). Compound **5** crystallizes in the monoclinic space group *C*2/*c* with four units per cell, while **6** crystallizes in the monoclinic space group $P2_1/c$ also with four units per cell.[10]

As depicted in Figures 1 and 2, the P_2N_2 rings are almost planar (deviation from planarity: $\sphericalangle$(N-P1-N-P2) = 2.29(7)° in **5**, $\sphericalangle$(N-P1-N-P2) = −5.5(1)° in **6**), but slightly distorted with two longer P–N bonds (**5**: $d(P1–N^{i}) = 1.813(2)$ and d(P2–

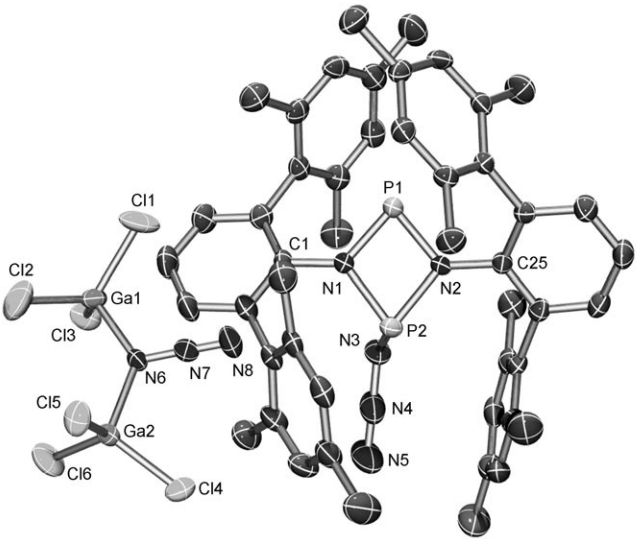
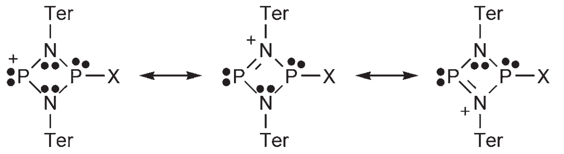


Figure 2. ORTEP drawing of the molecular structure of **6**. Thermal ellipsoids are set at the 50 % probability level (at 173 K); hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–N1 1.664(3), P1–N2 1.681(3), P1–P2 2.608(1), P2–N1 1.773(3), P2–N2 1.784(2), P2–N3 1.706(3), N1–C1 1.433(4), N2–C25 1.439(4), N3–N4 1.258(4), N4–N5 1.142(4), Ga1–N6 1.987(3), Ga1–Cl1 2.144(1), Ga1–Cl3 2.156(1), Ga1–Cl2 2.160(1), Ga2–N6 1.974(3), Ga2–Cl6 2.145(1), Ga2–Cl4 2.148(2), Ga2–Cl5 2.154(1), N6–N7 1.259(4), N7–N8 1.123(4); Ga2-N6-Ga1 125.5(1), N8-N7-N6 179.3(4), N1-P1-N2 84.6(1), N1-P2-N2 78.6(1), C1-N1-P1 131.0(2), P1-N1-P2 98.7(1), C25-N2-P1 127.4(2), P1-N2-P2 97.6(1), N5-N4-N3 174.0(5).[10]

N) = 1.736(2); **6**: d(P2–N1) = 1.773(3) and d(P2–N2) = 1.784(2) Å) and two considerably shorter P–N bonds (**5**: d(P1–N) = 1.664(2) and d(P2–N^i) = 1.614(2); **6**: d(P1–N1) = 1.664(3) and d(P1–N2) = 1.681(3) Å; cf. 1.656(2) Å in trimeric $[R_3N_3P_3Cl_2]^+[GaCl_4]^-$).[7c] The short P–N bonds between 1.61 and 1.68 Å are substantially shorter than the sum of the covalent radii (d_{cov}(N–P) = 1.8, d_{cov}(N=P) = 1.6 Å),[14] which indicates partial double-bond character for these P–N bonds (Scheme 3). For comparison, the P–NNN distance of 1.706(3) Å represents a typical single bond.[15] As shown on numerous occasions,[15,16] covalently bound azide groups such as P–NNN display a *trans*-bent configuration (relative to the P atom); **6** has a N5-N4-N3 bond angle of 174.0(5)°, while the bridging azide group attached to the two $GaCl_3$ moieties is almost linear (∢(N6-N7-N8) = 179.3(4)°).



Scheme 3. Lewis representation of *cyclo*-1,3-diphospha-2,4-diazenium cations **5** (X = Cl) and **6** (X = N_3).

Finally, we wanted to find out what happens when $GaCl_3$ is added to **4** with and without the 1,3-dipole molecule Me_3SiN_3 (Scheme 1, synthetic route B). When $GaCl_3$ is added to a solution of **4**, elimination of Me_3SiCl takes place. The formation of one phosphorus species, which is only stable in solution at low temperatures, is indicated by ^{31}P NMR spectroscopy ($\delta(^{31}P) = 147.5$ ppm ($\Delta\nu_{1/2} \approx 400$ Hz)) were observed. Presumably, after Me_3SiCl elimination TerN=PCl is formed, which reacts with $GaCl_3$ under chloride abstraction to form the labile $[TerN{=}P]^+[GaCl_4]^-$. The formation of tetrazaphosphole **3** when Me_3SiN_3 is added confirms the existence of $[TerN{=}P]^+[GaCl_4]^-$.

Then again, when a solution of Me_3SiN_3 was added to a solution of **4** in CH_2Cl_2 at −40 °C, no reaction occurred. Only upon adding $GaCl_3$ was an instantaneous reaction observed, as shown by ^{31}P NMR spectroscopy studies, resulting again in the formation of tetrazaphosphole **3**, the only final product. The formation of **3** was unequivocally demonstrated by X-ray crystallography (Figure 3) and NMR spectroscopy. The first tetrazaphosphole has only recently been introduced with a supermesityl group as stabilizing unit.[3,10] Interestingly, **3** and **6** possess the same molecular formula unit, and hence can be regarded as constitutional isomers.

In summary, **5** and **6** represent novel binary cyclic P^{III}/N four-membered heterocyclic cations with di- and tricoordinated P atoms and a delocalized π bond along the $NP^{(+)}N$ unit (Scheme 3). Obviously, starting the reaction from a cyclic precursor leads to chloride abstraction triggered by the action of $GaCl_3$, and hence to salt **5** or, when Me_3SiN_3 is present, to **6**. Starting from a noncyclic disguised dipolarophile such as $TerN(SiMe_3)PCl_2$ gives the expected formal [3+2] cyclization product **3** when $GaCl_3$ is present (Scheme 1). In contrast to Mes*N=PCl, TerN=PCl forms a stable dimer in the solid state and in solution. Since both bulky groups (Mes* and Ter) possess similar steric strain, a better electronic stabilization in monomeric Mes*N=PCl can be assumed.[10d] However, steric influences may play a role: the terphenyl groups are bulky but anisotropic, and the interleaving conformation shown in Figures 1 and 2 will certainly help to reduce the steric strain. Compound **6**, which was isolated by a formal $GaCl_3$-assisted Cl/N_3 exchange in **5**, represents an intriguing salt with an azide group in the cation and in the anion.

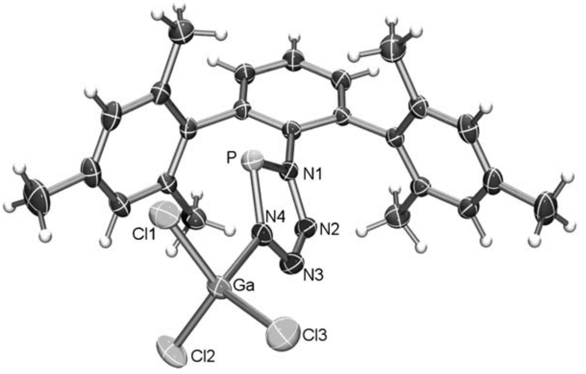


Figure 3. ORTEP drawing of the molecular structure of **3**. Thermal ellipsoids are set at the 50% probability level (at 173 K). Selected bond lengths [Å] and angles [°]: P–N4 1.641(1), P–N1 1.665(1), N1–N2 1.371(2), N1–C1 1.447(2), N2–N3 1.273(2), N3–N4 1.370(2), N4–Ga 1.988(1); N4-P-N1 87.76(6), N2-N1-P 114.28(9), N3-N2-N1 111.0(1), N2-N3-N4 112.7(1), N3-N4-P 114.27(9), N3-N4-Ga 117.85(9), P-N4-Ga 126.37(7).

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[10] See the Supporting Information: a) chemical shifts (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}); b) crystal data; c) full description of the experimental data, technique, and details; d) Natural bond orbital (NBO) partial charge calculations of a series of $R{-}N{=}P^{+}$ species; e) Although **5** and **6** are stable up to 210 and 140 °C, respectively, they slowly decompose when stored at RT.

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