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$GaCl_3$-Assisted Cyclization Reactions in Hypersilyl(trimethylsilyl)aminodichlorophosphine

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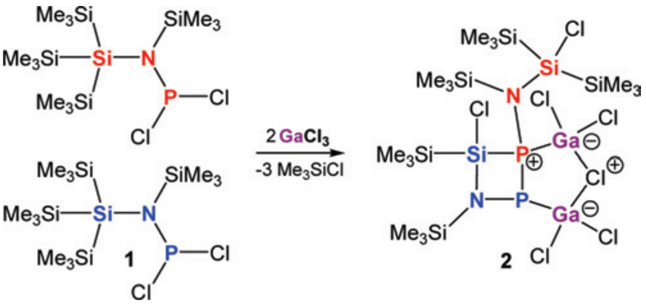
Hypersilyl(trimethylsilyl)aminodichlorophosphine, (hyp)N($SiMe_3$)PCl_2, was treated with $GaCl_3$, which resulted in the formation of an interesting novel bicycle, composed of a four-membered $SiNP_2$ ring and a five-membered P_2Ga_2Cl ring. In the presence of Me_3SiN_3, the same reaction provided access to a *cyclo*-2-phospha-4-sila-1,3-diazenium tetrachlorogallate. The free chloro-*cyclo*-phosphasiladiazane was obtained by the addition of nucleophilic bases.

Lewis-acid-assisted reactions such as [3 + 2] cyclizations, methyl/halogen exchange, or ring extension have attracted considerable interest in the last years.[1,2] With the help of such reactions, it was possible to generate a series of low-coordinated P^{III}/N and As^{III}/N heterocycles and cationic PN species bearing reactive multiple E−N bonds (E = P, As). Recent work in our group has focused on a new strategy for the ostensible generation and stabilization of cyclic and linear P^{III}/N cations utilizing both Lewis-acid-assisted reactions and nonaryl bulky groups such as the hypersilyl group [$(Me_3Si)_3Si$ = hyp]. The hypersilyl group was first introduced by Gilman and Harrell in 1966,[3] but tris(trimethylsilyl)silylamine and its lithium salt were not reported until 1993.[4]

Scheme 1. Reaction of **1** with $GaCl_3$ Leading to the Formation of Bicycle **2**



In the present work, we report on the preparation of hitherto unknown hypersilyl(trimethylsilyl)aminodichlorophosphine, (hyp)N($SiMe_3$)PCl_2 (**1**), which seemed to be an attractive candidate for a $GaCl_3$-assisted Me_3SiCl elimination, resulting in the formation of the kinetically stabilized hypersilylated iminochlorophosphine, (hyp)N═PCl. However, instead of (hyp)N═PCl, a surprising heterobicycle, involving only heteroatoms, was formed (Scheme 1).

Aminophosphine **1** is easily prepared in a two-step synthesis starting from *N*-hypersilyl-*N*-(trimethylsilyl)amine: (i) The lithium amide is formed in situ by the addition of *n*-BuLi in *n*-hexane at 0 °C. (ii) The reaction of lithium amide with PCl_3 at −30 °C leads to **1** in good yields (86%). The structure of **1** was determined from an X-ray crystallographic study of colorless monoclinic crystals grown from an *n*-hexane solution at −40 °C. The observed molecular structure (Figure 1) exhibits the expected geometry, with a short P−N distance [1.6451(9) Å; cf. the sum of the covalent radii $d_{cov}(N-P) = 1.8$ and $d_{cov}(N{=}P) = 1.6$ Å],[5] indicating partial double-bond character for this P−N bond due to hyperconjugation.[1,6]

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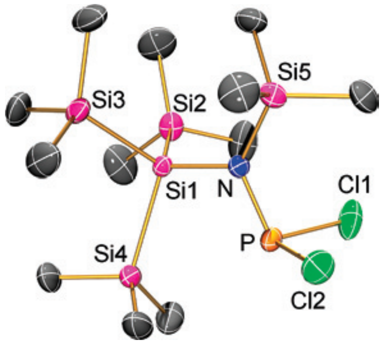


Figure 1. ORTEP drawing of the molecular structure of **1** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). See the text for values of selected metrical parameters.

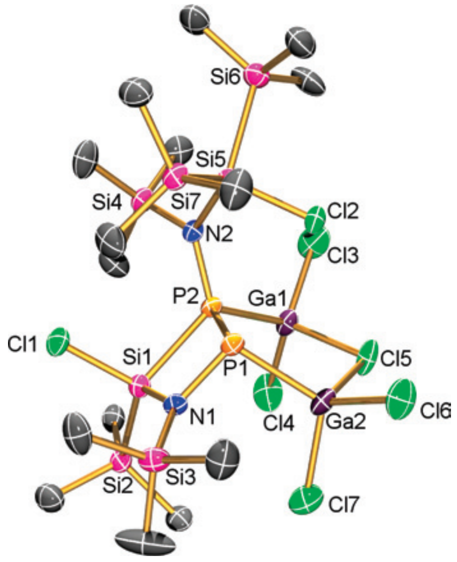
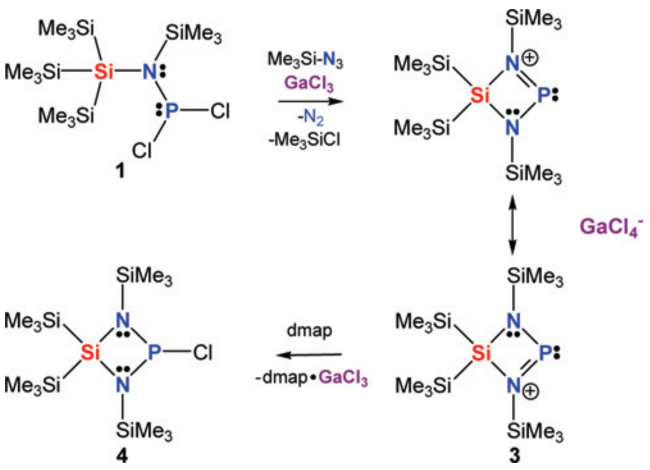


Figure 2. ORTEP drawing of the molecular structure of **2** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity). See the text for values of selected metrical parameters.

The reaction of **1** and $GaCl_3$ (1:1 mixture; Scheme 1) over the course of 4 h at −25 °C in CH_2Cl_2 gave a new compound with two ^{31}P NMR signals at 27.0 and 65.2 ppm [$^{1}J(^{31}P-^{31}P) = 192$ Hz] as the only product (isolated yield of compound **2** = 98%). The existence of two strongly coupled ^{31}P NMR signals clearly demonstrated the presence of an unexpected P−P bond. The product **2** was crystallized from CH_2Cl_2 at −80 °C, and an X-ray diffraction study confirmed the formation of a P−P bond and a surprising bicycle composed of five different heteroatoms (Figure 2). We do want to stress that this reaction can be reproduced always in high yields (>95%). To the best of our knowledge, neither a four-membered $SiNP_2$ nor a five-membered P_2Ga_2Cl cycle has been reported before. Furthermore, both structural motifs are unknown. Obviously, upon the addition of $GaCl_3$, the elimination of Me_3SiCl is triggered[1] and a formal Me_3Si/chlorine exchange[1g] occurs at the hypersilyl group.

Scheme 2. Reaction of **1** with a 1:1 Mixture of $GaCl_3$ and Me_3SiN_3 and the Proposed Reaction Mechanism Leading to the Formation of **3** and **4**, Respectively (after the Addition of a Base Such as dmap)



Compound **2**·CH_2Cl_2 crystallizes in the orthorhombic space group $Pna2_1$ with $Z = 4$. The Ga1−P2 and Ga2−P1 distances are 2.366(2) and 2.369(2) Å, respectively, while the distances P1−N1 and P2−N2 are significantly different [1.763(6) vs 1.677(8) Å]. The P1−P2 bond length is 2.217(2) Å, in accordance with the sum of the covalent radii (2.2 Å;[5] cf. 2.23−2.28 Å in azatriphosphabutadienes[7a] or 2.1374(9) Å in the three-membered $P_2C(R^1)MoR^2$ complex, where R^1 = adamantyl and R^2 = N(Ar)-*i*-Pr).[7b] The four-membered $SiNP_2$ ring is almost planar [deviation from planarity 6.6(2)°], while the five-membered P_2Ga_2Cl ring is nonplanar with torsion angles between 20 and 35°. The dihedral angle (N1−P1−P2−Ga1) between both rings is 112.6(2)°. The P1 atom adopts a trigonal-pyramidal coordination geometry [Σ(P1) = 292.2°], P2 a distorted tetrahedral geometry, and both nitrogen atoms are in a nearly trigonal-planar environment [Σ(N) = 358.1° (N1) and 360.0° (N2)]. The Si1−P2−P1 angle is rather small at 76.1(1)°. The N−P1−P2 angle is 89.5(2)°.

Despite the surprising formation of **2** in the reaction of **1** with $GaCl_3$, we carried out the same reaction in the presence of the 1,3 dipole molecule Me_3SiN_3. The idea was to cyclize iminochlorophosphine, (hyp)N═PCl (formed in situ after $GaCl_3$ addition), with Me_3SiN_3 yielding a tetrazaphosphole $GaCl_3$ adduct attached to a hypersilyl group.[1] The reaction of **1**, Me_3SiN_3, and $GaCl_3$ (1:1:1 mixture) over the course of 1 h at 0 °C in CH_2Cl_2 gave again a new unexpected compound (**3**) with a ^{31}P NMR signal at 394.4. ppm as the major product (Scheme 2). This phosphorus resonance was observed in the range typical for dicoordinated cationic phosphorus(III) compounds (cf. 365.7 ppm in 1-chloro-2,4-bis-*tert*-butyl-*cyclo*-1,3-diphospha-2,4-diazenium tetrachloridoaluminate).[11]

The solvent volume was then reduced to incipient crystallization in vacuo, and the solution was stored at −20 °C for 10 h, resulting in the deposition of colorless crystals of **3** (isolated yield: 91%). Single-crystal X-ray studies revealed a 1,3,4,4-tetrakis(trimethylsilyl)-*cyclo*-2-phospha-4-sila-1,3-diazenium tetrachlorogallate (Figure 3). Interestingly, treating

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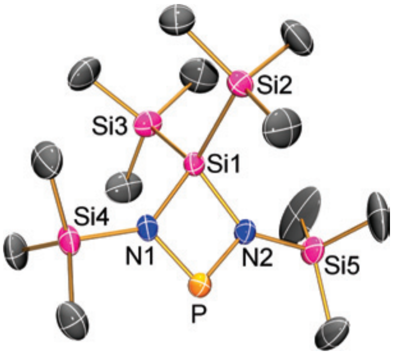

Figure 3. ORTEP drawing of the molecular structure of **3** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms and anion omitted for clarity). See the text for values of selected metrical parameters.

3 with bases such as tetrahydrofuran (THF) or 4-(dimethylamino)pyridine (dmap) affords neutral *cyclo*-phosphasiladiazane **4** and the THF·$GaCl_3$ and dmap·$GaCl_3$ adducts, respectively (Scheme 2). Because the dmap·$GaCl_3$ adduct precipitates in *n*-hexane, it is easily separated from neutral *cyclo*-phosphasiladiazane by filtration. The unexpected formation of **3** may be explained by an initial Staudinger reaction, followed by a Me_3SiCl elimination and an intramolecular cyclization step (Scheme 2).

cyclo-Phosphasiladiazanes[9] are known and may be synthesized in a variety of ways such as metal chloride induced cyclization of bis[bis(trimethylsilyl)amino]thiophosphoryl chlorides and the interactions of dimethyldichlorosilane with dilithiobis(amido)phosphines and of aminodichlorophosphines with dilithiobis(amido)dimethylsilanes.[10] All of these reactions lead to product mixtures, requiring additional separation steps. The previously reported displacement of $PbCl_2$ by PCl_3 from *cyclo*-plumbasiladiazane seems to be a much cleaner synthesis for *cyclo*-phosphasiladiazanes.[11] The new method presented here avoids the synthesis of plumbasiladiazane and represents a very clean, high-yielding approach.[12]

The only X-ray structure determination of a *cyclo*-2-phospha-4-sila-1,3-diazenium salt $[Me_2Si(N\text{-}t\text{-}Bu)_2P^+AlC1_4^-]$ was reported by Veith et al. with *t*-Bu groups attached to the nitrogen atoms.[9b] In accordance with that structural report, the local C_{2v} symmetry of the planar cation is slightly distorted with two short P−N distances [$d(\mathrm{P{-}N1}) = 1.639(1)$ Å, $d(\mathrm{P{-}N2}) = 1.640(1)$ Å; cf. $Me_2Si(N\text{-}t\text{-}Bu)_2P^+AlC1_4^- = 1.633(3)$ and $1.619(7)$ Å][9b] and two rather long Si−N bonds [$d(\mathrm{Si{-}N1}) = 1.807(1)$ Å and $d(\mathrm{Si{-}N2}) = 1.810(1)$ Å]. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$.

In conclusion, this work has demonstrated the successful use of hitherto unknown silylated aminodichlorophosphine **1** in $GaCl_3$-assisted reactions yielding an interesting fully characterized novel bicycle (**2**) composed of five different heteroatoms. Moreover, we present here an easy, high-yielding (>90%) synthetic procedure and full characterization of a new *cyclo*-2-phospha-4-sila-1,3-diazenium tetrachlorogallate (**3**) when Me_3SiN_3 is added in addition to $GaCl_3$. Furthermore, neutral *cyclo*-phosphasiladiazanes were synthesized by the addition of bases to **3**.

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Supporting Information Available: Experimental details, a table of crystal data, list of selected bond lengths and angles, and crystallographic information files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) **2**: To a stirred solution of **1** (0.873 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise $GaCl_3$ (0.387 g, 2.2 mmol) in CH_2Cl_2 (10 mL) at −60 °C over a period of 15 min. The resulting red solution is stirred at −25 °C for 4 h and is then warmed to ambient temperatures over a period of 1 h, resulting in a pale-orange solution. Removal of the solvent and drying in vacuo yields 1.767 g (1.96 mmol, 98%) of **2** as a pale-yellow solid. Mp: 82 °C (dec). Anal. Calcd (found): C, 20.02 (19.58); H, 5.04 (5.05); N, 3.11 (2.80). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ 65.2 (d, $^1J(^{31}P{-}^{31}P) = 192$ Hz), 24.2 −30.4 (m). $^{29}Si\{^1H\}$ NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ −10.8, −6.9, −3.3, 15.3, 16.0, 32.7. ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 0.32 (dm, 9H, $J(^{31}P{-}^1H) = 1.7$ Hz, $Si(C\mathit{H}_3)_3$), 0.36 (m, 9H, $Si(C\mathit{H}_3)_3$), 0.43 (m, 9H, $Si(C\mathit{H}_3)_3$), 0.50 (m, 9H, $Si(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ −0.98 (dm, $J(^{31}P{-}^{13}C) = 1.5$ Hz, $Si(\mathit{C}H_3)_3$), 0.02 (m, $Si(\mathit{C}H_3)_3$), 0.47 (dm, $J(^{31}P{-}^{13}C) = 7.1$ Hz, $Si(\mathit{C}H_3)_3$), 2.00 (dm, $J(^{31}P{-}^{13}C) = 8.1$ Hz, $Si(\mathit{C}H_3)_3$), 3.72 (dm, $J(^{31}P{-}^{13}C) = 3.5$ Hz, $Si(\mathit{C}H_3)_3$. Raman (10 mW, 25 °C, 705 scans, cm^{-1}): 2960 (3), 2901 (10), 2758 (1), 1408 (1), 1256 (1), 839 (1), 797 (1), 749 (1), 695 (1), 630 (2), 540 (1), 472 (1), 397 (1), 327 (1), 295 (1), 235 (1), 166 (2). **3**: To a stirred solution of **1** (2.184 g, 5.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise Me_3SiN_3 (0.634 g, 5.5mmol) in CH_2Cl_2 (5 mL) at −40 °C over a period of 5 min. To the resulting colourless solution was added dropwise $GaCl_3$ (0.968 g, 5.5 mmol) in CH_2Cl_2 (10 mL) at −40 °C over a period of 40 min. The resulting orange solution is warmed to 0 °C over a period of 1 h. After stirring for 30 min, the solution was concentrated in vacuo to incipient crystallization. Storage at −25 °C over a period of 10 h resulted in the deposition of colorless crystals. Removal of the supernatant by syringe and drying in vacuo yielded 2.697 g (4.56 mmol, 91%) of **3** as a colorless, crystalline solid. Mp: −101 °C (dec). Anal. Calcd (found): C, 24.37 (23.82); H, 6.14 (6.06); N, 4.74 (5.19). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2, 121.5 MHz): δ 394.4. ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): δ −12.5 (m, $Si(\mathit{Si}(CH_3)_3)_2$), 14.5 (m, $^2J(^{29}Si{-}^{31}P) = 2.8$ Hz, $N\mathit{Si}(CH_3)_3$)), 74 (m, $\mathit{Si}(Si(CH_3)_3)_2$). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): δ 0.39 (s, 18H, $Si(Si(C\mathit{H}_3)_3)_2$), 0.44 (d, 18H, $^4J(^1H{-}^{31}P) = 0.8$ Hz, $NSi(C\mathit{H}_3)_3$). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): δ −1.86 (s, $Si(Si(\mathit{C}H_3)_3)_2$), 1.76 (d, $^3J(^{13}C{-}^{31}P) = 4.7$ Hz, $NSi(\mathit{C}H_3)_3$). Raman (150 mW, 25 °C, 451 scans, cm^{-1}): 3068 (1), 2961 (6), 2900 (10), 2787 (1), 2733 (1), 1416 (2), 1267 (2), 1094 (2), 890 (4), 831 (4), 755 (3), 703 (3), 642 (5), 628 (6), 375 (3), 346 (7), 322 (4), 218 (4), 167 (8), 156 (8). MS (FAB^+, Cs, 20 keV, *p*-NBA matrix): 73 $[Si(CH_3)_3]^+$, 381 $[M_{cation} - Si(CH_3)_3 + 2H]^+$, 399 $[M_{cation} + Cl - H]^+$.