Phosphorus Ring Systems

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Low-Temperature Isolation of the Bicyclic Phosphinophosphonium Salt $[Mes^*_2P_4Cl][GaCl_4]$**

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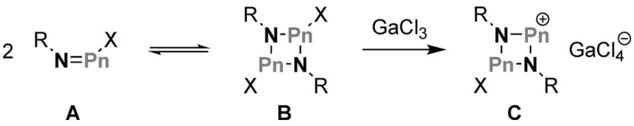
Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

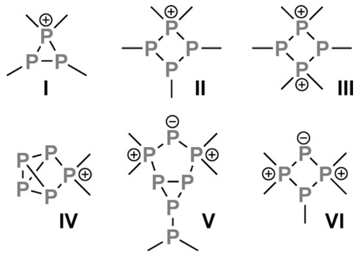
Abstract: *The reaction of $[ClP(\mu\text{-}PMes^*)]_2$ (**1**) with the Lewis acid $GaCl_3$ yielded a hitherto unknown tetraphosphabicyclo-[1.1.0]butan-2-ium salt, $[Mes^*P_4(Cl)Mes^*][GaCl_4]$ (**3**-$[GaCl_4]$), which incorporates a positively charged phosphonium center within its bicyclic P_4 scaffold. The formation of the title compound was studied by means of low-temperature NMR experiments. This led to the identification of an intermediate cyclotetraphosphenium cation, which was trapped by reaction with dimethylbutadiene (dmb). All of the compounds were fully characterized by experimental and computational methods.*

Ring systems composed of Group 15 elements (pnictogens, Pn) are a fascinating aspect of main-group chemistry.[1–3] In particular, (pseudo)halogen-substituted cyclic dipnictadiazanes (**B**, Scheme 1) proved to be versatile starting materials for the synthesis of (transient) compounds with NPn multiple bonds (for example, **A**) generated by cycloreversion reactions,[4–8] larger ring systems by subsequent cycloaddition reactions or ring expansion,[4,9,10] as well as cationic species which are formed by abstraction of halogen atoms (**C**).[11–15]

In this regard, we are currently interested in the reactivity of analogous ring systems solely based on phosphorus (that is, $[XP(\mu\text{-}PR)]_2$) to evaluate possible reaction routes to similar, unprecedented phosphorus species. For example, reports of cationic phosphorus ring systems include phosphinophosphonium frameworks (**I**–**III**, Scheme 2),[16–20] related cyclic and bicyclic polyphosphorus frameworks (**V**, **VI**)[21] and, in a wider sense, several cluster cations (**IV**),[22–25] as well as bicyclic systems with cationic substituents.[25,26] However, cyclic tetraphosphenium cations similar to **C** have not yet been reported.



Scheme 1. A formal equilibrium between monomeric iminopnictanes (**A**; Pn = P, As; X = (pseudo)halogen) and cyclodipnictadiazanes (**B**; Pn = P, As, Sb, Bi) depending on the steric strain of the substituent R gives rise to different reaction pathways, including formation of cyclodipnictadiazenium salts (**C**; Pn = P, As, Sb, Bi).



Scheme 2. Structural motifs found in cationic phosphorus ring systems.

Only recently we developed a synthesis for dichlorocyclotetraphosphane $[ClP(\mu\text{-}PMes^*)]_2$ (**1**, Mes* = 2,4,6-tri-*tert*-butylphenyl),[27] enabling us to study the reactivity of this little-known class of compounds.[28,29] Our approach focuses on the selective functionalization of the P_4 scaffold by substitution or abstraction of the Cl atoms, which is in contrast to the widely used method of direct functionalization of white phosphorus (P_4), for example, by use of Lewis acids and bases, transition metals, or singlet carbenes such as *N*-heterocyclic carbenes (NHCs) and cyclic alkylaminocarbenes (CAACs).[30–33]

Whereas the chemistry of cyclophosphanes with carbon- or nitrogen-based substituents has been well investigated,[34] no information about the reactivity of halogen substituted cyclotetraphosphanes has been reported. Herein, we wish to present results concerning the reaction of **1** with the Lewis acid $GaCl_3$.

In analogy to the synthesis of cyclodipnictadiazenium salts (**C**), a colorless dichloromethane solution of **1**·C_6H_5F was treated with $GaCl_3$ at low temperatures. Instantly, a deep-red coloration was observed. In situ ^{31}P NMR spectroscopy revealed formation of a transient cyclotetraphosphenium intermediate (**2**$^+$, Scheme 3), as indicated by a broadened, significantly downfield-shifted AM_2X spin system (358.9, 145.9, 88.6 ppm). The highest partial concentration of the intermediate was detected directly at the beginning of the

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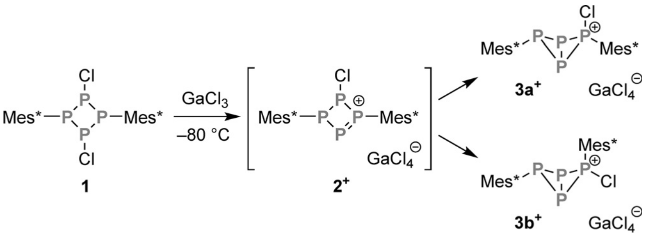


Scheme 3. Synthesis of [Mes*P_4(Cl)Mes*][$GaCl_4$] (**3**[$GaCl_4$]). The isomeric ratio between **3a**$^+$ and **3b**$^+$ varies from 1:8 (−50 °C, 3 h) to 3:4 (−80 °C, 12 h) depending on the reaction conditions.

reaction (ca. 40 % by mole fraction). Full conversion of **1** to **2**$^+$ could be confirmed by a trapping reaction (see below).

The resonances were assigned on the basis of computed NMR data (Supporting Information). The calculated gas-phase structure of **2**$^+$ (PBE0/6-31G(d,p)) reveals C_1 symmetry and incorporates a P=P double bond (2.05 Å; Wiberg bond index: 1.49; cf. 2.034(2) Å in Mes*P=PMes*)[35] that stabilizes the positive charge. In agreement with the Lewis formula, the highest partial charge is therefore found at one of the Mes*-substituted P atoms (+0.45 *e*), which adopts a nearly planar coordination environment ($\Sigma(\sphericalangle P) = 359.9°$). Even though the minimum structure displays four inequivalent P nuclei, a relatively fast exchange between two enantiomers accounts for both the observed NMR pattern and the signal broadening (Figure 1). As the dynamic equilibrium renders both Mes*-substituted P atoms equivalent, a single resonance at the center of their individual shifts ($\delta_{calc} = 206.5$, 48.6 ppm; $\delta_{av} = 127.6$ ppm) is expected. Taking this into consideration, the calculated and experimental data show reasonable agreement (Supporting Information, Table S7). Two other intermediates were observed at temperatures below −20 °C, which could not be identified unambiguously (Supporting Information, Figure S1).

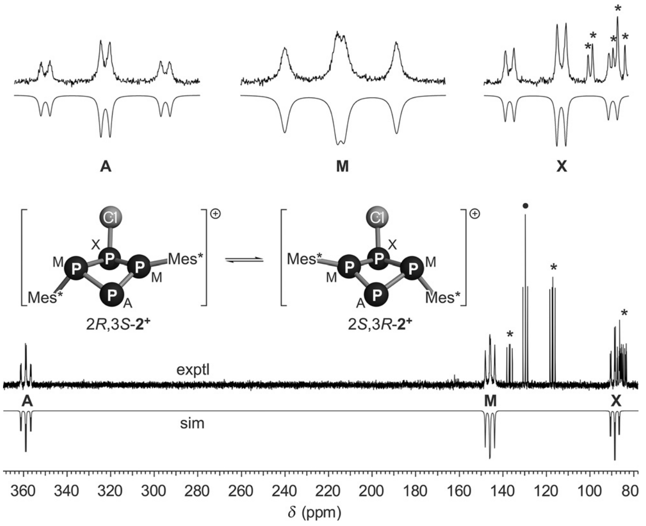


Figure 1. Experimental and simulated in situ ^{31}P NMR spectrum of the reaction of **1** and $GaCl_3$ (−60 °C). The AM_2X pattern is caused by a dynamic equilibrium between two enantiomers of **2**$^+$ (calculated structures). Labeled lines/signals are caused by starting material (●) and other intermediates (⋆).

The color of the reaction mixture faded slowly to orange/yellow over a period of one day at low temperatures. After full conversion of the starting material, two main products were formed, which were identified as *exo–exo* and *endo–exo* isomers of [Mes*P_4(Cl)Mes*]$^+$ (**3a**$^+$, **3b**$^+$, Scheme 3) on the basis of NMR data (85 % yield). Intriguingly, the chlorine atom of the reaction product is connected to one of the Mes*-substituted P atoms, resulting in the formation of a novel, bicyclic triphosphinophosphonium framework. According to DFT calculations, these constitutional isomers of **2**$^+$, which are formed after a formal 1,2-Cl shift, are energetically favored by 46.3 kJ mol^{-1} (**3a**$^+$) or 45.3 kJ mol^{-1} (**3b**$^+$) with respect to intermediate **2**$^+$ (ΔG^{298}).

Addition of *n*-pentane facilitated crystallization at −80 °C and afforded colorless crystals that were characterized as CH_2Cl_2/C_6H_5F solvate of **3a**[$GaCl_4$] (40 % yield of isolated product). The molecular structure was determined by single-crystal X-ray diffraction (Figure 2). All P−P bond lengths are within the range of typical single bonds (cf. $\Sigma r_{cov} = 2.22$ Å),[36] although the bonds to P1a (2.150(2) Å) are somewhat shortened owing to bond polarization. Similarly, the P1a−Cl1a bond (2.009(2) Å) is slightly shorter than the sum of covalent radii (2.10 Å).[36] A distorted tetrahedral coordination environment is found for P1a, which can be compared to tetracoordinate P atoms in cyclic phosphinohalophosphonium ions or bicyclic TerP$_4$Me·B(C_6F_5)$_3$ (Ter = 2,6-dimesitylphenyl).[18,32] All other P atoms exhibit typical trigonal pyramidal coordination (bond angles 58°–96°). The fold angle of the butterfly-shaped bicyclic P_4 scaffold amounts to 101.68(3)°, which compares well to known tetraphosphabicyclo[1.1.0]butane frameworks (88.6°–108.1°).[25,26,32,37–41] No close contacts are found between anion and cation. Several attempts to crystallize the *endo–exo* isomer **3b**[$GaCl_4$], which is actually formed in excess according to ^{31}P NMR spectra, remained futile.

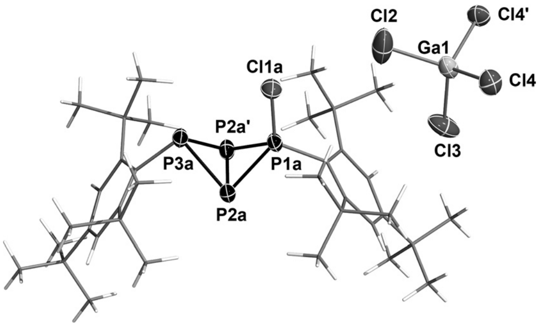


Figure 2. Molecular structure of **3a**[$GaCl_4$]. Ellipsoids are set at 50 % probability (173 K). Selected bond lengths [Å] and angles [°]: P1a–P2a 2.150(2), P1a–Cl1a 2.009(2), P2a–P2a′ 2.244(2), P2a–P3a 2.244(2); Cl1a-P1a-P2a 117.65(7), C1-P1A-Cl1a 118.7(2), P2a′-P1a-P2a 62.91(7), P1a-P2a-P2a′ 58.55(3), P3a-P2a-P2a′ 59.99(3), P1a-P2a-P3a 83.60(6), P2a′-P3a-P2a 60.02(7); P1a-P2a-P2a′-P3a −101.68(3).[56]

The solid-state Raman spectrum of **3a**[$GaCl_4$] (at −60 °C) shows characteristic bands at 340 cm^{-1} ($GaCl_4$ “breathing” mode), 485 cm^{-1} (P_4 deformation), 513 cm^{-1} (P_4Cl "breathing"), 588 cm^{-1} (P–C stretching at tricoodinate P), 615 cm^{-1} (P–Cl stretching), and 633 cm^{-1} (P–C stretching at tetracoordinate P). Upon warming, the sample started to decompose above 0 °C as indicated by decreasing signal intensities (Supporting Information, Figure S2).

To further investigate the electronic structure of **3a**$^+$ and **3b**$^+$, density functional theory (DFT) calculations were performed.[42] For both isomers, NBO[43] analysis revealed that the positive charge is mostly localized at the phosphonium center (P1, $+0.76\,e$), but also resides at the tricoordinate Mes* substituted atom (P3, $+0.37\,e$). The bridgehead atoms (P2) are only slightly positive ($+0.12\,e$), whereas the Cl atom bears a slightly negative charge ($-0.16\,e$). Thus, the overall charge of the P_4Cl scaffold amounts to $+1.21\,e$, or $+1.37\,e$ if only the P_4 unit is regarded. Comparison with neutral Mes*P_4Mes* ($+0.54\,e$, Supporting Information) or even dicationic $[(Ph_3As)P_4(AsPh_3)]^{2+}$ ($+0.12\,e$)[26] confirms the unique charge distribution within both isomers of **3**$^+$.

In the ^{31}P NMR spectrum, **3a**$^+$ and **3b**$^+$ are characterized by AMX$_2$ patterns (Figure 3). A characteristic high field shift is observed for the bridgehead atoms (P$_X$; **3a**$^+$: −214.5 ppm; **3b**$^+$: −226.4 ppm), which compares to known tetraphosphabicyclo[1.1.0]butanes (−220 to −370 ppm),[25,26,32,37–41,44–46] but is still shifted slightly downfield owing to the positive charge of the P_4 scaffold. The tricoordinate bridging atom (P$_M$) displays a moderate high-field shift (**3a**$^+$: −89.5 ppm; **3b**$^+$: −123.6 ppm) within the typical range, whereas the tetracoordinate P atom (P$_A$) is shifted significantly downfield (**3a**$^+$: +51.2 ppm; **3b**$^+$: +9.0 ppm), which has not yet been observed for nuclei within bicyclic P_4 frameworks. All of the experimental values are in good agreement with theoretical data (Supporting Information, Tables S8 and S9).

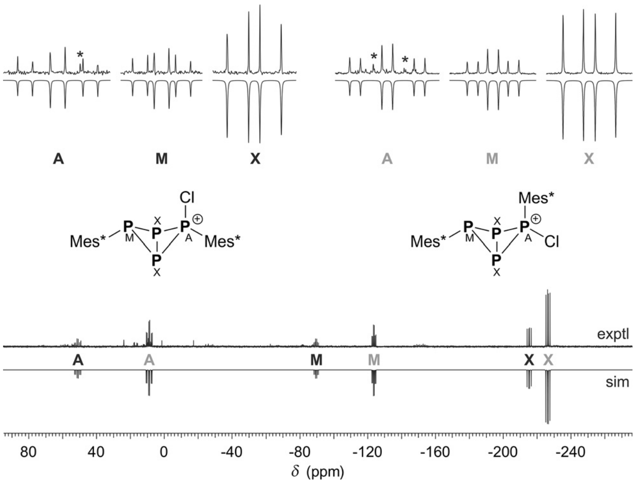
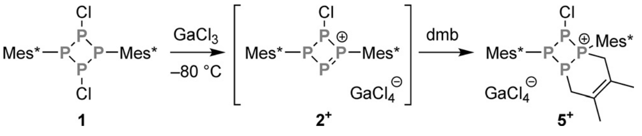


Figure 3. In situ ^{31}P NMR spectrum at 0 °C displaying the formation of **3a**$^+$ and **3b**$^+$. Starred lines in the enlarged section are caused by impurities that are due to incipient decomposition at this temperature.

At ambient temperature, solution NMR spectra indicate that **3a**$^+$ and **3b**$^+$ decompose within hours.[47] One of the decomposition products was identified as [Mes*P(H)(Cl)*t*Bu][GaCl$_4$] (**4**[GaCl$_4$]; Supporting Information). Remarkably, a *t*Bu group is transferred from a Mes* substituent to the P atom of **4**$^+$ in the course of this reaction, which demonstrates the intrinsic lability of **3a**$^+$ and **3b**$^+$. Displacement of *t*Bu groups from Mes* substituents has previously been observed in the presence of Lewis acids or under thermal conditions.[6,48–51]

In a next series of experiments, we aimed to further establish the identity of low-temperature intermediate **2**$^+$. For that purpose, **1** was treated with GaCl$_3$ in the presence of dimethylbutadiene (dmb) as trapping reagent.[52,53] This time, no red color was observed upon addition of GaCl$_3$. According to ^{31}P NMR data, the reaction led to quantitative formation of tetraphosphabicyclo[4.2.0]octenium salt **5**[GaCl$_4$] (Scheme 4), which can be regarded as [4+2] cycloaddition product of intermediate **2**$^+$ and dmb. In this vein, the trapping reaction also proved quantitative conversion of **1** to **2**$^+$ at low temperatures.



Scheme 4. Synthesis of [Mes*P_4(Cl)(C_6H_{10})Mes*][GaCl$_4$] (**5**[GaCl$_4$]).

At ambient temperature, cation **5**$^+$ is characterized by four broad signals in the ^{31}P NMR spectrum, indicating unresolved dynamic effects. Cooling to −80 °C revealed dynamic equilibria between several conformers or rotamers (Supporting Information, Figure S3). Heating to +80 °C barely improved the resolution of the NMR spectrum and led to slow decomposition of **5**$^+$. In the ^{1}H NMR spectrum, some of the signals are also significantly broadened, which is most likely due to hindered rotation of some *t*Bu groups.

Crystallization at 5 °C yielded colorless crystals of **5**-[GaCl$_4$]·CH_2Cl_2 (yield of isolated product after workup: 45 %; see the Supporting Information). The solid-state structure was determined by single-crystal X-ray diffraction (Figure 4).

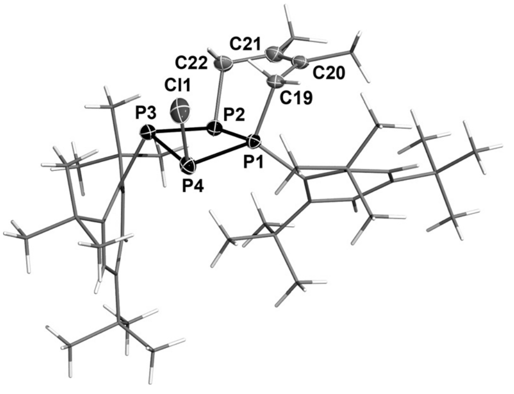


Figure 4. Molecular structure of **5**$^+$.[56] Ellipsoids are set at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: P1–P2 2.195(1), P1–C19 1.846(3), C19–C20 1.514(4), C20–C21 1.334(4), C21–C22 1.500(4), P2–C22 1.871(3), P4–Cl1 2.068(1); P2-P1-P4 91.78(4), C19-P1-P2 102.3(1), C19-P1-P4 116.1(1); P1-P2-P4-P3 159.03(1).

The bicyclic system is folded along the P1–P2 and C19–C22 axes (angles between least squares planes: P3-P4-P1-P2/P1-P2-C22-C19/C22-C19-C20-C21 72.1°/63.2°). The P_4 ring system is rather flat (fold angle: 159°), but well within typical parameters (110°–173°).[54,55] P1 sits in a distorted tetrahedral environment, and the other P atoms exhibit trigonal pyramidal coordination. The P1–P2 bond (2.195(1) Å) is slightly shorter than the other three P–P bonds (av. 2.25 Å). The structural data of the P_4 ring system correspond to other known cyclotriphosphinophosphonium ions.[16–18] The Mes* moiety at P1 is highly distorted owing to Pauli repulsion between the *o*-*t*Bu groups and the $P_4C_6H_{10}$ scaffold; the P atom is bent out of the least-squares plane of the phenyl ring by 52.1°. No close contacts are found between anion and cation. As expected, the positive charge is essentially localized at P1 (+0.92 *e*) according to NBO analysis. The partial charges of the other P atoms are only slightly positive (av. +0.32 *e*). To exclude the possibility that **5**$^+$ was formed by a "reverse" reaction of **3a**$^+$ or **3b**$^+$ with dmb, a solution of both salts was treated with the latter. This did not lead to the formation of **5**$^+$; in fact, no reaction was observed after two hours based on ^{31}P NMR data.

In conclusion, the synthesis of the first tetraphosphabicyclo[1.1.0]butan-2-ium salt, **3**[GaCl$_4$], which incorporates a positively charged, bicyclic P_4 scaffold, is achieved by selective chlorine abstraction starting from [ClP(μ-PMes*)]$_2$ (**1**). **3**[GaCl$_4$] is temperature-sensitive and only stable at low temperatures. The formation of **3**$^+$ was studied by means of low-temperature NMR experiments. This led to the discovery of tetraphosphenium intermediate **2**$^+$, which could be identified on the basis of DFT calculations. Moreover, a trapping reaction with dmb could provide chemical evidence for the identity of **2**$^+$. Currently, we are investigating the reactivity of **1** with other Lewis acids and under different conditions to diversify the product scope.

Keywords: bicyclic compounds · NMR spectroscopy · phosphorus cations · phosphorus compounds · ring systems

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[42] The Supporting Information includes details about syntheses and characterization of all compounds as well as computational details.

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[56] CCDC 1053909 (**3a**[$GaCl_4$]), CCDC 1053910 (**4**[$GaCl_4$]), CCDC 1053911 (**5**[$GaCl_4$]), and CCDC 1053912 (**6**) 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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