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Preparation of the $[(DippNP)_2(P_4)_2]^{2+}$-Dication by the Reaction of $[DippNPCl]_2$ and a Lewis Acid with P_4

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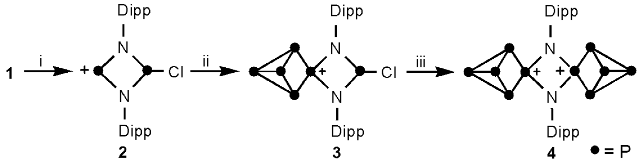
The activation and functionalization of white phosphorus by *N*-heterocyclic carbenes[1] and carbene-like main group element fragments[2] is of considerable current interest. Carbene-analogous phosphenium cations display a pronounced ambiphilic nature which renders their behavior both Lewis acidic and Lewis basic. Their electrophilic character comes to the fore in element−element bond insertion reactions,[3] making them interesting species for the systematic investigation of P_4 functionalization. Only recently, the first structurally characterized inorganic cationic P_5 cluster $[P_5Br_2]^+$ was obtained *via* phosphenium insertion by Krossing and coworkers.[4] Our solvent-free approach to consecutively insert the phosphenium cation $[Ph_2P]^+$ into P−P[5a,b] bonds of P_4 resulted in the formation of unprecedented phosphorus-rich cationic clusters $[Ph_2P_5]^+$, $[Ph_4P_6]^{2+}$, and $[Ph_6P_7]^{3+}$.[5c] In this communication, we report on the functionalization of P_4 formally through the cationic bifunctional Lewis acid $[DippNP]_2^{2+}$ obtained from *cyclo*-1,3-diphospha-2,4-diazane $[DippNPCl]_2$ (**1**). This has enabled the targeted preparation of novel mono- and dicationic phosphorus-rich clusters **3**$[GaCl_4]$•C_6H_5F and **4**$[Ga_2Cl_7]_2$ (Scheme 1).

Scheme 1. Reaction of **1** with $GaCl_3$ and P_4[a]



[a] (i) 1 eq. $GaCl_3$, C_6H_5F, rt, 10 min, (ii) 1 eq. P_4, C_6H_5F, rt, 2 h; (iii) 3 eq. $GaCl_3$, P_4 C_6H_5F, rt, 6 h.

Cyclic phosphenium cation **2** can be generated from **1** in the presence of the Lewis acid $GaCl_3$.[6] The addition of one eq. $GaCl_3$ to a solution of **1** in C_6H_5F afforded an instant color change of the initially colorless solution to deep red. $^{31}P\{^1H\}$ NMR investigation of the reaction mixture showed a new broad signal (C_6D_6 capillary, rt, $\delta = 242.3$ ppm, $\Delta\nu_{1/2} = 104$ Hz) shifted downfield compared to the sharp signal of **1** (*cis* isomer, $\delta = 210.5$ ppm, $\Delta\nu_{1/2} = 10$ Hz),[7] indicating the formation of cation **2**.[8a] The subsequent addition of one eq. P_4 gave rise to a clear, pale orange solution within 2 h (Scheme 1). The ^{31}P NMR spectrum of the reaction mixture revealed the exclusive formation of monocation **3**, which showed an A_2MVXZ spin system ($\delta_A = -346.7$ ppm, $\delta_M = 85.1$ ppm, $\delta_V = 152.7$ ppm, $\delta_X = 168.2$ ppm, $\delta_Z = 197.5$ ppm; $^1J_{AV} = -139.7$ Hz, $^1J_{AX} = -139.9$ Hz, $^1J_{MV} = -282.5$ Hz, $^1J_{MX} = -293.4$ Hz, $^2J_{AM} = 16.4$ Hz, $^2J_{VX} = 57.0$ Hz, Figure 1).[8b,9] The resonances for this spin system are in an approximate ratio of 2:1:1:1:1. Similar to other N_2P_2 systems,[7,10] the two ring phosphorus atoms of **3** do not couple, resulting in the observation of a singlet for the tri-coordinate phosphorus atom (s, $\delta_Z = 197.5$ ppm). The very air- and moisture-sensitive material was isolated as the $[GaCl_4]^-$ salt as fluorobenzene solvate.

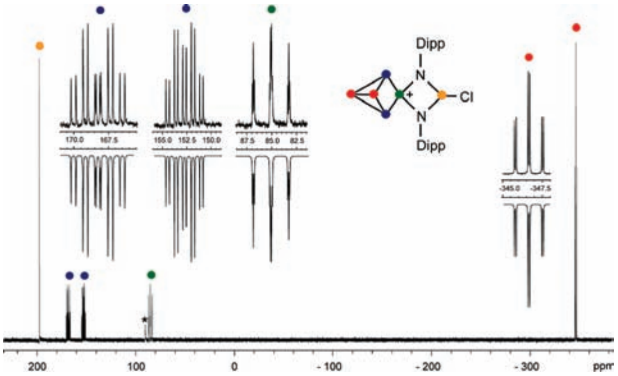


Figure 1. ^{31}P NMR spectrum of cation **3** (in C_6H_5F, C_6D_6-capillary, 25 °C; 161.94 MHz). Full spectrum (bottom) and expansions (inset) showing the experimental (up) and fitted (down) spectra;[9] a very small amount of an unidentified side-product is indicated by an asterisk.[8b]

A single-crystal X-ray study of [**3**]$[GaCl_4]$•C_6H_5F (Figure 2) confirmed the insertion of **2** into one of the P−P bonds of P_4. The structural features of the P_5 core are comparable to $[Ph_2P_5]^+$.[5c] The P−P bonds involving the four-coordinate phosphorus center P1 and the P4−P5 bond (2.1462(7) − 2.164(1) Å) are significantly shorter than the remaining P−P bonds (2.2461(8) − 2.2535(8) Å). Comparably short P−P distances have been observed in other compounds with cationic four-coordinate phosphorus centers and strained phosphorus cages.[2i,11] The P−N bonds between the tri-coordinate phosphorus atom P6 and N1 or N2 (1.733(2), 1.732(2) Å) are typical for neutral diphosphadiazanes.[12] In contrast, the P−N bonds involving the phosphonium center P1 are significantly shorter (1.662(2), 1.669(2) Å).

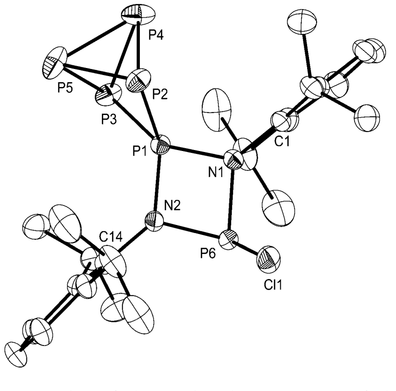


Figure 2. ORTEP plot of the molecular structure of the cation **3** in **3**$[GaCl_4]\cdot C_6H_5F$. Thermal ellipsoids at 50% probability (hydrogen atoms, counteranion and C_6H_5F omitted for clarity). Selected bond lengths (Å): P6−Cl1 2.0788(7), P6−N1 1.733(2), P6−N2 1.732 (2), P1−N1 1.669(2), P1−N2 1.662(2), P1−P2 2.1518(7), P1−P3 2.1462(7), P2−P4 2.2535(8), P2−P5 2.2461(8), P3−P4 2.2484(8), P3−P5 2.2472(8), P4−P5 2.164(1).

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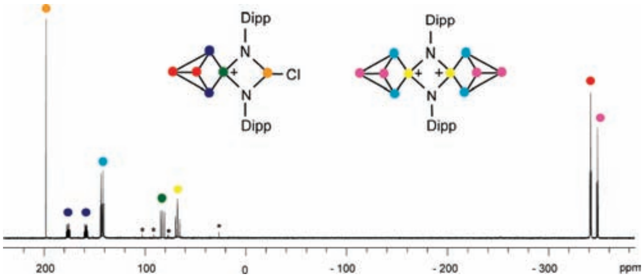

Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $\mathbf{3}[GaCl_4]$ and $\mathbf{4}[Ga_2Cl_7]_2$ (in C_6H_5F, C_6D_6-capillary, 25 °C; 161.94 MHz); very small amounts of unidentified side-products are indicated by an asterisk.[8b]

The reaction of two equiv. of P_4 with cation **2** and an excess of Lewis acid (**2**, $GaCl_3$ 1:4) in C_6H_5F resulted in the formation of a pale-yellow solution with small amounts of orange-yellow precipitate (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of the filtrate is depicted in Figure 3. Beside the resonances of monocation **3**, signals of a new A_2MX_2 spin system ($\delta_A = -341.8$ ppm, $\delta_M = 67.4$ ppm, $\delta_X = 142.3$ ppm; $^1J_{AX} = -320.3$ Hz, $^1J_{MX} = -135.2$ Hz, $^2J_{AM} = 21.9$ Hz) in a ratio of 2:1:2 indicate the formation of a new species in approximately 60% yield.[8b] The resonances for the A_2MX_2 spin system are consistent with two C_{2v}-symmetric P_5 cages bridged by two imido groups, suggesting the formation of dication **4** (Figure 3). $\mathbf{4}[Ga_2Cl_7]$ crystallized as a conglomerate with $\mathbf{3}[GaCl_4]$. The postulated structure in solution was confirmed by X-ray diffraction (Figure 4). To our knowledge, dication **4** represents the first structurally characterized example of two homoatomic P_5 cages fused *via* an imido bridge. In the solid state, dication **4** is centrosymmetric, consistent with the A_2MX_2 pattern observed in the $^{31}P\{^1H\}$ NMR spectrum. The bond lengths and angles in the P_5 cores of dication **4** follow a similar trend as observed for monocation **3**. The N_2P_2 ring is planar with a short P1−N1 bond (1.684(2) Å). The pronounced short character of the P−N bonds in the P_2N_2 core might account for an increased reactivity. In solution, dication **4** is not very stable and readily decomposes to an insoluble orange material at room temperature. The $^{31}P\{^1H\}$ NMR spectrum of the reactions mixture after ~12 h shows an additional complex set of signals. This indicates the formation of a further oligomer which we believe to be cation $[(DippNP)_3(P_4)Cl_2]^+$, presumably resulting from a condensation of cations **2** and **4**. This unusual process is currently being investigated. Details will be reported in a subsequent full paper.

In summary, the synthesis of the unique phosphorus-rich organophosphorus cation **4** has been achieved by stepwise insertion of the disguised bifunctional Lewis acid $[DippNP]_2^{2+}$ into the P−P bonds of two P_4 tetrahedra. The utilization of bifunctional phosphenium cations[13] represents a rational and potentially versatile synthetic method for the assembly of large clusters using P_4 as a building block. Due to the cationic charge such cluster may be amenable to a host of subsequent transformations. Studies directed at the synthesis of further cationic clusters and the reactivity of **3** and **4** are in progress.

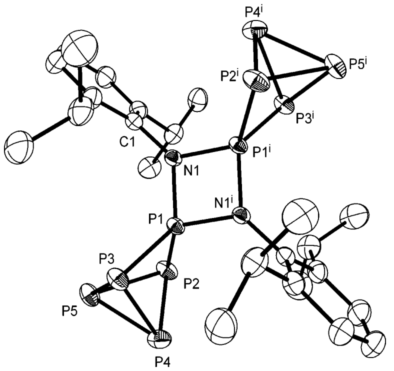

Figure 4. ORTEP plot of the molecular structure of the cation **4** in $\mathbf{4}[Ga_2Cl_7]_2$. Thermal ellipsoids at 50% probability (hydrogen atoms and counteranions omitted for clarity). Selected bond lengths (Å): N1−P1 1.684(2), P1−P2 2.1388(7), P1−P3 2.1380(7), P2−P4 2.2603(8), P2−P5 2.2450(8), P3−P4 2.2598(8), P3−P5 2.2425(8), P4−P5 2.1659(9); [symmetry code: (i) $-x,-y+1,-z$].

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Supporting Information Available: Full experimental and spectroscopic data for compounds $\mathbf{2}[Ga_2Cl_7]$ and $\mathbf{3}[GaCl_4]\cdot C_6H_5F$ and selected data for $\mathbf{4}[Ga_2Cl_7]_2$ (including $^{31}P-^{31}P$ DQF COSY), and X-ray crystallographic data for $\mathbf{3}[GaCl_4]$ and $\mathbf{4}[Ga_2Cl_7]_2$ (CCDC numbers 743848, 743849). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) (a) Only a broad signal for **2** is observed in the $^{31}P\{^1H\}$ NMR spectrum due to fluxional behaviour. The observed chemical shift strongly depends on the $GaCl_3$ concentration. Cation **2** was isolated as $\mathbf{2}[Ga_2Cl_7]$ when more than 2eq. of $GaCl_3$ are used. (b) For experimental details and spectroscopic data see Supporting Information.

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