## Preparation of Cationic $[(R_2N)P_5Cl]^+$ -Cage Compounds from $[(R_2N)PCl]^+$ and $P_4$

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Dedicated to Professor Wolfgang Beck on the Occasion of His 80th Birthday

Keywords: P<sub>4</sub> activation; Phosphorus; Cations; Main group elements; Structure elucidation

**Abstract.** The reaction of several amino-substituted mono- and dichlorophosphanes  $(R_2N)_nPCl_{3-n}$  (n = 2, R = i-Pr; n = 1, R = i-Pr, Cy) with GaCl<sub>3</sub> to form phosphenium cations [(i-Pr<sub>2</sub>N)<sub>2</sub>P]<sup>+</sup> (**13**<sup>+</sup>) and  $[(R_2N) PCl]^+$  (**14a,b**<sup>+</sup>) has been investigated. The isolation and fully characterization of the first amino- and chloro-substituted phosphenium cation **14b**[GaCl<sub>4</sub>] was accomplished. The insertion of these phosphenium ions into P–P bonds of dissolved P<sub>4</sub> was examined. Amino- and

#### Introduction

A plethora of anionic and neutral phosphorus cage and ring compounds have been discovered and described in literature.<sup>[1]</sup> However, the field of cationic polyphosphorus derivatives is still underdeveloped and mostly limited to *catenated* and cyclic compounds.<sup>[2]</sup> Only recently, the first structurally characterized cationic phosphorus cages  $[P_5X_2]^+$  (X = Br, I, Cl) (1<sup>+</sup>) were reported obtainable from the reaction of  $P_4$  and  $PX_3$  in the presence of the silver salt  $Ag[Al(OR)_4]$  (OR = perfluorinated aliphatic alkoxide).<sup>[3]</sup> Similar to other carbene like main group compounds<sup>[4]</sup> phosphenium cations are anticipated to undergo P-P bond insertion reactions because of their amphiphilic nature.<sup>[5]</sup> Therefore, we investigated room temperature molten media obtained from various stoichiometric combinations of Ph2PCl and GaCl3. These mixtures can be used as sources of the elusive phosphenium cation  $[R_2P]^+$  (2<sup>+</sup>, R = Ph).<sup>[6]</sup> Thus, dissolution of P<sub>4</sub> in such melts at elevated temperatures resulted in the stepwise formation of cationic cage compounds  $[Ph_2P_5]^+(3^+), [Ph_4P_6]^{2+}(4^{2+}), and [Ph_6P_7]^{3+}(5^{3+}, Scheme 1).^{[7]}$ In addition, we also examined mixtures of dichlorophosphanes  $RPCl_2$  (R = aryl, alkyl) and Lewis acids  $ECl_3$  (E = Al, Ga) in fluorobenzene solution. These mixtures are suitable sources of  $[RPC1]^+$  (6<sup>+</sup>) ions and provide access to a multitude of asymmetrically substituted cationic cage compounds  $[RP_5C1]^+$  (7<sup>+</sup>) (Scheme 1).<sup>[8]</sup> This approach can be applied to various chlorophosphanes, thus, the number of highly functionalized cationic

E-Mail: jweigand@uni-muenster.de [a] Institut für Anorganische und Analytische Chemie Universität Münster structures of [14b][GaCl<sub>4</sub>] and [15b][Ga<sub>2</sub>Cl<sub>7</sub>] are presented and, furthermore, the intriguing NMR spectra of the  $P_5^+$ -cations 15a,b<sup>+</sup> are discussed. P<sub>5</sub><sup>+</sup>-cage compounds has been extended to zwitterionic and cationic P<sub>5</sub>-cages from four-membered phosphorus-nitrogen (8<sup>+</sup> 9<sup>2+1</sup>)<sup>[9]</sup> and phosphorus mitrogen metal betarocycles (10<sup>+</sup>

chloro-substituted phosphenium cations 14a,b<sup>+</sup> readily form the corre-

sponding P5<sup>+</sup>-cages 15a,b<sup>+</sup>. No reaction was observed for the less elec-

trophilic diamino-substituted phosphenium cation 13<sup>+</sup>. The molecular

cationic P<sub>5</sub>-cages from four-membered phosphorus-nitrogen  $(\mathbf{8}^+, \mathbf{9}^{2+})^{[9]}$  and phosphorus-nitrogen-metal heterocycles  $(\mathbf{10}^+, \mathbf{11})^{[10]}$  by P–P bond insertion reactions of the respective phosphenium cations (Scheme 2). Unstabilized phosphenium cations  $[\mathbf{R}_2\mathbf{P}]^+$  ( $\mathbf{2}^+, \mathbf{R} = aryl$ , alkyl) are elusive because of their highly electrophilic nature<sup>[9]</sup>, and only N-stabilized phosphenium cations (e.g.  $\mathbf{R} = NCy_2$ , Ni-Pr<sub>2</sub>) have been reported to form stable salts in which the phosphorus atom is indeed divalent.<sup>[10]</sup>



Scheme 1. Cationic phosphorus cages and phosphenium cations.

In our present contribution we report on the reactions of amino-substituted mono- and dichlorophosphanes  $(R_2N)_nPCl_{3-n}$  (n = 2, R = i-Pr; n = 1, R = i-Pr, Cy) with the Lewis acid GaCl<sub>3</sub>. Both types of derivatives react with GaCl<sub>3</sub> to form the corresponding phosphenium cations [(i-Pr<sub>2</sub>N)<sub>2</sub>P]<sup>+</sup> (**13**<sup>+</sup>) and  $[(R_2N)PCl]^+$  (**14a**,**b**<sup>+</sup>) (a: R = *i*-Pr, b: R = Cy; Scheme 3).

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Scheme 2. Cationic phosphorus cages from four-membered heterocycles.

However, only cations  $14a,b^+$  undergo insertion reactions into one P–P bond of the P<sub>4</sub> tetrahedron to yield the corresponding cationic cages  $[(R_2N)P_5Cl]^+$  ( $15a,b^+$ ). In course of our investigations, we also succeeded in the isolation and characterization of the first amino- and chloro-substituted phosphenium cation ( $14b^+$ ) as tetrachlorogallate salt. The dependency of the chemical shift of the phosphenium cations in response to the stoichiometric combination of GaCl<sub>3</sub> and chlorophosphanes is also discussed.



Scheme 3. Amino-substituted phosphenium cations and phosphorus cages.

#### **Results and Discussion**

The reaction of chlorophosphanes of the type  $R_2PCl$  and  $RPCl_2$  (R = aryl, alkyl) with halide abstracting agents such as  $Me_3SiOTf$  or AgOTf or Lewis acids ( $ECl_3$ , E = Ga, Al) yields a variety of products, involving phosphanylphosphonium cations and Lewis acid-base adducts between the phosphane and  $ECl_3$ .<sup>[13]</sup> Other structural variations are also discussed.<sup>[8, 13b]</sup> Related reactions of amino-substituted chlorophosphanes and Lewis acids or halide abstracting agents have been investigated previously and do not show the structural variety as observed for the alkyl- or aryl-substituted chlorophosphanes.<sup>[14]</sup> However, a series of phosphenium ions [ $(R_2N)_2P$ ]<sup>+</sup> ( $\mathbf{13}^+$ ) were isolated and utilized for example as *NHP* ligands (*N*-Heterocyclic *P*hosphenium) in transition metal chemistry.<sup>[15]</sup> Very few examples of phosphenium ions of the form [ $(R_2N)_2PR'$ ]<sup>+</sup> (R =

*i*-Pr;  $R' = Mes^{[16]}$ , *ortho*-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub><sup>[17]</sup>) are known and structurally characterized. We were interested if cation 13<sup>+</sup> can insert into P-P bonds of the P4 tetrahedron. The formation of cation  $13^+$  is achieved upon addition of GaCl<sub>3</sub> to  $(i-Pr_2N)_2PCl$ in almost quantitative yield.<sup>[17]</sup> However, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture of P<sub>4</sub>, (*i*-Pr<sub>2</sub>N)<sub>2</sub>PCl and GaCl<sub>3</sub> in a 1:1:1 ratio in fluorobenzene showed only the formation of cation 13<sup>+</sup> (Scheme 4) and unreacted P<sub>4</sub> ( $\delta = -521.0$  ppm), the formation of cation  $16^+$  was not observed. The outcome of this reaction was found to be independent of the reaction stoichiometry of (i-Pr<sub>2</sub>N)<sub>2</sub>PCl and GaCl<sub>3</sub> (see experimental section). This might be explained with the decreased electrophilicity of cation  $13^+$  attributed to the optimal overlap of the lone pairs of electrons at the nitrogen atoms with the empty p-type orbital of the divalent phosphorus atom.<sup>[18]</sup> This is in sharp contrast to the related four-membered phosphenium cations derived from  $[DippNPC1]_2$  which give cations 8<sup>+</sup> and 9<sup>2+</sup> upon reaction with P<sub>4</sub> in the presence of GaCl<sub>3</sub> in various stoichiometries.<sup>[9]</sup> In order to increase the electrophilicity of phosphenium cations, replacement of one substituent in  $[(R_2N)_2P]^+$  by a chloride should result in a pronounced reactivity. Thus, the corresponding dichlorophosphanes (i-Pr<sub>2</sub>N)PCl<sub>2</sub> and (Cy<sub>2</sub>N)PCl<sub>2</sub> should yield the phosphenium cations 14a,b<sup>+</sup> which are expected to display an enhanced electrophilicity. Cations 14a.b<sup>+</sup> are known and have been used for the syntheses of phospholes and nitrogen-phosphorus heterocycles.<sup>[19]</sup> However, their isolation has not been reported so far. Therefore, we investigated the reactions of (i-Pr<sub>2</sub>N)PCl<sub>2</sub> and (Cy<sub>2</sub>N)PCl<sub>2</sub> with GaCl<sub>3</sub> in 1 : 1 and 1:2 stoichiometries (Figure 1). The addition of one equivalent GaCl<sub>3</sub> to a C<sub>6</sub>H<sub>5</sub>F solution of  $(i-Pr_2N)PCl_2$  or  $(Cy_2N)PCl_2$  induced the formation of the expected phosphenium cations  $14a^+$ and 14b<sup>+</sup>. This is indicated by remarkable low field shifts observed in <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the reaction mixtures (n =1; **14a**<sup>+</sup>:  $\delta$  = 292.4 ppm,  $v_{1/2}$  = 105 Hz; **14b**<sup>+</sup>:  $\delta$  = 309.8 ppm,  $v_{1/2} = 110$  Hz, Figure 1) compared to the chemical shifts of the corresponding phosphanes (*i*-Pr<sub>2</sub>N)PCl<sub>2</sub>:  $\delta = 167.7$  ppm,  $v_{1/2}$ = 105 Hz; (Cy<sub>2</sub>N)PCl<sub>2</sub>:  $\delta$  = 167.7 ppm,  $v_{1/2}$  = 90 Hz).<sup>[20]</sup> The increased low-field shift of  $14b^+$  might be best explained by the less favored overlap of the free lone pair of electrons at the more sterically demanding Cy2N-substituent compared to the *i*-Pr-substituted species  $14a^{+}$ .<sup>[21]</sup> In addition, the chemical shifts of the phosphenium ions strongly depend on the amount of Lewis acid added to the reaction mixture. A second equivalent of GaCl<sub>3</sub> leads to the formation of [Ga<sub>2</sub>Cl<sub>7</sub>]<sup>-</sup> anions<sup>[22]</sup> accompanied with a significant low field shift of the respective phosphenium cations **14a**,**b**<sup>+</sup> (n = 2; **14a**<sup>+</sup>:  $\delta = 340.0$  ppm,  $v_{1/2}$ = 145 Hz; **14b**<sup>+</sup>:  $\delta$  = 350.1 ppm,  $v_{1/2}$  = 514 Hz; Figure 1). A comparable reliance of the <sup>31</sup>P{<sup>1</sup>H} NMR resonances of phos-



Scheme 4. Attempted reaction of  $P_4$  with chlorophosphane 13 in the presence of Lewis acid GaCl<sub>3</sub>.

phenium cations on the nature of the corresponding anions has been reported for cyclodiphosphadiazenium salts.<sup>[23]</sup>



**Figure 1.**  ${}^{31}P{}^{1}H$  NMR investigation of mixtures of (*i*-Pr<sub>2</sub>N)PCl<sub>2</sub> or (Cy<sub>2</sub>N)PCl<sub>2</sub> with GaCl<sub>3</sub> in fluorobenzene in various stoichiometries (C<sub>6</sub>D<sub>6</sub> capillary, C<sub>6</sub>H<sub>5</sub>F).

The additional increase in line broadening of the resonances can be explained by the dynamic equilibrium dissociation of  $[Ga_2Cl_7]^-$  to  $[GaCl_4]^-$  and  $GaCl_3$ .<sup>[8]</sup> The salt **14b**[GaCl\_4] was obtained as analytically pure colorless solid in excellent yield (81%) by the slow addition of *n*-hexane to the fluorobenzene solution of the 1:1 reaction of (Cy<sub>2</sub>N)PCl<sub>2</sub> and GaCl<sub>3</sub>. Compound  $14b[GaCl_4]$  was fully characterized and a section of the crystal structure is depicted in Figure 2. This compound crystallizes in the orthorhombic space group  $P2_12_12_1$  as a racemic twin with four formula units in the unit cell. 14b[GaCl<sub>4</sub>] represents the first structural characterized chloro-substituted phosphenium cation. The P1–N1 bond length (1.608(2) Å), which is comparable to known diamino-substituted phosphenium cations,<sup>[17, 24]</sup> is substantially shorter than a typical P-N single bond  $(d_{cov}(P-N) = 1.8 \text{ Å}; d_{cov}(P=N) = 1.6 \text{ Å})^{[25]}$  indicating double bond character. The nitrogen atom exhibits a planar arrangement (angular sum 359.9(1)°) indicating sp<sup>2</sup> hybridization and is located in the plane spanned by the atoms P1, Cl1 and the ipso-carbon atoms of the cyclohexyl groups (dihedral angles  $6.7(2)^{\circ}$ ,  $177.2(1)^{\circ}$ ). The angle involving the phosphorus atom is rather acute (Cl1-P1-N1: 104.50(7)°) compared to known phosphenium cations of type  $13^+$  (e.g. in [((*i*-Pr)<sub>2</sub>N)  $_{2}P][GaCl_{4}]: 117.07(7)^{\circ}),^{[17]}$  and is indicative of the higher electrophilicity of chloro-substituted phosphenium cations. The molecular structure of 14b[GaCl<sub>4</sub>] shows two very short interatomic Cl...P contacts (P1...Cl2 3.060(1) Å, P1...Cl4<sup>i</sup> 3.207(9) Å) (symmetry operation i = -1+x, y, z) between the anions and cations which are close to the sum of the van der Waals radii  $(r_{A(P)} + r_{D(Cl)} = 3.55 \text{ Å})^{[26]}$ . This interaction leads to the formation of one-dimensional strands along the [100] axis ((Cl2-P1-Cl2<sup>i</sup>: 166.27(3) °, P1-Cl2-P1<sup>i</sup>: 166.27(3) °; Figure 2). Considering the second interatomic contact involving Cl4<sup>*i*</sup>, the phosphorus atom shows a distorted bisphenoidal geometry (N1–P1–Cl4<sup>*i*</sup>: 166.27(3)°, Cl1–P1–Cl4<sup>*i*</sup>: 88.79(3)°).



**Scheme 5.** Reaction of  $P_4$  with dichlorophosphanes ( $R_2N$ )PCl<sub>2</sub> (R = i-Pr, Cy) in the presence of the Lewis acid GaCl<sub>3</sub>.



**Figure 2.** Cut-out of the crystal structure of compound **14b**[GaCl<sub>4</sub>]. Thermal ellipsoids at 50% probability (hydrogen atoms are omitted for clarity). Selected bond lengths /Å and angles /°: P1–Cl1 2.0026(8), P1–N1 1.608(2), N1–C1 1.496(3), N1–C7 1.525(3), P1–Cl2<sup>*i*</sup> 3.291(1), P1–Cl4<sup>*i*</sup> 3.207(1); N1–P1–Cl1 104.50(7), N1–P1–Cl4<sup>*i*</sup> 132.68(6), Cl1–P1–Cl4<sup>*i*</sup> 88.79(3), Cl2–P1–Cl2<sup>*i*</sup> 166.27(3), C1–N1–P1 129.0(1), C7–N1–P1 113.3(1), C1–N1–C7 129.0(1); *i*) –1+*x*, *y*, *z*.

The reaction of  $P_4$ ,  $(Cy_2N)PCl_2$  and  $GaCl_3$  in a 1:1:1 ratio in  $C_6H_5F$  solution has been performed to investigate the ability of cation **14b**<sup>+</sup> to insert in one of the P–P bonds of  $P_4$  (Scheme 5).

<sup>31</sup>P{<sup>1</sup>H}-NMR investigation of the reaction mixture exhibits incomplete conversion to the corresponding cationic  $P_5^+$ -cage 15b<sup>+</sup> in an approximate yield of 60 % (Figure 3). Remaining  $P_4$ and phosphenium cation  $14b^+$  can be observed in the reaction mixture. The separation of compound 15b[GaCl<sub>4</sub>] from the reaction mixture was difficult, since cation 15b<sup>+</sup> is in equilibrium with cation 14b<sup>+</sup> and P<sub>4</sub>. Similar results were obtained employing a second equivalent GaCl<sub>3</sub> or using (*i*-Pr<sub>2</sub>N)PCl<sub>2</sub> (Scheme 5; see experimental section). However, layering the reaction mixture of the 1:1:2 stoichiometry with n-hexane at -35 °C yields crystalline 15b[Ga<sub>2</sub>Cl<sub>7</sub>], suitable for X-ray diffraction, as a conglomerate including 14b[GaCl<sub>4</sub>]. A view of the molecular structure of the cation  $15b^+$  in  $15b[Ga_2Cl_7]$  is depicted in Figure 3. The P<sub>5</sub><sup>+</sup>-cage in cation 15b<sup>+</sup> displays nearly identical bond lengths and angles compared to other reported [RP<sub>5</sub>Cl]<sup>+</sup>-cations (2.151(9) to 2.258(5) Å).<sup>[9]</sup> Similarly to the latter cages, the bonds between the bridging (P2, P3) and tetracoordinate phosphorus atoms (P1) and the P4-P5 bond in cation 15b<sup>+</sup> are slightly shorter by approximately 0.07 Å (2.1573(6) to 2.1981(6) Å) than the remaining P–P bonds (2.2385(6) to 2.2460(6) Å). The short P4-P5 bond length is typical for the bridgehead bond in related bicyclo[1.1.0]-tetraphosphane moieties.<sup>[27]</sup> Likewise, the P1-N1 bond in 15b<sup>+</sup> is shortened (1.612(2) Å) because of electrostatic interaction. In accordance to the molecular structure of 15b<sup>+</sup> an ABMX<sub>2</sub> spin system is observed within the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the reaction mixtures (Figure 3).<sup>[28]</sup> This is the result of the  $C_{S}$ symmetry of the P<sub>5</sub><sup>+</sup>-moiety. The chemical shifts and coupling



**Figure 3.** a) left: <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the 1:1:1 reaction of P<sub>4</sub>, (Cy<sub>2</sub>N)PCl<sub>2</sub> and GaCl<sub>3</sub>. (C<sub>6</sub>H<sub>5</sub>F, C<sub>6</sub>D<sub>6</sub> capillary, 300 K; insets show experimental (upwards) and fitted spectra (downwards); \* marks small amounts of unidentified side products; **15b**<sup>+</sup> exhibits an ABMX<sub>2</sub> spin system:  $\delta_A = -271.8$  ppm,  $\delta B = -264.8$  ppm,  $\delta_M = 33.7$  ppm,  $\delta_X = 116.2$  ppm, <sup>1</sup>*J*(P<sub>A</sub>P<sub>X</sub>) = -152.7 Hz, <sup>1</sup>*J*(P<sub>B</sub>P<sub>X</sub>) = -145.9 Hz, <sup>1</sup>*J*(P<sub>A</sub>P<sub>B</sub>) = -167.1 Hz, <sup>1</sup>*J*(P<sub>M</sub>P<sub>X</sub>) = -277.8 Hz, <sup>2</sup>*J*(P<sub>A</sub>P<sub>M</sub>) = 17.8 Hz, <sup>2</sup>*J*(P<sub>B</sub>P<sub>M</sub>) = 23.1 Hz; b) right: ORTEP plot of the molecular structure of the cation in **15b**[Ga<sub>2</sub>Cl<sub>7</sub>]. Thermal ellipsoids at 50% probability (hydrogen atoms and anion are omitted for clarity). Selected bond lengths /Å and angles /°: P1-Cl1 2.0523(5), P1-N1 1.612(2), N1-C1 1.500(2), N1-C7 1.500(2), P1-P2 2.1621(6), P1-P3 2.1573(6), P2-P4 2.2385(6), P2-P5 2.460(6), P3-P4 2.2424(6), P3-P5 2.2394(6), P4-P5 2.1981(6); C7-N1-C1 119.4(1), N1-P1-Cl1 110.99(5), P3-P1-P2 91.42(2), P1-P2-P4 83.73(2), P1-P3-P5 82.38(2), P2-P4-P3 87.27(2), P4-P2-P5 58.70(2), P5-P4-P2 60.82(2).

constants of 15b<sup>+</sup> exhibit some interesting characteristics compared to other  $C_{\rm S}$ -symmetric [RP<sub>5</sub>Cl]<sup>+</sup>-cations (R = alkyl, aryl).<sup>[8]</sup> Within alkyl- and aryl-substituted [RP<sub>5</sub>Cl]<sup>+</sup>-cage compounds the chemical shifts of the phosphonium moiety shift to higher field with decreasing electronegativity of the corresponding substituents (ranging from 99 ppm (R = t-Bu) to 26 ppm (R =  $C_6F_5$ )).<sup>[8]</sup> An opposite trend was described for the phosphorus atoms adjacent to the phosphonium moiety (ranging from 44 ppm (R = t-Bu) to 83 ppm (R =  $C_6F_5$ )).<sup>[8]</sup> Thus, the resonance of the phosphonium moiety of 15b+  $(\delta_{M} = 33.7 \text{ ppm})$  and the resonance of the adjacent phosphorus atoms ( $\delta_x = 116.2$  ppm) emphasize the electronegative character of the amino-substituent. Between the phosphonium moiety and the bridgehead phosphorus atoms (P4/P5) two different  ${}^{2}J_{PP}$  coupling constants are observed ( ${}^{2}J(P_{A}P_{M}) = 17.8$  Hz,  ${}^{2}J(P_{B}P_{M}) = 23.1 \text{ Hz}$ ). Also the  ${}^{1}J_{PP}$  coupling constants from the bridgehead phosphorus atoms to the neighbouring ones exhibit different values  $({}^{1}J(P_{A}P_{X}) = -152.7 \text{ Hz}, {}^{1}J(P_{B}P_{X}) = -$ 145.9 Hz). By comparison of these values with known  $[RP_5C1]^+$ ,  $[R_2P_5]^+$  and  $[P_5X_2]^+$ -cations (R = alkyl, aryl; X = Cl, Br, I) the A part of the spin system can be assigned to the phosphorus atom in closer proximity to the Cl-substitutent due to the set of smaller coupling constants.<sup>[3, 7, 8]</sup>

## Conclusions

The reactions of amino-substituted mono- and dichlorophosphanes  $(R_2N)_nPCl_{3-n}$  (n = 2, R = i-Pr; n = 1, R = i-Pr, Cy) with various amounts of the Lewis acid GaCl<sub>3</sub> have been investigated. In all cases the formation of phosphenium ions  $(13^+, 14a,b^+)$  was observed. The isolation and characterization of the first amino- and chloro-substituted phosphenium cation  $[14b][GaCl_4]$  was achieved. The ability of insertion reactions into P–P bonds of the P<sub>4</sub> tetrahedron was examined. Whereas chloro-substituted phosphenium cations  $14^+$  undergo P–P bond insertion reactions to form the amino-substituted cations  $[(R_2N)P_5Cl]^+$  (**15a,b**<sup>+</sup>) no reaction was observed for the diamino-substituted phosphenium cation  $[(i-Pr_2N)_2P]$  (**13**<sup>+</sup>). This study gives an insight into the properties relevant for phosphenium cations to undergo reactions with P<sub>4</sub> and extends the number of cationic P<sub>5</sub><sup>+</sup>-cage compounds to amino-substituted derivates. This will help to design appropriate chlorophosphane precursor for the transformation of P<sub>4</sub> into cationic polyphosphorus compounds.

### **Experimental Section**

All reactions were carried out in either a glove box or using standard Schlenk techniques under an inert Ar atmosphere. Dry, oxygen-free solvents were employed. P4 was dried with (CH3)3SiCl and recrystallized from CS2 prior to use. Reagent grade GaCl3 and (i-Pr2N)2PCl were used as received from commercial suppliers. (i-Pr<sub>2</sub>N)PCl<sub>2</sub> and (Cy<sub>2</sub>N)PCl<sub>2</sub> were prepared according to the previously described methods.<sup>[29]</sup> NMR spectra were measured at 300 K on a Bruker AVANCE III 400 or a Bruker AVANCE II 200 spectrometer, and spectra were referenced either to residual solvent (1H, 13C) or externally [31P (H<sub>3</sub>PO<sub>4</sub>), <sup>27</sup>Al (Al(NO<sub>3</sub>)<sub>3</sub>), <sup>71</sup>Ga (Ga(NO<sub>3</sub>)<sub>3</sub>)]. Chemical shifts are reported in ppm. J values are reported in Hz. CD<sub>2</sub>Cl<sub>2</sub> was purchased from Sigma-Aldrich and stored over 3 Å molecular sieves prior to use. To obtain <sup>31</sup>P{<sup>1</sup>H} NMR spectra of reaction mixtures, a C<sub>6</sub>D<sub>6</sub>-capillary was inserted into the NMR tube. For compounds which give rise to a higher order spin systems in their <sup>31</sup>P{<sup>1</sup>H} NMR spectra, the resolution-enhanced <sup>31</sup>P{<sup>1</sup>H} spectra were transferred to the software program gNMR, version 5.0, by Cherwell Scientific.<sup>[30]</sup> The full lineshape iteration procedure of gNMR was applied to obtain the best match of the calculated to the experimental spectra along with the assignment of all the peaks revealed in the resolution-enhanced spectra. The signs for the  ${}^{1}J({}^{31}P,{}^{31}P)$  coupling constants were set negative and all other signs obtained accordingly.<sup>[31]</sup> Melting points were recorded on an electrothermal melting point apparatus in sealed capillaries under Argon atmosphere and are uncorrected. Infrared (IR) spectra were recorded using a Bruker Vertex 70 spectrometer. Elemental analyses



were performed on a Vario EL III CHNS elemental analyzer at the IAAC, University of Münster.

Recrystallization of [14b][GaCl<sub>4</sub>] from fluorobenzene by *n*-hexane diffusion gave single crystals suitable for X-ray diffraction. Layering 1:1:2 reaction mixtures of (Cy<sub>2</sub>N)PCl<sub>2</sub>, P<sub>4</sub> and GaCl<sub>3</sub> with *n*-hexane gave single crystals of [15b][Ga<sub>2</sub>Cl<sub>7</sub>] suitable for X-ray analysis. Single crystals of [14b][GaCl<sub>4</sub>] and [15b][Ga<sub>2</sub>Cl<sub>7</sub>] were mounted in Paratone oil and transferred to the cold N2 gas stream of a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(1) K (graphite-monochromated Mo- $K_a$  radiation with  $\lambda = 0.71073$  Å). Crystal data: [14b][GaCl<sub>4</sub>], C<sub>12</sub>H<sub>22</sub>Cl<sub>5</sub>GaNP, FW = 458.25, orthorhombic, space group  $P2_12_12_1$ , Z = 4, a = 6.9315(4) Å, b = 16.584(1)Å, c = 16.734(1) Å,  $a = 90^{\circ}$ ,  $\beta = 90^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 1923.7(2) Å<sup>3</sup>, F(000)= 928, T = 153(1),  $\mu = 2.198$ , 9161 reflections collected, 5159 reflections unique ( $R_{int} = 0.0283$ ), 4620 reflections observed ( $F > 2\sigma$  (F)). The final was  $R_1 = 0.0344$  and  $wR_2 = 0.0662$  (all data). CCDC-871709; [15b][Ga<sub>2</sub>Cl<sub>7</sub>], C<sub>12</sub>H<sub>22</sub>Cl<sub>8</sub>Ga<sub>2</sub>NP<sub>5</sub>, FW = 758.20, monoclinic, space group  $P2_1/n$ , Z = 4, a = 9.2899(5) Å, b = 25.734(1) Å, c = 11.9087(7)Å, V = 2786.3(3) Å<sup>3</sup>, F(000) = 1496, T = 153(1),  $\mu = 2.992$ , 29837 reflections collected, 7198 reflections unique ( $R_{int} = 0.0234$ ), 6360 reflections observed ( $F > 2\sigma$  (F)). The final was  $R_1 = 0.0265$  and  $wR_2$ = 0.0494 (all data) CCDC-871709. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x

<sup>31</sup>P{<sup>1</sup>H} NMR Experiments of (*i*-Pr<sub>2</sub>N)<sub>2</sub>PCl/GaCl<sub>3</sub>/P<sub>4</sub> Mixtures: A suspension of P<sub>4</sub> (0.5 mmol) in a solution of (*i*-Pr<sub>2</sub>N)<sub>2</sub>PCl (0.5 mmol) and GaCl<sub>3</sub> (0.5(i)/1.0(ii) mmol) in CH<sub>2</sub>Cl<sub>2</sub> ((i), 2 mL or C<sub>6</sub>H<sub>5</sub>F ((ii), 2 mL),<sup>[32]</sup> respectively) was stirred for 12 h at room temperature after which <sup>31</sup>P{<sup>1</sup>H} spectra were recorded ((i), CH<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>-capillary, 25 °C):  $\delta$  = 304.7 ([(*i*-Pr<sub>2</sub>N)<sub>2</sub>P][GaCl<sub>4</sub>],  $v_{1/2}$  = 50 Hz), 521.5 (P<sub>4</sub>); ((ii), C<sub>6</sub>H<sub>5</sub>F, C<sub>6</sub>D<sub>6</sub>-capillary, 25 °C,):  $\delta$  = 315.7 ([(*i*-Pr<sub>2</sub>N)<sub>2</sub>P][Ga<sub>2</sub>Cl<sub>7</sub>],  $v_{1/2}$  = 35 Hz), 521.5 (P<sub>4</sub>)).

<sup>31</sup>P{<sup>1</sup>H} NMR Experiments of (R<sub>2</sub>N)PCl<sub>2</sub>/GaCl<sub>3</sub> Mixtures: (R = *i*-Pr, Cy). A solution of (R<sub>2</sub>N)PCl<sub>2</sub> (0.5 mmol) and GaCl<sub>3</sub> (0.5/ 1.0 mmol) in C<sub>6</sub>H<sub>5</sub>F (2 mL) was stirred for 15 min at room temperature after which <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded (Figure 1).

<sup>31</sup>P{<sup>1</sup>H} NMR Experiments of (Cy<sub>2</sub>N)PCl<sub>2</sub>/GaCl<sub>3</sub>/P<sub>4</sub> Mixtures: A suspension of P<sub>4</sub> (0.5 mmol) in a solution of (Cy<sub>2</sub>N)PCl<sub>2</sub> (0.5 mmol) and GaCl<sub>3</sub> (0.5(i)/1.0 mmol(ii)) in C<sub>6</sub>H<sub>3</sub>F (2 mL) was stirred for 12 h at room temperature after which <sup>31</sup>P{<sup>1</sup>H} spectra were recorded ((i): Figure 3, (ii): <sup>31</sup>P{<sup>1</sup>H} NMR spectrum was found to be similar to (i)).

<sup>31</sup>P{<sup>1</sup>H} NMR Experiments of (*i*-Pr<sub>2</sub>N)PCl<sub>2</sub>/GaCl<sub>3</sub>/P<sub>4</sub> Mixtures: A suspension of P<sub>4</sub> (0.5 mmol) in a solution of (*i*-Pr<sub>2</sub>N)PCl<sub>2</sub> (0.5 mmol) and GaCl<sub>3</sub> (0.5(*i*)/1.0 mmol(*ii*)) in C<sub>6</sub>H<sub>3</sub>F (2 mL) was stirred for 12 h at room temperature after which <sup>31</sup>P{<sup>1</sup>H} spectra were recorded. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of (*i*) and (*ii*) were found to be similar to the data obtained for (Cy<sub>2</sub>N)PCl<sub>2</sub>. [(*i*-Pr<sub>2</sub>N)P<sub>5</sub>Cl]<sup>+</sup> (**15a**<sup>+</sup>) (C<sub>6</sub>H<sub>5</sub>F, C<sub>6</sub>D<sub>6</sub>-capillary, 25 °C): ABMX<sub>2</sub> spin system: ( $\delta_A = -274.6$  ppm,  $\delta_B = -266.6$  ppm,  $\delta_M = 33.1$  ppm,  $\delta_X = 118.0$  ppm, <sup>1</sup>J(P<sub>A</sub>P<sub>X</sub>) = -152.9 Hz, <sup>1</sup>J(P<sub>B</sub>P<sub>X</sub>) = -144.4 Hz, <sup>1</sup>J(P<sub>A</sub>P<sub>B</sub>) = -161.3 Hz, <sup>1</sup>J(P<sub>M</sub>P<sub>X</sub>) = -278.3 Hz, <sup>2</sup>J(P<sub>A</sub>P<sub>M</sub>) = 18.1 Hz, <sup>2</sup>J(P<sub>B</sub>P<sub>M</sub>) = -24.0 Hz.

**Synthesis of [14b][GaCl<sub>4</sub>]:** To a solution of  $(Cy_2N)PCl_2$  (1.0 mmol) in  $C_6H_5F$  (5 mL) GaCl<sub>3</sub> (1.0 mmol) was added. The reaction mixture was stirred for 1 h at room temperature accompanied by the formation of small amounts of a white precipitate. *n*-Hexane (2 mL) was slowly added to complete precipitation. The white solid was isolated, washed with *n*-hexane (3 x 2 mL) and dried in vacuo. **[14b]**[GaCl<sub>4</sub>] Yield: 81 % (370 mg, 0.8 mmol); m.p. 110.0–110.6 °C; **IR** (KBr, 25 °C, (cm<sup>-1</sup>)): 2937 (vs), 2857 (w), 1447 (s), 1386 (vw), 1257 (vw), 1165 (w), 1144

(vw), 1064 (s), 1014 (w), 947 (w), 894 (m), 610 (w), 550 (m), 504 (vw), 430 (vw); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta = 1.16-1.28$  (2H, m, CH<sub>2</sub>), 1.37-1.50 (4H, m, CH<sub>2</sub>), 1.70-1.85 (6H, m, CH<sub>2</sub>), 1.90-1.98 (4H, m, CH<sub>2</sub>), 2.02-2.09 (4H, m, CH<sub>2</sub>), 4.11-4.23 (2H, m, CH); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta = 25.0$  (2C, s, CH<sub>2</sub>), 26.3 (4C, s, CH<sub>2</sub>), 34.6 (4C, d, <sup>3</sup>J<sub>PC</sub> = 6.9 Hz), 65.8 (2C, d, CH, <sup>3</sup>J<sub>PC</sub> = 6.4 Hz); <sup>71</sup>Ga{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta = 250.7$  (1 Ga, s(br),  $v_{1/2} = 5000$  Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta = 250.7$  (1 Ga, s(br),  $v_{1/2} = 113$  Hz); elemental analysis for C<sub>12</sub>H<sub>22</sub>Cl<sub>5</sub>GaNP (458.27): calcd. N: 3.1 C: 31.4, H 4.8; found: N: 2.8 C 30.8, H 4.7 %.

#### Acknowledgement

We gratefully acknowledge the Fonds der Chemischen Industrie (FCI) (fellowship for M.H.H.), the European Phosphorus Science Network (PhoSciNet CM0802) and the Deutsche Forschungsgemeinschaft (DFG) (WE 4621/2–1). J.J.W. thanks *Prof. F. Ekkehardt Hahn* (WWU Münster) for his generous support.

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Received: March 20, 2012 Published Online: May 15, 2012