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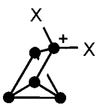
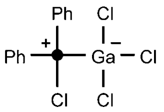
Formation of $[Ph_2P_5]^+$, $[Ph_4P_6]^{2+}$, and $[Ph_6P_7]^{3+}$ Cationic Clusters by Consecutive Insertions of $[Ph_2P]^+$ into P–P Bonds of the P_4 Tetrahedron**

Jan J. Weigand, Michael Holthausen, and Roland Fröhlich*

Many transition-metal complexes containing a broad variety of degraded or aggregated P_n units, resulting from P_4 activation, have been discovered and described.[1–3] In comparison, the functionalization of P_4 with main-group fragments represents a new and rapidly developing field. Recently, Bertrand and co-workers have found that carbenes react with white phosphorus, with or without inducing its fragmentation or aggregation[4]. Similarly, heavier carbene-like main-group-element derivatives containing Al,[5] Ga,[6] Tl,[7] and Si,[8] insert into the P–P bonds of the P_4 tetrahedron.[9] Krossing and co-workers have reported the insertion of in situ-prepared, highly electrophilic, carbene-analogous $[PX_2]^+$ cations (X = Br, I) into one of the P–P bonds of P_4, yielding phosphorus-rich binary cage cations $[P_5X_2]^+$ (**1**, see below). Although highly reactive, these cations could be successfully isolated using non-oxidizing, weakly coordinating counteranions of type $[Al(OR)_4]^-$ (OR = polyfluorinated aliphatic alkoxide).[10] In contrast to the well-developed chemistry of oligophosphorus anions,[11] **1** represents the only structurally characterized cationic homoatomic phosphorus cluster reported.



1 X = Br, I



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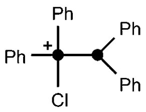

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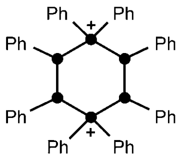
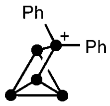
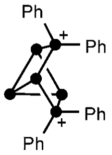


4 ● = P

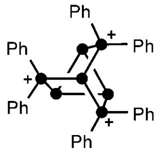
We recently reported that a room-temperature molten medium **M**, consisting of the donor–acceptor complex $[Ph_2PCl\rightarrow GaCl_3]$ (**2**), the chloro(diphenylphosphanyl)diphenylphosphonium cation **3**, and the counteranions $[Ga_nCl_{3n+1}]^-$ ($n = 1, 2, 3$) can be readily obtained from the binary $Ph_2PCl/GaCl_3$ system. This melt is a reactive source of the diphenylphosphenium cation $[Ph_2P]^+$, which inserts into P–P bonds of $(PhP)_5$, to give the 2,3,4,5-*cyclo*-tetraphosphanyl-1,4-diphosphonium dication **4**.[12,13] As an acceptor for phosphenium insertion, P_4 should be more viable to accommodate multiple charges and, hence, the formation of larger cationic clusters than the monocationic species **1** is conceivable. Herein, we report the targeted preparation of mono- to tricationic clusters $[Ph_2P_5]^+$ (**5**), $[Ph_4P_6]^{2+}$ (**6a**), $[Ph_6P_7]^{3+}$ (**7a**, see below)[14] by reaction of P_4 in the room-temperature molten medium **M** with varied stoichiometries and reaction conditions such as temperature and reaction time.



5

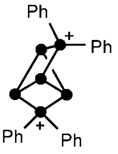


6a

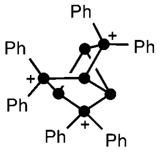


7a

● = P

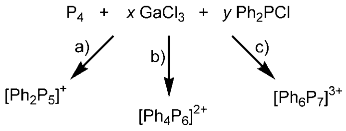


6b



7b

The reaction of P_4 with an excess of Ph_2PCl in freshly prepared molten medium **M** ($P_4/Ph_2PCl/GaCl_3$ 1:8:5) at 70 °C for 7 h gave rise to a clear, pale yellow honey-like melt (Scheme 1 b). The $^{31}P\{^1H\}$ NMR spectrum (Figure 1 a) of the dissolved melt in CH_2Cl_2 revealed two new spin systems, A_2MX_2 (**5**: $\delta_A = -292.0$, $\delta_M = -5.4$, $\delta_X = 19.7$ ppm, $^1J(P_A,P_X) = -139.7$, $^1J(P_M,P_X) = -212.2$, $^2J(P_A,P_M) = 8.3$ Hz) and ABMM′XX′ (**6a**: $\delta_A = -231.7$, $\delta_B = -213.0$, $\delta_M =$



Scheme 1. Reaction of P_4 with $GaCl_3$ and Ph_2PCl where a) $x = 1$, $y = 1$; (60 °C for 45 min.); b) $x = 8$, $y = 5$ (70 °C for 7 h); c) $x = 6$, $y = 3$ (60 °C for 1 h than 100 °C for 12 h).

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[*] Dr. J. J. Weigand, M. Holthausen
Institut für Anorganische und Analytische Chemie
Universität Münster
Corrensstrasse 30, 48149 Münster (Germany)
Fax: (+49) 251-83-33108
E-mail: jweigand@uni-muenster.de
Dr. R. Fröhlich
Organisch-Chemisches Institut, Universität Münster (Germany)

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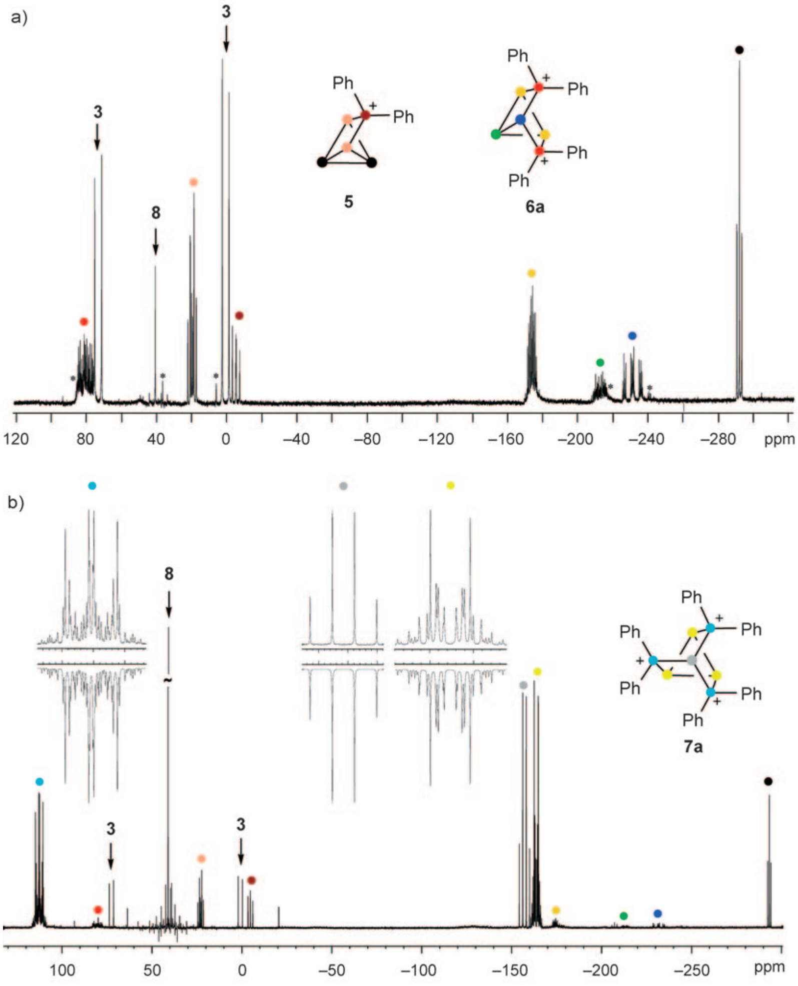

Figure 1. a) $^{31}P\{^1H\}$ NMR spectrum (101.26 MHz) of the reaction mixture according to Scheme 1 a) after 7 h at 70 °C and dissolved in CH_2Cl_2. Signals assigned to unknown side-products are labeled with asterisks; b) $^{31}P\{^1H\}$ NMR spectrum (161.94 MHz) of the reaction mixture according to Scheme 1 c) after 12 h at 100 °C and dissolved in CH_2Cl_2. Expansions (inset) show the experimental (up) and fitted[16] (down) spectra for cation **7a**. Signals assigned to decomposition products and other compounds are labeled according to a).

-174.4, $\delta_X = 80.5$ ppm),[15,16] the presence of the phosphanyl–phosphonium cation **3** (two doublets, $\delta = 75.8$, -0.6 ppm, $^1J(P,P) = -380.1$ Hz), and small amounts of the $[Ph_2PClH]^+$ cation **8**,[17] which is a decomposition product, presumably resulting from solvent activation.[18]

The proton-coupled ^{31}P NMR spectrum of the reaction mixture showed only an additional splitting of the downfield resonance at 41 ppm ($^1J(P,H) = 581.0$ Hz) resulting from the one-bond coupling of the hydrogen to the phosphorus atom in **8**. The resonances for the A_2MX_2 spin system can be assigned to the monocation **5** as shown in Figure 1.

The resonances for the ABMM′XX′ spin system with an approximate ratio of 1:1:2:2 suggest the formation of the dicationic species **6a**, containing four chemically inequivalent phosphorus atoms. Two second-order resonances with relative intensities of 1:2, representing an AA′XX′X″X‴ spin system, would be expected for the symmetrical isomer **6b** which may, therefore, only be present in concentrations below the detection limit. The P_6 cage arrangement proposed for **6a** is unprecedented and, to our knowledge, there are only two related neutral tricyclic hexaphosphanes, reported by Jutzi and co-workers.[19] The variable temperature $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture (temperature profile down to 200 K) indicated no dynamic behavior of cations **5** and **6a** in CD_2Cl_2 solution. The monocation **5** was formed quantitatively as a tetrachlorogallate salt by the 1:1:1 reaction of P_4, Ph_2PCl, and $GaCl_3$ (Scheme 1 a) at 60 °C within 45 minutes as a pale yellow, crystalline material (71 % yield).[18] Compound **5**$[GaCl_4]$ is very air- and moisture-sensitive but is stable for at least six months at room temperature. The $^{13}C\{^1H\}$ NMR spectrum of **5**$[GaCl_4]$ in CD_2Cl_2 showed a characteristic, large $^1J(C,P)$ value of 48.6 Hz with smaller long-range couplings of $J < 13$ Hz. The monocation **5** is very stable in CD_2Cl_2 solution and, after two weeks, there were no indications of decomposition or rearrangement in the $^{31}P\{^1H\}$ NMR sample. The C_{2v}-symmetric P_5 cage, as already deduced in solution from the $^{31}P\{^1H\}$ NMR spectrum, was also confirmed in the solid state by single-crystal X-ray diffraction. A view of the molecular structure of the nearly C_{2v}-symmetric cation **5** is shown in Figure 2. **5**$[GaCl_4]$ crystallizes in the triclinic space group $P\bar{1}$ with three

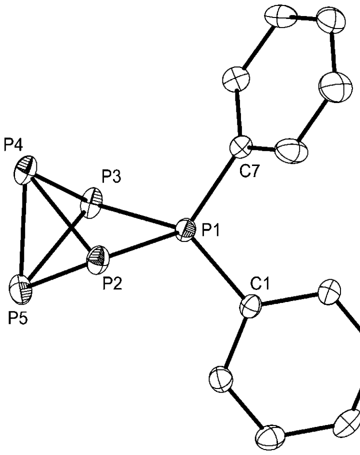

Figure 2. ORTEP representation of the molecular structure of the cation **5** in **5**$[GaCl_4]$. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and counteranions are omitted for clarity. Only one cation of the asymmetric unit is shown. Selected bond lengths [Å] and angles [°]: P1–C1 1.792(3), P1–C7 1.789(3), P1–P2 2.182(1), P1–P3 2.186(1), P2–P4 2.244(1), P2–P5 2.239(1), P3–P5 2.249(1), P3–P4 2.245(1), P4–P5 2.179(1); C1-P1-C7 108.4(1), C1-P1-P2 115.5(1), C7-P1-P3 112.9(1), P2-P1-P3 88.28(4), P1-P2-P4 84.76(4), P1-P3-P5 86.38(4), P2-P4-P3 85.33(4), P3-P5-P2 85.34(4), P4-P2-P5 58.18(3), P5-P3-P4 58.01(3).

formula units in the unit cell. The three crystallographically different cations display nearly identical bond lengths and angles. However, in two of the three cations the phenyl groups are disordered. The P—P bond lengths in **5** (ranging from 2.179(1) to 2.249(1) Å) are very close to the values found in the $[P_5Br_2]^+$ ion (ranging from 2.150(7) to 2.262(8) Å).[10] The bonds between the tri- and tetracoordinated phosphorus atoms and the P4—P5 bond in cation **5** are approximately 0.07 Å shorter than the remaining P—P bonds and are even shorter than those in P_4 (2.220 Å). The P4—P5 bond length is reminiscent of both the related strained SiP_4 cage compound (2.159(2) Å)[8d] and of bicyclo[1.1.0]tetraphosphanes, R_2P_4 (R = organyl) which display relatively short P—P bridgehead bonds (2.120 Å).[20] It has been observed in several examples, that P—P distances involving a cationic four-coordinate phosphorus center are generally slightly shorter.[13,21,22]

Attempts to form dication **6a** by a stoichiometric reaction of P_4 and the melt **M** ($P_4/Ph_2PCl/GaCl_3$ 1:2:2) resulted in mixtures of **3**, **5**, **6a**, and **8** from which it has not been possible to isolate cation **6a**. Besides the isolation of dication **6a**, we were interested in the possibility of inserting more than two $[Ph_2P]^+$ cations into the P_4 framework. However, only mixtures of **3**, **5**, and **6a** were formed when the $GaCl_3$ mole fraction was lower than 0.5. In these mixtures, it can be assumed that gallium is present entirely in the tetrachlorogallate $[GaCl_4]^-$ form. Hence, the melt is considered to be a basic medium in which highly positively charged cations might not be stable.[23] Subsequently, we increased the amount of $GaCl_3$ by performing a 1:3:6 reaction of P_4, Ph_2PCl, and $GaCl_3$ (Scheme 1c) at 100 °C, hence, switching to an acidic medium. Indeed, a clean reaction occurred, with the formation of one major product. From this melt, pure, colorless crystals of the heptachlorodigallate salt **7a**$[Ga_2Cl_7]_3$ were grown at 100 °C within 12 h. The crystals were washed with small amounts of 1,2-difluorobenzene and pentane, giving analytically pure **7**$[Ga_2Cl_7]_3$ in moderate yield (40 %). Compound **7a**$[Ga_2Cl_7]_3$ is extremely moisture- and air-sensitive and melts between 85–87 °C. The compound crystallized in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. To our knowledge, the $[Ph_6P_7]^{3+}$ cation (**7a**) represents the first structurally characterized homoatomic phosphorus cage with a positive charge greater than one. In the solid state, trication **7a** takes the form of a P_7 cage with a typical nortricyclane (tricyclo[2.2.1.0^{2,6}]heptane) skeleton, reminiscent of the $[P_7]^{3-}$ trianion or P_4S_3 (Figure 3).[24,25] However, **7a** incorporates three tetracoordinated phosphonium centers in the bridging positions. Hence, the molecular structure has approximate C_3 symmetry. The bond lengths and angles follow a similar trend to that in the monocation **5**.

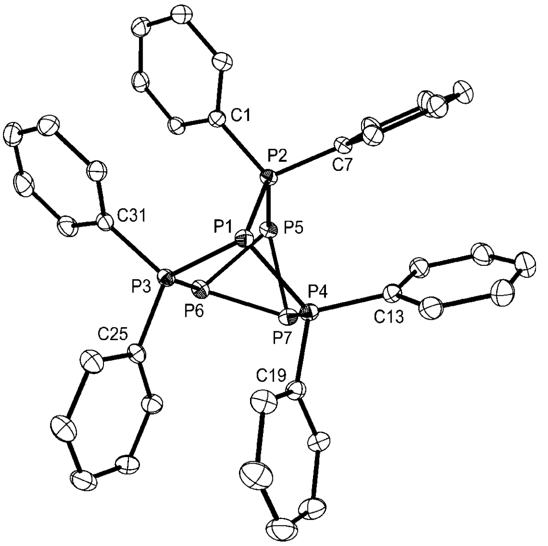

Figure 3. ORTEP representation of the molecular structure of the cation **7a** in **7a**$[Ga_2Cl_7]_3$. Thermal ellipsoids are set at 50 % probability. Hydrogen atoms and counteranions are omitted for clarity. Selected bond lengths [Å] and angles [°]: P2—C1 1.784(3), P2—C7 1.791(3), P1—P2 2.223(1), P1—P3 2.218(1), P1—P4 2.219(1), P2—P5 2.27(1), P3—P6 2.224(1), P4—7 2.227(1), P5—P6 2.215(1), P6—P7 2.219(1), P5—P7 2.220(1); C1-P2-C7 109.3(1), C1-P2-P1 113.3(1), C7-P2-P1 106.4(1), P3-P1-P2 91.89(4), P4-P1-P2 91.49(4), P3-P1-P4 91.61(4), P1-P2-P5 109.31(4), P2-P5-P6 101.08(4), P2-P5-P7 104.02(4), P6-P5-P7 60.06(3).

Consistently with the solid state structure, the $^{31}P\{^1H\}$ NMR spectrum of **7a**$[Ga_2Cl_7]_3$ in CD_2Cl_2 solution at room temperature (Figure 1b) features three resonances which display a complex AA′A″BXX′X″ spin pattern with relative intensities of 3:1:3, resulting from the C_3 symmetry of the cation. There are no indications of the formation of the asymmetric isomer **7b** in the spectrum. Iterative analyses[16] of the complex spectrum, performed at two external field strengths, revealed a first order resonance for the tricoordinated apical phosphorus atom at $\delta_B = -157.1$ ppm represented by a quartet, indicating only a coupling to the three bridging phosphorus atoms ($^1J(B,X) = {}^1J(B,X') = {}^1J(B,X'') = -306.1$ Hz, $^2J(B,A) = {}^2J(B,A') = {}^2J(B,A'') = 0$ Hz). The coupling patterns for the basal phosphorus atoms at $\delta_A = -163.7$ ppm and the bridging phosphonium centers at $\delta_X = 112.6$ ppm are complex, owing to second order effects ($^1J(A,X) = {}^1J(A',X') = {}^1J(A'',X'') = -397.0$ Hz , $^1J(A,A') = {}^1J(A,A'') = {}^1J(A',A'') = -220.4$ Hz, $^2J(X,X') = {}^2J(X,X'') = {}^2J(X',X'') = 16.5$ Hz, $^2J(A,X') = {}^2J(A,X'') = {}^2J(A',X'') = 14.2$ Hz). Full spectroscopic characterization of **7a**$[Ga_2Cl_7]_3$ was hampered by its limited stability in solution. Elemental analysis indicated that **7a**$[Ga_2Cl_7]_3$ could be isolated as a pure compound from the reaction mixture.[18] However, it readily decomposes as soon as dissolved in CD_2Cl_2, forming **6a**, **5**, **3**, and **8** (Figure 1b). A detailed investigation, to understand the decomposition of trication **7a** in solution, is currently underway.

In summary, the solvent-free method represents a powerful strategy for the functionalization of the P_4 tetrahedron to form new cationic phosphorus-rich organophosphorus cage and cluster systems, as illustrated by the formation of mono- to trications **5**, **6a**, and **7a**, by the consecutive insertion of $[Ph_2P]^+$ into P—P bonds of the P_4 tetrahedron. The trication **7a** was only formed in cases where the reaction was carried out in acidic media ($GaCl_3$ mole fraction > 0.5), indicating that insertion of $[Ph_2P]^+$ strongly depends on the presence of an excess of Lewis acid to prevent the detrimental presence of Cl^- ions, which decompose **7a** by nucleophilic attack. We are currently investigating the reactivity of various other Lewis acid/chloropnictogen systems with P_4 and the behavior of the reaction products in organic solvents.

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Keywords: cations · cluster compounds · phosphorus · solvent-free synthesis · structure elucidation

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[14] Possible isomers, **6a**/**6b** for the dications and **7a**/**7b** for the trications, assuming that two or more positive phosphonium centers are not situated adjacent to each other.

[15] The NMR spectrum of **6a** could not be simulated owing to its complexity. For the assignment of the phosphorus nuclei see the 2D ^{31}P–^{31}P COSY NMR spectrum provided in the Supporting Information.

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