

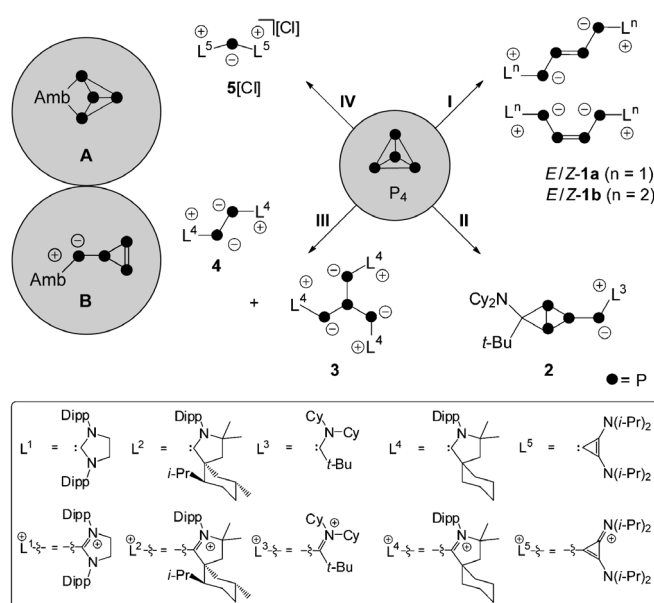
[3+2] Fragmentation of an $[RP_5Cl]^+$ Cage Cation Induced by an N-Heterocyclic Carbene**

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Dedicated to Professor Bernt Krebs on the occasion of his 75th birthday

The transformation of white phosphorus with ambiphilic main-group element compounds (Amb; for example, carbenes, silylenes, phosphonium ion salts) has given new impetus to the field of P_4 activation. Depending on the nature of Amb, these reactions proceed by two distinct reaction mechanisms.^[1] If Amb is of predominantly electrophilic character, the reaction commences with an electrophilic attack on P_4 . A subsequent rearrangement yields cage compounds of type **A** (Scheme 1). The overall reaction corresponds to a formal insertion of Amb into a P–P bond of the P_4 tetrahedron. Several main-group-element-centered compounds,^[2] and especially those featuring a Group 15 element, react according to this mechanism. For example, reactions were reported yielding several remarkable cage cations, such as P_4NO^+ ,^[3] $P_5X_2^+$ ($X = I, Br, Cl$)^[4] and a series of intriguing polyphosphorus cages featuring organo substituents.^[5]

If the nature of Amb is predominantly nucleophilic, the reaction of Amb and P_4 commences with a nucleophilic attack. A subsequent rearrangement gives a *cyclo*-triphosphirene-type structure **B** (Scheme 1). The formation of **B** is favored by the propensity of Amb to accept electron density from the adjacent P atom.^[1] Carbenes **L** are ambiphiles with predominantly nucleophilic character^[6] and react accordingly. Mainly *N*-heterocyclic carbenes (NHC) and cyclic or acyclic alkyl amino carbenes (*cAAC* or *aAAC*) were investigated in reactions with P_4 .^[7,8] In all cases a *cyclo*-triphosphirene of type **B** was reported as an intermediate. However **B** is elusive, and distinct reaction pathways occur depending on the electronic and steric features of **L**. Bertrand and co-workers reacted P_4 with carbene **L**¹ or **L**² in a 1:2 stoichiometry and obtained *E/Z*



Scheme 1. Carbene-induced transformation and fragmentation reactions of P_4 . I) For example + 2 **L**², *n*-hexane, RT; **E-1a** 65%; II) + 3 **L**³, Et₂O, RT, 2 h, 66%; III) + 3 **L**⁴, Et₂O, RT, 2 h; **3** 67%, **4** 12%; IV) + 3 **L**⁵, thf, RT, 12 h, CHCl₃, 30 min, 74%. Dipp = 2,6-diisopropylphenyl. Only one representative resonance structure for **L**ⁿ and for **L**ⁿ⁽⁺⁾ is depicted.

isomers **1a,b** via an intermediate of type **B** (Scheme 1, **I**).^[7] Bicyclic compound **2** results from the reaction of an intermediate of type **B** with the alkylamino carbene **L**³ by a cycloaddition reaction involving the triphosphirene P–P double bond (**II**).^[8] Compound **3** results from a ring-opening reaction of **B** with two equivalents of **L**⁴, which is accompanied by the formation of a small amount of **4** as side product (**III**).^[8] A [3+1] fragmentation of the P_4 tetrahedron was achieved using the less sterically demanding carbene **L**⁵ in a 3:1 reaction with P_4 .^[8] The P_1 fragment was identified as cation **5**⁺, and a compound of unknown constitution featuring a P_3 moiety was indicated in the ³¹P NMR spectrum of the reaction mixture (**IV**).^[8] In this context we investigated the reaction of DippP₅Cl⁺ cage compound **6**[GaCl₄] with NHC **L**⁶ and obtained intriguing, novel polyphosphorus compounds. A solution of **L**⁶ in CH₂Cl₂ was added dropwise to a solution of **6**[GaCl₄] in CH₂Cl₂ at –78 °C (Scheme 2). A red reaction mixture was obtained, which turned yellow after slow warming to ambient temperature. The remarkable cationic bicyclo[1.1.0]tetraphosphane **7**⁺ was identified as the major product in this reaction.^[9] Apparently, a nucleophilic attack of

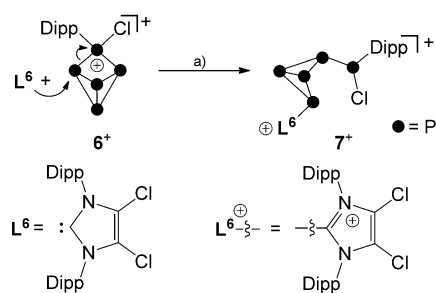
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Scheme 2. Reaction of $6[\text{GaCl}_4]$ with carbene L^6 in a 1:1 stoichiometry. a) CH_2Cl_2 , -78°C , 2 h, $-78^\circ\text{C} \rightarrow \text{RT}$, 12 h. Anions are omitted for clarity.

L^6 on a P atom adjacent to the phosphonium moiety in 6^+ occurs.

This leads to the cleavage of the P–P bond between these atoms. The molecular structure of 7^+ is shown in Figure 1 and provides a rare example of a molecular structure of an *endo,exo*-substituted bicyclo[1.1.0]tetraphosphane. The bicyclic P_4 moiety reveals a less pronounced folding ($\text{P}2 \cdots \text{P}3$: $3.055(1) \text{ \AA}$) than in derivatives featuring substituents in *exo,exo*-positions (av. $2.75 \text{ \AA}$).^[10] A short intramolecular distance between the atoms P1 and P3 ($3.035(1) \text{ \AA}$) is observed. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture shows the complex multiplet resonances of the ACEMX spin system of 7^+ (Supporting Information, Figure S2.2.1).^[9] The $^{31}\text{P}\{^1\text{H}\}$ NMR parameters indicate a non-symmetrical molecular structure. Thus, the rotation around the P–P bond involving the Dipp-substituted P atom is hindered. The *endo,exo*-substitution of 7^+ causes an extraordinary large $^3J(\text{PP})$ coupling constant ($^3J(\text{PP}) = 244.6 \text{ Hz}$) involving the chloro- and imidazoliumyl-substituted P atoms. The observed small amounts of remaining cation 6^+ and other unidentified species together with the instability of 7^+ in the reaction mixture prevented the isolation and full characterization of

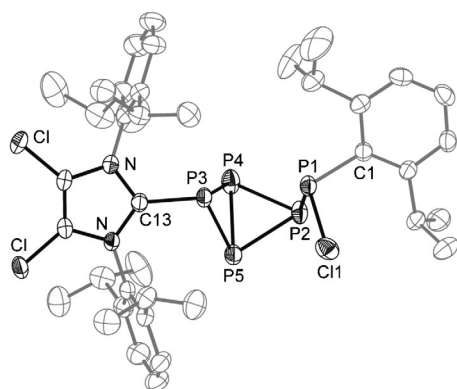


Figure 1. Molecular structure of cation 7^+ in $7[\text{GaCl}_4] \cdot \text{CH}_2\text{Cl}_2$ (ellipsoids are set at 50% probability; hydrogen atoms and solvate molecules are omitted for clarity). Selected bond lengths [$\text{\AA}$] and calculated values in parentheses: C1–P1 $1.834(2)$ (1.830), C13–P3 $1.852(2)$ (1.865), P1–Cl1 $2.0735(9)$ (2.089), P1...P3 $3.035(1)$ (3.204), P2...P3 $3.055(1)$ (3.118), P1–P2 $2.2274(9)$ (2.227), P2–P4 $2.2174(9)$ (2.272), P2–P5 $2.2170(9)$ (2.233), P3–P4 $2.2056(8)$ (2.271), P3–P5 $2.2129(8)$ (2.262), P4–P5 $2.182(1)$ (2.204).

the latter. However, the formation of 7^+ might constitute the first step of a disassembly of the $\text{DippP}_5\text{Cl}^+$ cation 6^+ into smaller fragments.

We investigated the reaction of $6[\text{GaCl}_4]$ with L^6 in a ratio of 1:3 (Figure 2, top). A suspension of $6[\text{GaCl}_4]$ in $\text{C}_6\text{H}_5\text{F}$ was added to a solution of L^6 in $\text{C}_6\text{H}_5\text{F}$ at -40°C within five

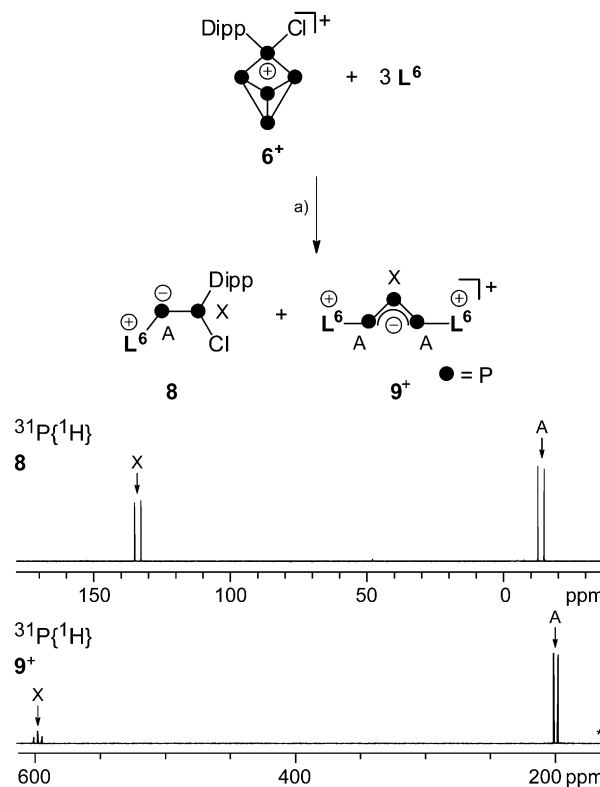


Figure 2. Top: Reaction of $6[\text{GaCl}_4]$ with carbene L^6 in a 1:3 stoichiometry. a) $\text{C}_6\text{H}_5\text{F}$, -40°C , 5 min, $-40^\circ\text{C} \rightarrow \text{RT}$, 3 h; **8** 87%, **9** $[\text{GaCl}_4]$ 89%; anions are omitted. Bottom: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **8** (C_6D_6 , RT) and **9** $[\text{GaCl}_4]$ (CD_2Cl_2 , RT). A small amount of an unidentified side product is marked with an asterisk.^[9]

minutes. At -40°C a deep-red reaction mixture was obtained which turned into a deep green solution upon warming to ambient temperature. $^{31}\text{P}\{^1\text{H}\}$ NMR investigation of the reaction mixture (Supporting Information, Figure S2.3.1) revealed the nearly quantitative fragmentation of the P_5^+ core of 6^+ into a P_2 (**8**) and a P_3^+ species (**9** $^+$). The former was isolated in very good yields (87%) by removal of all volatiles from the reaction mixture and extraction of the obtained green solid with *n*-hexane/benzene (10:1). Compound **8** is of a deep-yellow color ($\lambda_{\text{max}} = 410 \text{ nm}$), which is attributed to its inversely polarized phosphalkene moiety.^[11] Salt **9** $[\text{GaCl}_4]$ was obtained as an analytically pure, green solid in very good yields (89%) by washing the residue with benzene. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the isolated compounds are depicted in Figure 2. The resonance of the X part of the AX spin system of **8** ($\delta(\text{P}_\text{X}) = 133.8 \text{ ppm}$) is in the typical range of chloro-substituted phosphanes.^[12] The chemical shift of $\delta(\text{P}_\text{A}) = -13.7 \text{ ppm}$ is comparable to those of inversely polarized phosphalkenes.^[11] The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum

reveals a doublet of doublet resonance for the C2 atom of the imidazoliumyl substituent ($\delta(\text{C-2}) = 172.1$ ppm, $^1J(\text{CP}_\text{A}) = 127.2$ Hz, $^2J(\text{CP}_\text{X}) = 24.0$ Hz). The isopropyl groups of the Dipp groups of the imidazoliumyl substituent of **8** are diastereotopic owing to the chiral P_X atom and reveal a twofold set of resonances in the ^1H NMR spectrum. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9** $[\text{GaCl}_4]$ exhibits an A_2X spin system ($\delta(\text{P}_\text{A}) = 199.4$ ppm, $\delta(\text{P}_\text{X}) = 597.9$ ppm, $^1J(\text{P}_\text{A}\text{P}_\text{X}) = -508.3$ Hz), indicating a C_s - or a C_2 -symmetric molecular structure. The P_X atom resonates at remarkable low field and compares well with the respective chemical shifts of the central P atom of metal-coordinated triphosphaallyl derivatives.^[13] The chemical shift of the A part is between those of related P-substituted, inversely polarized phosphaaalkenes ((*E*)-**1a** $\delta(\text{P}) = 63.0$ ppm; Scheme 1)^[7b] and imidazoliumyl-substituted diphosphenes (for example, $[\text{L-P=P-L}]^{2+}$ $\delta(\text{P}) = 452$ ppm).^[14] The magnitude of the $^1J(\text{PP})$ coupling constant ($^1J(\text{P}_\text{A}\text{P}_\text{X}) = -508.3$ Hz) agrees well with those typically observed for diphosphenes.^[15] The ^1H NMR spectrum of **9** $[\text{GaCl}_4]$ shows one set of resonances corresponding to the Dipp substituents. This indicates chemically equivalent imidazoliumyl substituents and a free rotation around the C-P_A bonds. The resonance of the C2 atoms of the imidazoliumyl substituent ($\delta(\text{C2}) = 161.9$ ppm) is shifted to higher field compared to **8**. This is in line with a decreased P–C double-bond character.^[11] The Raman spectrum of **9** $^+$ is dominated by a prominent band corresponding to the overlapping intense asymmetric and symmetric stretching modes of the P_3 moiety ($\nu_{\text{asym/sym}}(\text{P-P-P}) = 566$ cm^{-1}).^[9] Similar intense bands are reported for the symmetric stretching modes of diphosphenes (for example, RP=PR ($\text{R} = \text{Si}(\text{SiMe}_3)_3$), $\nu_{\text{sym}}(\text{P-P}) = 591$ cm^{-1} ;^[16] $\text{R} = \text{Mes}^*$, $\nu_{\text{sym}}(\text{P-P}) = 610$ cm^{-1}).^[17] The intensive green color of **9** $[\text{GaCl}_4]$ results from a strong absorption maximum at $\lambda_{\text{max}} = 696$ nm, which is assigned to a $\text{n} \rightarrow \pi^*$

transition. A second absorption maximum at $\lambda = 443$ nm corresponds to a $\pi \rightarrow \pi^*$ transition. Similar transitions are reported for diphosphenes.^[15] The molecular structure of **9** $^+$ is shown in Figure 3 (left). An interaction of the P_3 moiety with the anion or solvate molecules was not observed. This might be explained by the significant steric demand of the imidazoliumyl substituents. The P–P bond lengths are almost equal (P1-P2 2.093(1) Å, P3-P2 2.091(1) Å) and between lengths expected for a typical P–P single (2.22 Å) and double bond (2.00 Å).^[15] The P–C bonds (C1-P3 1.815(2) Å, C28-P1 1.814(3) Å) are shorter than the respective bonds in imidazoliumyl-substituted phosphanes (av. C–P 1.85 Å),^[18] indicating some degree of P–C double-bond character. A very acute P–P–P angle (P3-P2-P1 : 87.2(4)°) and a short intramolecular distance between both terminal P atoms ($\text{P3} \cdots \text{P1}$ 2.878(1) Å) are observed.^[19] Such acute P–P–P angles are characteristic features of triphosphaallyl moieties.^[13]

To gain a detailed understanding of the bonding situation in **9** $^+$, quantum chemical calculations were carried out at BP86/def2-TZVPP on the model compound $\text{L}'_2\text{P}_3^+$ (**9** $^+$, $\text{L}' = 1,3\text{-dimethylimidazol-2-ylidene}$).^[9] The optimized geometry of **9** $^+$ is in good agreement with the experimental values (Figure 3, left). The comparatively large deviation of the P3-P2-P1 angle can be explained with the very soft bending potential of the P_3 fragment. The analysis of the Kohn–Sham molecular orbitals (MO) reveals that the LUMO, HOMO, and HOMO–4 of **9** $^+$ are closely related to the classical π system of the C_3 allyl anion (Figure 3, middle). The LUMO corresponds to an antibonding π^* -type orbital. The HOMO reveals a node at the central P atom and two p-type lobes at the terminal P atoms. The HOMO–4 corresponds to a bonding π -type orbital. The nearly degenerated orbitals HOMO–2 (–0.27 eV), HOMO–3 (–0.27 eV), and HOMO–7 (–0.33 eV) are dominated by contributions from the lone

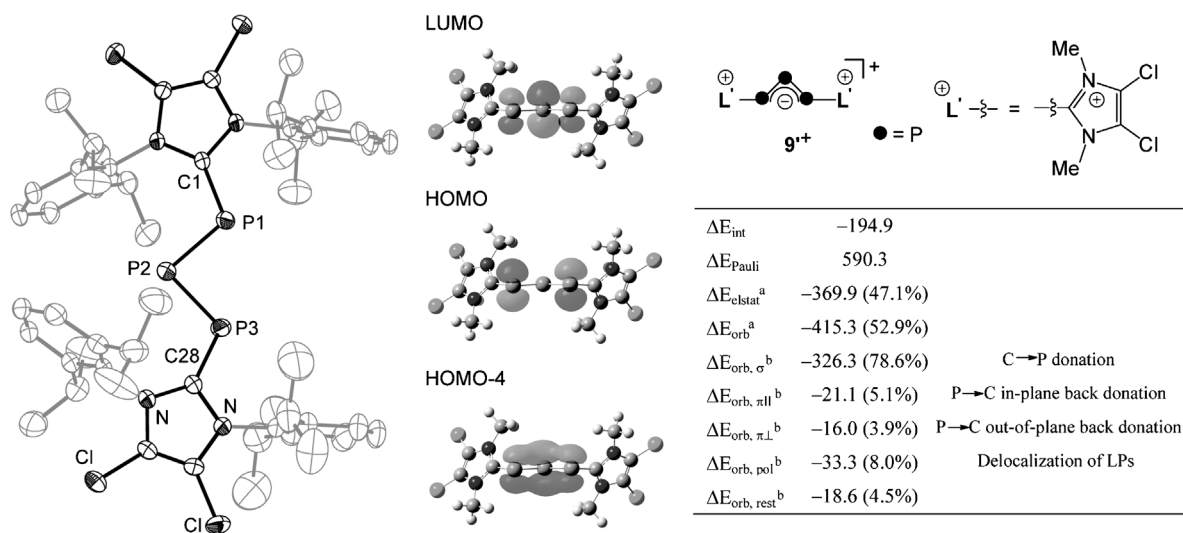
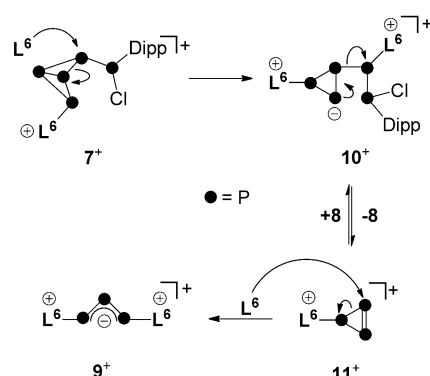


Figure 3. Left: molecular structure of cation **9** $^+$ in **9** $[\text{GaCl}_4] \cdot 2(\text{CH}_2\text{Cl}_2)$ (ellipsoids are set at 50% probability; hydrogen atoms and solvate molecules are omitted for clarity). Selected bond lengths [Å] and angles [°], calculated values in parentheses: C1–P3 1.815(2) (1.827), C28–P3 1.814(3) (1.826), P1–P2 2.093(1) (2.111), P3–P2 2.091(1) (2.111); P3–P2–P1 87.2(4) (101.4). Middle: selected molecular orbitals of **9** $^+$: LUMO (–0.17 eV), HOMO (–0.24 eV), HOMO–4 (–0.32 eV). Right: EDA–NOCV results [kcal mol $^{-1}$] for **9** $^+$ (BP86/TZ2P+). Electronic configuration of the fragments: P_3^+ singlet, $2\text{L}'$ singlet. [a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. [b] Percentage values in parentheses give the contribution to the orbital interaction ΔE_{orb} .^[9]

pairs of electrons on the P atoms. An energy decomposition analysis with natural orbitals for chemical valence (EDA-NOCV)^[20] was performed for 9^+ , where P_3^+ and $2L^+$ are taken as interacting fragments. The dominant contribution (78.6%) to the orbital interactions comes from the σ -type donation $\Delta E_{\text{orb},\sigma}$ of the lone-pair donor orbitals of L into empty P_3^+ orbitals via $(+/+)$ and $(+/-)$ combination $L \rightarrow P_3^+ \leftarrow L$. The other contributions, which are much less important, come from in-plane and out-of-plane π -type back donation and from delocalization of the lone pairs. The σ donation of the ligands nearly cancels the positive charge of the P_3^+ fragment in the molecule. The calculated NBO partial charge of the P_3 moiety in 9^+ is +0.10 e.

A reaction sequence explaining the [3+2]-fragmentation of $6[\text{GaCl}_4]$ to 8 and $9[\text{GaCl}_4]$ on the basis of experimental evidence and quantum chemical calculations is proposed in Scheme 3.^[9] The reaction of $\text{DippP}_5\text{Cl}^+$ cage 6^+ with the first



Scheme 3. Proposed reaction sequence of the formation of 9^+ .

equivalent L^6 yields 7^+ as experimentally observed species (see above). The nucleophilic attack of a second carbene L^6 occurs at the *endo*-substituted P atom of 7^+ and initiates a P–P bond cleavage in the P_3 rings, yielding intermediate 10^+ . The formation of 10^+ is calculated to be weakly exergonic ($\Delta G_R^{298} = -5.1 \text{ kcal mol}^{-1}$). Subsequently, this intermediate intramolecularly eliminates 8 to yield the elusive triphosphirane derivate 11^+ in an endergonic reaction ($\Delta G_R^{298} = 14.3 \text{ kcal mol}^{-1}$), which however is energetically accessible. Cation 11^+ is related to **B** which constitutes the key intermediate in carbene-induced P_4 activation (Scheme 1).^[7,8] The nucleophilic attack of a third equivalent of L^6 on the P–P double bond of 11^+ initiates a ring-opening, yielding 9^+ . This final step is highly exergonic ($\Delta G_R^{298} = -28.9 \text{ kcal mol}^{-1}$) and provides the driving force for the overall reaction.

In summary, the [3+2]-fragmentation of $\text{DippP}_5\text{Cl}^+$ cage cation 6^+ with three equivalents $\text{NHC } L^6$ gives the P_2 species 8 and the P_3^+ species 9^+ . Cation 9^+ is the first triphosphaallyl derivate that is not stabilized in the coordination sphere of a metal atom. The mechanism of the [3+2]-fragmentation was elucidated and proceeds by the *endo,exo*-substituted butterfly-type cation 7^+ . The proposed reaction mechanism is supported by quantum chemical calculations. The ease of this reaction (high yields, multi-gram scale) together with the

facile accessibility of $6[\text{GaCl}_4]$ from P_4 renders 8 and 9^+ as potential precursors for a plethora of interesting subsequent transformation reactions and may give access to new, hitherto unknown polyphosphorus compounds.

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- [1] a) M. Scheer, G. Balazs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236; b) V. A. Milyukov, Y. H. Budnikova, O. G. Sinyashin, *Russ. Chem. Rev.* **2005**, *74*, 781; c) N. A. Giffin, J. D. Masuda, *Coord. Chem. Rev.* **2011**, *255*, 1342.
- [2] a) D. Holschumacher, T. Bannenberg, K. Ibrom, C. G. Daniliuc, P. G. Jones, M. Tamm, *Dalton Trans.* **2010**, *39*, 10590; b) G. Prabusankar, A. Doddi, C. Gemel, M. Winter, R. A. Fischer, *Inorg. Chem.* **2010**, *49*, 7976; c) Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull, C. E. Hughes, *Angew. Chem.* **2004**, *116*, 3525; *Angew. Chem. Int. Ed.* **2004**, *43*, 3443; d) W. Uhl, M. Benter, *Chem. Commun.* **1999**, 771; e) C. Dohmeier, H. Schnöckel, C. Robl, U. Schneider, R. Ahlrichs, *Angew. Chem.* **1994**, *106*, 225; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 199; f) Y. Xiong, S. Yao, M. Brym, M. Driess, *Angew. Chem.* **2007**, *119*, 4595; *Angew. Chem. Int. Ed.* **2007**, *46*, 4511.
- [3] T. Köchner, S. Riedel, A. J. Lehner, H. Scherer, I. Raabe, T. A. Engesser, F. W. Scholz, U. Gellrich, P. Eiden, R. A. Paz Schmidt, D. A. Plattner, I. Krossing, *Angew. Chem.* **2010**, *122*, 8316; *Angew. Chem. Int. Ed.* **2010**, *49*, 8139.
- [4] a) I. Krossing, I. Raabe, *Angew. Chem.* **2001**, *113*, 4544; *Angew. Chem. Int. Ed.* **2001**, *40*, 4406; b) M. Gonsior, I. Krossing, L. Müller, I. Raabe, M. Jansen, L. van Wüllen, *Chem. Eur. J.* **2002**, *8*, 4475; c) A. Bihlmeier, M. Gonsior, I. Raabe, N. Trapp, I. Krossing, *Chem. Eur. J.* **2004**, *10*, 5041.
- [5] a) J. J. Weigand, M. H. Holthausen, R. Fröhlich, *Angew. Chem.* **2009**, *121*, 301; *Angew. Chem. Int. Ed.* **2009**, *48*, 295; b) M. H. Holthausen, J. J. Weigand, *J. Am. Chem. Soc.* **2009**, *131*, 14210; c) M. H. Holthausen, C. Richter, A. Hepp, J. J. Weigand, *Chem. Commun.* **2010**, *46*, 6921; d) M. H. Holthausen, K.-O. Feldmann, S. Schulz, A. Hepp, J. J. Weigand, *Inorg. Chem.* **2012**, *51*, 3374; e) M. H. Holthausen, J. J. Weigand, *Z. Anorg. Allg. Chem.* **2012**, *638*, 1103.
- [6] H. M. Tuononen, R. Roesler, J. L. Dutton, P. J. Ragnogna, *Inorg. Chem.* **2007**, *46*, 10693.
- [7] a) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2007**, *119*, 7182; *Angew. Chem. Int. Ed.* **2007**, *46*, 7052; b) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2007**, *129*, 14180.
- [8] O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638; *Angew. Chem. Int. Ed.* **2009**, *48*, 5530.
- [9] See the Supporting Information for further details.
- [10] a) E. Niecke, R. Rüger, B. Krebs, *Angew. Chem.* **1982**, *94*, 553; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 544; b) A. R. Fox, R. J. Wright, E. Rivard, P. P. Power, *Angew. Chem.* **2005**, *117*, 7907; *Angew. Chem. Int. Ed.* **2005**, *44*, 7729; c) M. Donath, E. Conrad, P. Jerabek, G. Frenking, R. Fröhlich, N. Burford, J. J. Weigand, *Angew. Chem.* **2012**, *124*, 3018; *Angew. Chem. Int. Ed.* **2012**, *51*, 2964.
- [11] L. Weber, *Eur. J. Inorg. Chem.* **2000**, 2425.
- [12] Y. Carpenter, N. Burford, M. D. Lumsden, R. McDonald, *Inorg. Chem.* **2011**, *50*, 3342.
- [13] a) M. Scheer, C. Kuntz, M. Stubenhofer, M. Linseis, R. F. Winter, M. Sierka, *Angew. Chem.* **2009**, *121*, 2638; *Angew. Chem. Int. Ed.* **2009**, *48*, 2600; b) M. Scheer, S. Deng, O. J. Scherer, M.

- Sierka, *Angew. Chem.* **2005**, *117*, 3821; *Angew. Chem. Int. Ed.* **2005**, *44*, 3755; c) P. Jutzi, U. Meyer, *Phosphorus and Sulfur* **1988**, *40*, 275; d) N. Wiberg, A. Wörner, H.-W. Lerner, K. Karaghiosoff, D. Fenske, G. Baum, A. Dransfeld, P. von R. Schleyer, *Eur. J. Inorg. Chem.* **1998**, 833; e) V. Thelen, D. Schmidt, M. Nieger, E. Niecke, W. W. Schoeller, *Angew. Chem.* **1996**, *108*, 354; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 313.
- [14] O. Back, B. Donnadiou, P. Parameswaran, G. Frenking, G. Bertrand, *Nat. Chem.* **2010**, *2*, 369.
- [15] L. Weber, *Chem. Rev.* **1992**, *92*, 1839.
- [16] V. Cappello, J. Baumgartner, A. Dransfeld, M. Flock, K. Hassler, *Eur. J. Inorg. Chem.* **2006**, 2393.
- [17] a) H. Hamaguchi, M. Tasumi, M. Yoshifuji, N. Inamoto, *J. Am. Chem. Soc.* **1984**, *106*, 508; b) I. A. Garbuzova, L. A. Leites, S. S. Bulkavo, *J. Mol. Struct.* **1997**, *411*, 467.
- [18] J. J. Weigand, K.-O. Feldmann, F. D. Henne, *J. Am. Chem. Soc.* **2010**, *132*, 16321.
- [19] $r_{\text{cov}}(\text{P}, \text{P}) = 2.02 \text{ \AA}$, $\Sigma r_{\text{vdW}}(\text{P}, \text{P}) = 3.80 \text{ \AA}$; A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
- [20] M. P. Mitoraj, A. Michalak, T. Ziegler, *J. Chem. Theory Comput.* **2009**, *5*, 962.