Angewandte Chemie International Edition

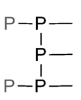
DOI: 10.1002/anie.201201414

Phosphorus Compounds

One-Pot Syntheses of Cationic Polyphosphorus Frameworks with Two-, Three-, and Four-Coordinate Phosphorus Atoms by One-Pot Multiple P–P Bond Formations from a P_1 Source**

*Kai-Oliver Feldmann and Jan J. Weigand**

The structural diversity of neutral and anionic cyclic and cage-like polyphosphorus frameworks (for example **1**,[1] $\mathbf{2}^{2-}$[2]) is based on the two bonding motifs **A** and **B**.[3] These comprise two- and three-coordinate phosphorus atoms that feature at least two P–P bonds. Only one compound featuring two- and four-coordinate P atoms (**C**, **3**[4]) was reported. In the realm of cationic polyphosphorus frameworks this series is extended by an array of *cyclo*-phosphinophosphonium ion frameworks[5] (e.g. **D**, $\mathbf{4}^{2+}$[6]) and phosphorus-rich cationic cage compounds[7,8] that are composed of three- and four-coordinate P atoms. Polyphosphorus frameworks featuring a combination of two-, three-, and four-coordinate P atoms (**E**) have been elusive to date. Herein we present the first examples of cyclic ($\mathbf{5}^+$) and bicyclic ($\mathbf{6a,b}^+$, a: R = Cy, b: R = Ph) cationic polyphosphorus frameworks displaying bonding motif **E**. These cations result from the reaction of our recently reported trication $\mathbf{7}^{3+}$[9] (Scheme 1) as a P_1 synthon with secondary phosphanes in an unprecedented combination of comproportionative and base-induced reductive P–P bond formations.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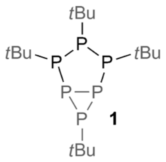
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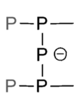
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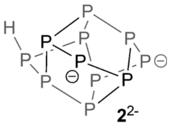
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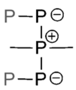
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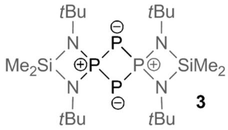
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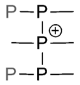
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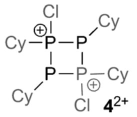
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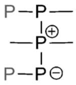
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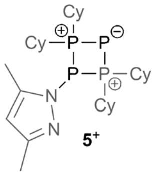
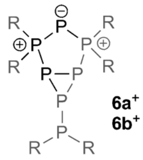
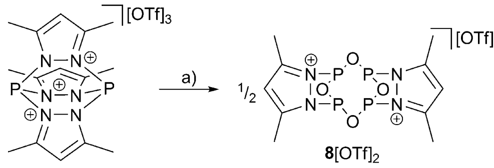

$\mathbf{5}^+$


$\mathbf{6a}^+$ (R = Cy)
$\mathbf{6b}^+$ (R = Ph)

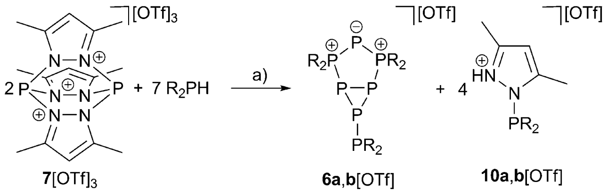


Scheme 1. P–O bond formation by hydrolysis of **7**[OTf]$_3$. a) 2 H_2O, CH_3CN, −2 **9**[OTf] (3,5-dimethylpyrazolium triflate).

Established synthetic methods are inadequate for the preparation of cations displaying bonding motive **E**. Key to the success for the preparation of cations $\mathbf{5}^+$ and $\mathbf{6a,b}^+$ was the realization that multiple-charged P^{III}-centered cations show a propensity to reductively form P^I species in the presence of a Lewis base.[10] In contrast, we recently demonstrated that P-centered trication $\mathbf{7}^{3+}$ yields the unprecedented cation $\mathbf{8}^{2+}$ (Scheme 1) upon careful hydrolysis.[9,11] The +3 oxidation state of the P atoms is retained in this reaction.

We were therefore interested to establish whether cation $\mathbf{7}^{3+}$ can also be reduced to P^I compounds upon reactions with Lewis bases and whether this can be exploited for base-induced reductive P–P coupling reactions. This would constitute a novel synthetic approach towards P–P bond formation and contrast the previously reported protolysis reaction.

The addition of 3.5 equivalents of the Lewis basic phosphane Cy_2PH to a suspension of **7**[OTf]$_3$ in CH_2Cl_2 at room temperature yielded an orange solution (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum[12] of the reaction mixture revealed the clean formation of two phosphorus-containing products indicated by the presence of an AMNN′XZZ′ spin



Scheme 2. Reaction of **7**[OTf]$_3$ with a secondary phosphane R_2PH. a) CH_2Cl_2, −**9**[OTf], −**11**; **6a**[OTf]/**10a**[OTf]: R = Cy, 12 h, RT, 45 %; **6b**[OTf]/**10b**[OTf]: R = Ph, 3 h, RT, not isolated.

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[**] We gratefully acknowledge the FCI (fellowship for K.-O.F.), the European Phosphorus Science Network (PhosSciNet CM0802), and the DFG (WE 4621/2-1). J.J.W. thanks Prof. F. Ekkehardt Hahn (WWU Münster) for his generous support, one of the referees for very helpful comments, and Prof. Robert Wolf (Universität Regensburg) for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201201414.

system for compound **6a**[OTf] and a singlet ($\delta = 84.4$ ppm) for compound **10a**[OTf].[12] Furthermore, the ^{1}H NMR spectrum indicated the formation of 3,5-dimethylpyrazolium triflate (**9**[OTf]) and 3,5-dimethylpyrazole (**11**). Compounds **9**[OTf], **10a**[OTf], and **11** can be conveniently separated by evaporation of all volatiles from the reaction mixture under reduced pressure and extraction with Et_2O. Compound **6a**[OTf] remains as analytically pure orange solid in moderate yield (45%). Compound **10a**[OTf] was obtained by fractional crystallization from the Et_2O extract (54%).

Figure 1 shows the $^{31}P\{^1H\}$ NMR spectrum of **6a**[OTf] and the molecular structure of **6a**$^+$ in **6a**[OTf]$\cdot 0.5\,C_6H_5F$. Crystals suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **6a**[OTf] in fluorobenzene. The molecular structure reveals a bicyclic P_7 framework composed of an envelope shaped five-membered ring and a three-membered ring. These are annulated in a way that P1 and P6 are located above the plane spanned by P2, P3, P4, and P5. This results in a rather short distance between the phosphorus atoms P1 and P6 (3.500(8) Å). Similar conformations were observed in the neutral bicyclic hexaphosphanes $t\mathrm{Bu}_4P_6$ (**1**)[1] and $\mathrm{Cp^*}_4P_6$.[13] The shortest P–P bonds (P1–P2 2.120(1) Å, P1–P3 2.121(1) Å) in cation **6a**$^+$ are observed between the two- and three-coordinate P atoms. Similar bond lengths have been observed for structurally related cations (for example, 2.137(6) Å in $[Ph_3P{-}P{-}PPh_3][AlCl_4]$[10a]). According to an NBO[14] (natural bond orbital) analysis on the DFT (B3LYP/6-311G(2d)) optimized structure of **6a**$^+$,[12] this shortening is a result of donation of electron density from the p-type lone pair of electrons on P1 into the σ* orbitals of the adjacent P–P ($\mathrm{LP(p)}_{P1}\rightarrow\sigma^*_{P2-P4}$ 7.24 kcal mol^{-1}, $\mathrm{LP(p)}_{P1}\rightarrow\sigma^*_{P3-P5}$ 7.19 kcal mol^{-1}) and P–C ($\mathrm{LP(p)}_{P1}\rightarrow\sigma^*_{P2-C}$ 10.61 kcal mol^{-1}, $\mathrm{LP(p)}_{P1}\rightarrow\sigma^*_{P3-C}$ 10.51 kcal mol^{-1}) bonds. These secondary interactions also result in a slight elongation of the P2–P4 (2.230(1) Å) and P3–P5 (2.235(1) Å) bonds in comparison to related bonds between three- and four-coordinate P atoms (for example 2.1952(6) Å in 1,2,3,4-tetracyclohexyl-1-methylcyclotetraphosphan-1-ium triflate).[15]

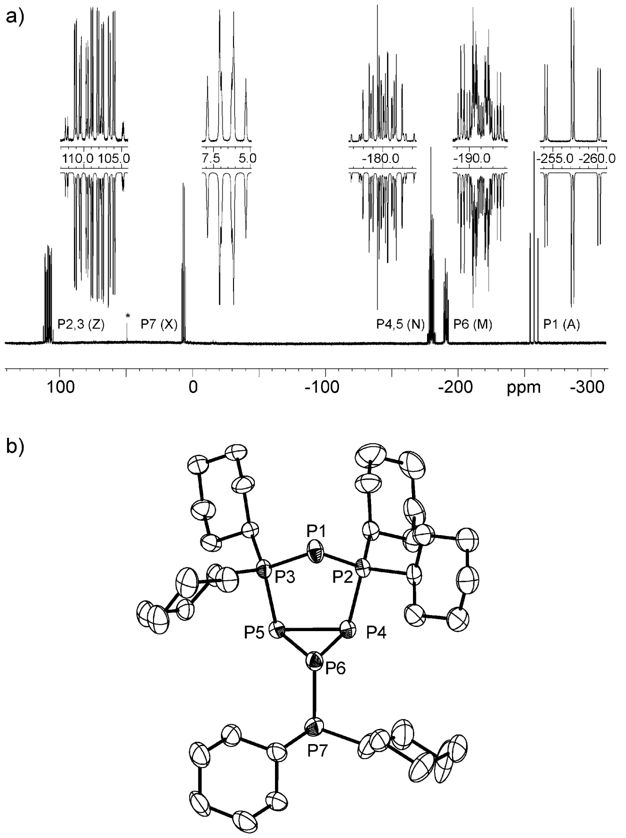
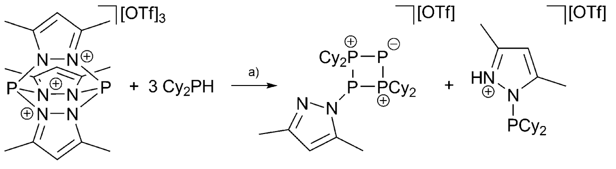


Figure 1. a) $^{31}P\{^1H\}$ NMR spectrum of **6a**[OTf] (CD_2Cl_2, 300 K). Insets show experimental (upwards) and fitted spectra (downwards); ⋆ indicates very small amounts of **10a**[OTf]. AMNN′XZZ′ spin system [ppm, Hz]: $\delta_A = -257.2$ (1P), $\delta_M = -190.9$ (1 P), $\delta_N = -180.0$ (2P), $\delta_X = 6.6$ (1 P), $\delta_Z = 108.5$ (2 P); $^1J(P_AP_Z) = {^1J}(P_AP_Z{'}) = -478.3$, $^1J(P_MP_N) = {^1J}(P_MP_{N'}) = -169.6$, $^1J(P_MP_X) = -156.9$, $^1J(P_NP_Z) = {^1J}(P_{N'}P_{Z'}) = -334.0$, $^1J(P_NP_{N'}) = -295.4$, $^2J(P_AP_N) = {^2J}(P_AP_{N'}) = -2.3$, $^2J(P_MP_Z) = {^2J}(P_MP_{Z'}) = 38.4$, $^2J(P_NP_X) = {^2J}(P_{N'}P_X) = 135.9$, $^2J(P_NP_{Z'}) = {^2J}(P_{N'}P_Z) = -11.9$, $^2J(P_ZP_{Z'}) = -5.2$, $^3J(P_AP_M) = 46.1$, $^3J(P_XP_Z) = {^3J}(P_XP_{Z'}) = 7.2$, $^4J(P_AP_X) = -3.5$). b) Molecular structure of the cation in **6a**[OTf]$\cdot 0.5\,C_6H_5F$ (hydrogen atoms omitted for clarity, ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: P2–P1 2.120(1), P2–P4 2.230(1), P4–P5 2.201(1), P4–P6 2.206(1), P6–P5 2.206(1), P6–P7 2.243(2), P3–P1 2.121(1), P3–P5 2.235(1), P1⋯P6 3.500(8); P2-P1-P3 93.19(5), P1-P2-P4 112.44(5), P1-P3-P5 112.61(5), P5-P4-P2 101.31(5), P5-P4-P6 60.07(4), P6-P4-P2 96.79(5), P4-P5-P6 60.07(4), P4-P5-P3 101.41(5), P6-P5-P3 95.85(5), P4-P6-P5 59.86(4), P4-P6-P7 95.15(5), P5-P6-P7 95.67(5); [P2,P3,P4,P5]-[P4,P5,P6] 89.2, [P2,P3,P4,P5]-[P1,P2,P3] 141.4.

The $^{31}P\{^1H\}$ NMR spectrum of **6a**[OTf] shows several remarkable features that can be attributed to its unique bicyclic structure. The signals for the phosphorus atoms of the three-membered ring of **6a**$^+$ (P_N $\delta = -180.0$ ppm, P_M $\delta = -190.9$ ppm) are shifted upfield compared to phosphanyl-substituted *cyclo*-triphosphanes (e.g. $\delta = -157.2$ ppm for 2,3-bis(*tert*-butyl)-1-(*tert*-butylchlorophosphanyl)-*cyclo*-triphosphane).[16] The chemical shifts of the bridgehead (P_N) and four-coordinate phosphorus atoms (P_Z: $\delta = 108.6$ ppm) are best compared to the structurally related dication $[Ph_4P_6]^{2+}$ ($\delta = -174.4$ and 80.5 ppm, respectively).[8a] The signal of the two-coordinate P atom (P_A, $\delta = -257.2$ ppm) is shifted upfield compared to related acyclic triphosphenium ions ($\delta = -229$ ppm for $(n\mathrm{Bu})_3P{-}P{-}P(n\mathrm{Bu})_3{}^+$).[10a] This may be attributed to the rather acute angles in the five-membered ring.[17] The magnitude of the coupling constants between the two- and four-coordinate P atoms in **6a**$^+$ ($^1J(P_AP_Z) = -478.3$ Hz) is significantly larger than that between the three- and four-coordinate nuclei ($^1J(P_NP_Z) = -334.0$ Hz), which is in accordance with previous observations.[18] Furthermore, they are found to be smaller than in acyclic derivatives. This observation can be attributed to the lower s-orbital character of the respective P–P bonding orbitals in the cyclic structure of **6a**$^+$.[19]

To gather information on the reaction mechanism of the formation of **6a**[OTf], we investigated the reaction of **7**$[OTf]_3$ with various amounts of Cy_2PH. The addition of three equivalents of Cy_2PH to a suspension of **7**$[OTf]_3$ in CH_2Cl_2 at room temperature again yielded an orange solution (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture[12] after 4 h revealed the clean formation of only two phosphorus-containing products. A singlet ($\delta = 84.4$ ppm) indicated the formation of the pyrazoliumyl-substituted phosphane **10a**[OTf], and the presence of an AMX_2 spin



7[OTf]$_3$ **5**[OTf] **10a**[OTf]

Scheme 3. Reaction of **7**[OTf]$_3$ with Cy$_2$PH in a 1:3 ratio. a) −**9**[OTf], CH$_2$Cl$_2$, 4 h, RT.

system is indicative of the formation of the four-membered ring compound **5**[OTf]. The ^{1}H NMR spectrum indicated the formation of **9**[OTf] as the only other by-product. The isolation of compound **5**[OTf] (yield of isolated product: 40%) followed the same procedure as for **6a**[OTf].

The molecular structure of **5**$^+$ is depicted in Figure 2. The bond lengths follow the same trends as already discussed for **6a**$^+$, and the angles are largely dictated by the four-membered ring geometry.[20] Interestingly, the P4–N1 bond in **5**$^+$ (1.716(2) Å; Wiberg bond index $\mathrm{WBI_{P\text{-}N}} = 0.7752$) is significantly shorter than the respective P–N bond in **10a**$^+$ (P1–N1 1.775(1) Å, Figure 3; $\mathrm{WBI_{P\text{-}N}} = 0.6551$).[12] It has been previously observed that protonation of the sp^2-type lone pair of electrons of P-pyrazole moieties leads to a significant lengthening and weakening of the P–N bond.[11] The ^{31}P{^{1}H} NMR spectrum of dissolved **5**[OTf] (CD$_2$Cl$_2$, 300 K) is depicted in Figure 3. The chemical shift of the four-coordinate P atoms ($\mathrm{P_X}$, $\delta = 53.2$ ppm) is in the expected range for phosphonium moieties in four-membered rings.[6] The signal of the three-coordinate phosphorus atom in **5**$^+$ is shifted to higher field compared to the related acyclic derivative Cy$_2$PP(pyr)PCy$_2$ ($\delta = 29.0$ ppm; pyr = 3,5-dimethylpyrazolyl).[21] This may be rationalized by the rather acute angles in the four-membered ring, resulting in increased shielding similar to the observations made for **6a**[OTf].

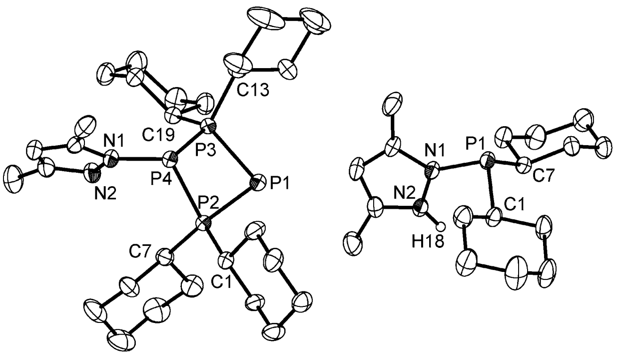


Figure 2. Molecular structures of the cations **5**$^+$ and **10a**$^+$ in **5**[OTf] and **10a**[OTf] (hydrogen atoms omitted for clarity, ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: **5**$^+$: P1–P2 2.1387(7), P1–P3 2.1356(7), P2–P4 2.2143(7), P3–P4 2.2162(7), P4–N1 1.716(2), P2–C1 1.839(2), P2–C7 1.834(2), P3–C13 1.845(2), P3–C19 1.831(2); P2-P1-P3 84.11(3), P1-P2-P4 92.58(3), P1-P3-P4 92.61(3), P2-P4-P3 80.52(2). **10a**$^+$: P1–N1 1.775(1), P1–C1 1.850(2), P1–C7 1.845(2).

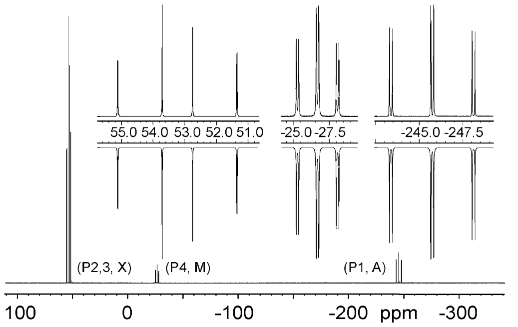
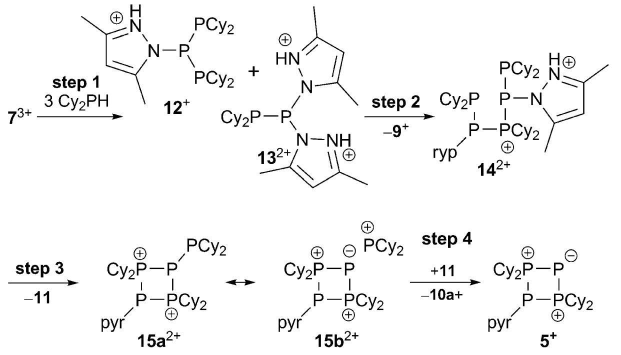


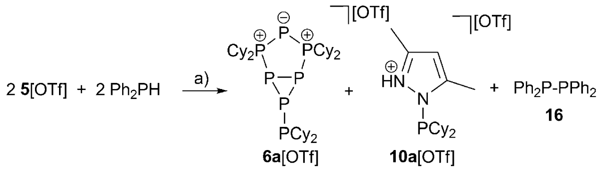
Figure 3. ^{31}P{^{1}H} NMR spectrum of **5**[OTf] (CD$_2$Cl$_2$, 300 K). Insets show experimental (upwards) and fitted spectra (downwards). AMX$_2$ spin system [ppm, Hz]: $\delta_A = -245.7$ (1P), $\delta_M = -26.7$ (1P), $\delta_X = 53.2$ (2P); $^1J(\mathrm{P_AP_X}) = -382.8$, $^1J(\mathrm{P_MP_X}) = -227.3$, $^2J(\mathrm{P_AP_M}) = -26.9$.

The formation of **5**$^+$ can be understood mechanistically in terms of several subsequent substitution steps, followed by a base-induced reduction (Scheme 4). Step 1 most likely involves the formation of intermediates **12**$^+$ and **13**$^{2+}$. This step is a protolysis reaction, which is related to the reaction of **7**$^{3+}$ with water.[9] Subsequently, monocation **12**$^+$ may substitute one pyrazoliumyl substituent in dication **13**$^{2+}$, forming dicationic intermediate **14**$^{2+}$ and 3,5-dimethylpyrazolium ion (**9**$^+$) after deprotonation (step 2). Similarly, an intramolecular substitution reaction of intermediate **14**$^{5+}$ yields dication **15**$^{2+}$ via the loss of 3,5-dimethylpyrazole (**11**, step 3). These reaction steps are related to our recent report that pyrazolyl-substituted phosphanes react with secondary phosphanes to form P–P bonds via the elimination of pyrazole[21] and constitute a variation of the classical preparation of phosphanylphosphonium moieties.[5] The lower covalent bond order of the P–P single bond in **15**$^{2+}$ as a result of a substantial bond polarity (canonical structure **15b**$^{2+}$ vs. **15a**$^{2+}$) can be assumed by analogy with investigations on *P*-phosphanyldiazaphopholenes.[22] In combination with a base-induced redox reaction (pyrH, **11**), this rationalizes the formation of cation **5**$^+$ via the elimination of **10a**$^+$ in step 4.



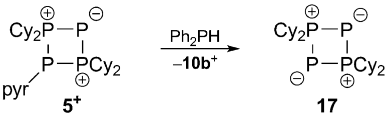
Scheme 4. Proposed mechanism for the formation of **5**$^+$.

We could confirm that compound **5**$^+$ is an intermediate in the formation of cation **6a**$^+$ by reacting **5**[OTf] with either 0.5 equiv of Cy$_2$PH or 1 equiv of Ph$_2$PH. The reaction of the latter with **5**[OTf] yields **6a**[OTf], **10a**[OTf], 3,5-dimethylpyrazole (**11**), and remarkably diphosphane **16** (Scheme 5).[12]

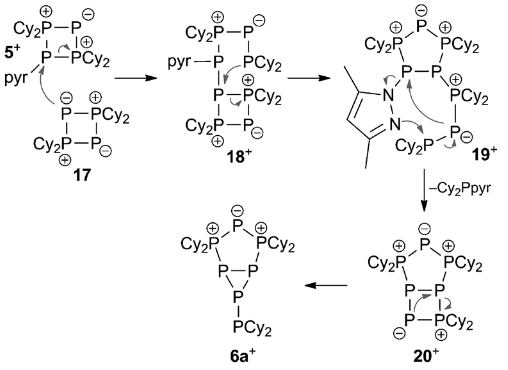


Scheme 5. Reaction of **5**[OTf] with Ph_2PH in a 1:1 ratio. a) −**11**, CH_2Cl_2, 15 h, RT.

The $[R_2P]$ moiety of the secondary phosphane is not incorporated into the framework of **6a**$^+$. This observation has significant implications for the mechanism of the formation of cation **6a**$^+$. We propose that the reaction of cation **5**$^+$ and Ph_2PH yields the elusive neutral intermediate **17** (Scheme 6). A related tetraphosphete (**3**) has been previously prepared.[4] The formation of **6a**$^+$ is then initiated by a nucleophilic attack of **17** on the three-coordinate phosphorus atom of **5**$^+$ according to Scheme 7.[23] This attack most likely results in the cleavage of the P–P bond involving one of the four-coordinate P atoms and the formation of intermediate **18**$^+$. This mode of attack generates a Lewis basic phosphanyl moiety, which can undergo intramolecular nucleophilic attack, and furthermore results in an umpolung of the initially two-coordinate phosphorus atom of compound **17**. Thus, the intramolecular attack may result in the formation of intermediate **19**$^+$, in which the thermodynamically favored five-membered ring[3b] of **6a**$^+$ is present. Intermediate **19**$^+$ may then eliminate Cy_2Ppyr, yielding the fused bicyclo[3.2.0]heptaphosphane-1,3-ium cation **20**$^+$. This type of framework is known for polyphosphanes.[24] However, intermediate **20**$^+$ may rearrange to the bicyclo[3.1.0]hexaphosphane-1,3-ium cation **6a**$^+$, which is thermodynamically more favored owing to the presence of fused five- and three-membered rings.[3b]

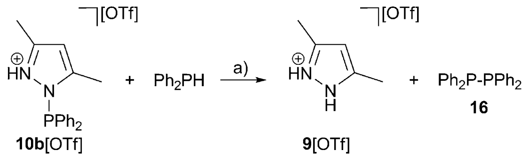


Scheme 6. Formation of intermediate **17** from cation **5**$^+$ and Ph_2PH.



Scheme 7. Plausible mechanism of the formation of cation **6a**$^+$.

A side product of the synthesis of compound **6a**[OTf] is the pyrazoliumyl-substituted phosphane **10a**$^+$. This cation results from the protonation of the formed Cy_2Ppyr by [pyrH][OTf] (**9**[OTf]). The latter is formed along with diphosphane **16** from a comproportionation reaction of the intermediately formed cation **10b**$^+$ and Ph_2PH, which was confirmed by a test reaction (Scheme 8).[12] Thus, all observed products are accounted for by the proposed mechanism.



Scheme 8. Formation of **16** from **10b**[OTf] and Ph_2PH. a) CH_2Cl_2, 3 h, RT.

The formation of a diphosphane as side product is predominant in case of Ph_2PH. However, the formation of $Cy_2P{-}PCy_2$ was not observed in reactions of **7**$[OTf]_3$ or **5**[OTf] with Cy_2PH. Apparently, the formation of **10b**$^+$ is not as favorable as the formation of **10a**$^+$. This explains why the reaction of **7**$[OTf]_3$ and 3.5 equiv of Ph_2PH proceeds less selectively, preventing the isolation of **6b**[OTf] (Scheme 2).[25] Futhermore, we found that **6b**[OTf] decomposes in solution comparably fast to copious amounts of insoluble orange residue and **16**. The low stability of **6b**$^+$ is in line with previous observations of substituent effects on polyphosphanes. Cyclohexyl substituents were found to yield products of higher stability than those with phenyl substituents.[26] Nevertheless, we obtained single crystals of **6b**[OTf] co-crystallized with **9**[OTf] as an *n*-hexane solvate from concentrated solutions of the reaction mixture layered with *n*-hexane at −35 °C. The structural parameters of the molecular structure of **6b**$^+$ (depicted in the Supporting Information) are very similar to those of **6a**$^+$.

In summary, remarkable cationic polyphosphorus compounds **6a,b**$^+$ were synthesized. These species represent the first examples of polyphosphorus cations that feature two-, three-, and four-coordinate phosphorus atoms in direct connectivity. Overall, eight P–P bonds are formed by a unique combination of protolysis and base-induced reductive P–P coupling reactions. The syntheses of cations **6a**,**b**$^+$ is an example of the distinct reactivity of phosphorus-centered cations compared to neutral and anionic phosphorus-containing compounds. We hope that further studies of the reactivity of phosphorus-centered cations will make complexity in phosphorus chemistry more accessible, broaden the structural variety of polyphosphorus compounds, and may also inspire the development of new synthetic methods for related p-block-element compounds.

Received: February 20, 2012
Revised: April 30, 2012
Published online: June 15, 2012

Keywords: phosphorus-centered cations · polyphosphorus frameworks · P–P bond formation · reductive coupling · structure elucidation

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