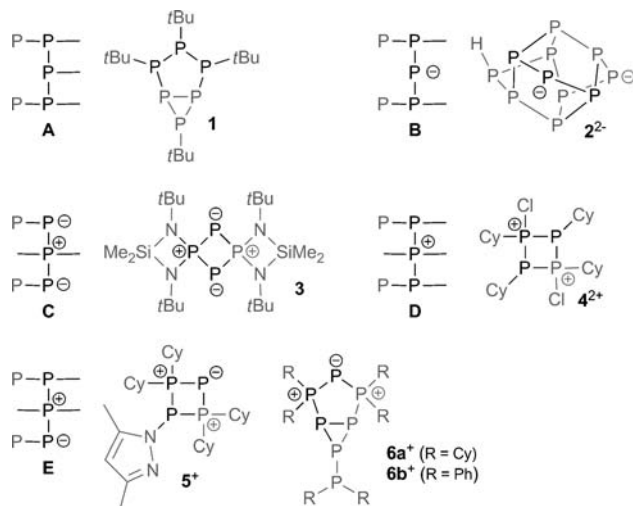


Phosphorus Compounds

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_I Source**

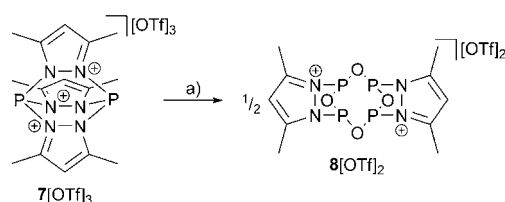
Kai-Oliver Feldmann and Jan J. Weigand*

The structural diversity of neutral and anionic cyclic and cage-like polyphosphorus frameworks (for example **1**,^[1] **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**, **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 (**5**⁺) and bicyclic (**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 **7**^{3+ [9]} (Scheme 1) as a P_I synthon with secondary phosphanes in an unprecedented combination of comproportionative and base-induced reductive P–P bond formations.

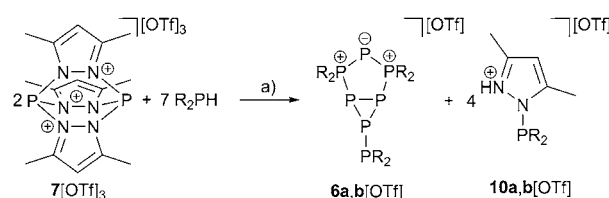


Scheme 1. P–O bond formation by hydrolysis of **7**[OTf]₃. a) 2 H₂O, CH₃CN, –2 **9**[OTf] (3,5-dimethylpyrazolium triflate).

Established synthetic methods are inadequate for the preparation of cations displaying bonding motive **E**. Key to the success for the preparation of cations **5**⁺ and **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 **7**³⁺ yields the unprecedented cation **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 **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 Cy₂PH to a suspension of **7**[OTf]₃ in CH₂Cl₂ at room temperature yielded an orange solution (Scheme 2). The ³¹P{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 R₂PH. a) CH₂Cl₂, –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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system for compound **6a**[OTf] and a singlet ($\delta = 84.4$ ppm) for compound **10a**[OTf].^[12] Furthermore, the ^1H 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6a**[OTf] and the molecular structure of **6a**⁺ in **6a**[OTf]·0.5 $\text{C}_6\text{H}_5\text{F}$. 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 $t\text{Bu}_4\text{P}_6$ (**1**)^[1] and Cp^*P_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 $[\text{Ph}_3\text{P}-\text{P}(\text{PPh}_3)[\text{AlCl}_4]]^{[10a]}$). 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 (LP(p)_{P1}→ σ^* _{P2–P4} 7.24 kcal mol^{−1}, LP(p)_{P1}→ σ^* _{P3–P5} 7.19 kcal mol^{−1}) and P–C (LP(p)_{P1}→ σ^* _{P2–C} 10.61 kcal mol^{−1}, LP(p)_{P1}→ σ^* _{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]

The $^{31}\text{P}\{^1\text{H}\}$ 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 $[\text{Ph}_4\text{P}_6]^{2+}$ ($\delta = -174.4$ 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 $(n\text{Bu})_3\text{P}-\text{P}(n\text{Bu})_3^+$).^[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**⁺ ($^1J(\text{P}_\text{A}\text{P}_\text{Z}) = -478.3$ Hz) is significantly larger than that between the three- and four-coordinate nuclei ($^1J(\text{P}_\text{N}\text{P}_\text{Z}) = -334.0$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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

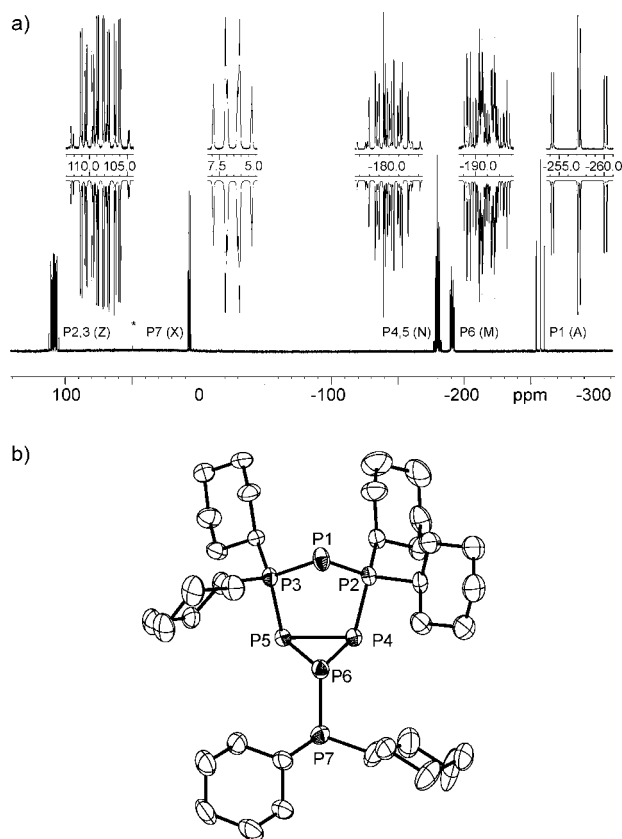
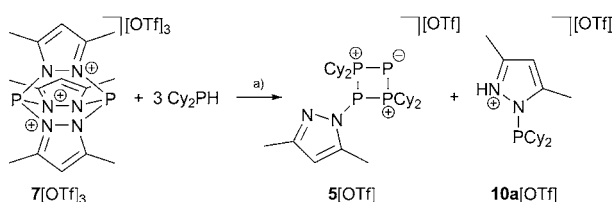


Figure 1. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6a**[OTf] (CD_2Cl_2 , 300 K). Insets show experimental (upwards) and fitted spectra (downwards); * indicates very small amounts of **10a**[OTf]. AMN'XZZ' spin system [ppm, Hz]: $\delta_\text{A} = -257.2$ (1P), $\delta_\text{M} = -190.9$ (1P), $\delta_\text{N} = -180.0$ (2P), $\delta_\text{X} = 6.6$ (1P), $\delta_\text{Z} = 108.5$ (2P); $^1J(\text{P}_\text{A}\text{P}_\text{Z}) = ^1J(\text{P}_\text{A}\text{P}_\text{Z}) = -478.3$, $^1J(\text{P}_\text{M}\text{P}_\text{N}) = ^1J(\text{P}_\text{M}\text{P}_\text{N}) = -169.6$, $^1J(\text{P}_\text{M}\text{P}_\text{X}) = -156.9$, $^1J(\text{P}_\text{N}\text{P}_\text{Z}) = ^1J(\text{P}_\text{N}\text{P}_\text{Z}) = -334.0$, $^1J(\text{P}_\text{N}\text{P}_\text{N}) = -295.4$, $^2J(\text{P}_\text{A}\text{P}_\text{N}) = ^2J(\text{P}_\text{A}\text{P}_\text{N}) = -2.3$, $^2J(\text{P}_\text{M}\text{P}_\text{Z}) = ^2J(\text{P}_\text{M}\text{P}_\text{Z}) = 38.4$, $^2J(\text{P}_\text{N}\text{P}_\text{X}) = ^2J(\text{P}_\text{N}\text{P}_\text{X}) = 135.9$, $^2J(\text{P}_\text{N}\text{P}_\text{Z}) = ^2J(\text{P}_\text{N}\text{P}_\text{Z}) = -11.9$, $^2J(\text{P}_\text{Z}\text{P}_\text{Z}) = -5.2$, $^3J(\text{P}_\text{A}\text{P}_\text{M}) = 46.1$, $^3J(\text{P}_\text{X}\text{P}_\text{Z}) = ^3J(\text{P}_\text{X}\text{P}_\text{Z}) = 7.2$, $^4J(\text{P}_\text{A}\text{P}_\text{X}) = -3.5$). b) Molecular structure of the cation in **6a**[OTf]·0.5 $\text{C}_6\text{H}_5\text{F}$ (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.



Scheme 3. Reaction of $7[OTf]_3$ with Cy_2PH in a 1:3 ratio. a) $-9[OTf]$, CH_2Cl_2 , 4 h, RT.

system is indicative of the formation of the four-membered ring compound $5[OTf]$. The 1H 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

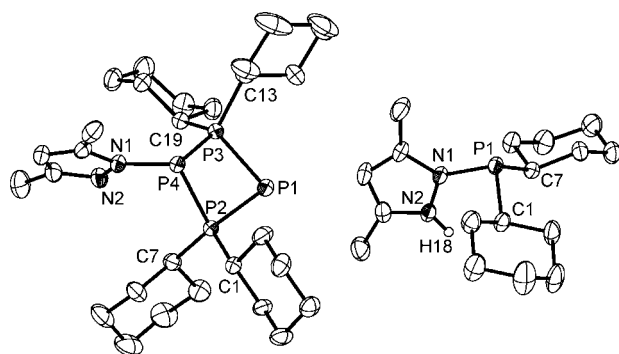


Figure 2. Molecular structures of the cations 5^+ and $10a^+$ in $5[OTf]$ and $10a[OTf]$ (hydrogen atoms omitted for clarity, ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: 5^+ : P1–P2 2.1387(7), P1–P3 2.1356(7), P2–P4 2.2143(7), P3–P4 2.2162(7), P4–N1 1.716(2), P2–C1 1.839(2), 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).

ring geometry.^[20] Interestingly, the P4–N1 bond in 5^+ (1.716(2) Å; Wiberg bond index $WBI_{P-N} = 0.7752$) is significantly shorter than the respective P–N bond in $10a^+$ (P1–N1 1.775(1) Å, Figure 3; $WBI_{P-N} = 0.6551$).^[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 $^{31}P\{^1H\}$ NMR spectrum of dissolved $5[OTf]$ (CD_2Cl_2 , 300 K) is depicted in Figure 3. The chemical shift of the four-coordinate P atoms (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 $Cy_2PP(pyr)PCy_2$ ($\delta = 29.0$ 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 $6a[OTf]$.

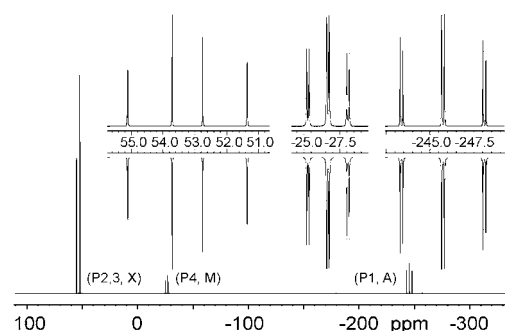
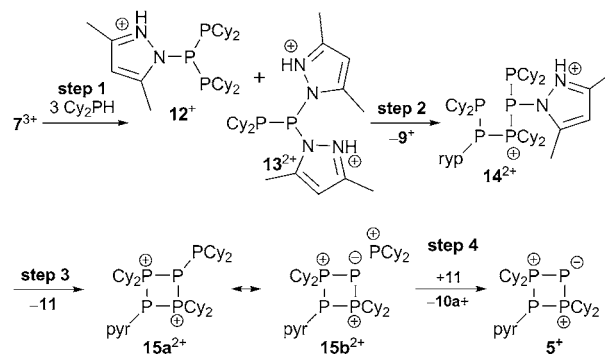


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $5[OTf]$ (CD_2Cl_2 , 300 K). Insets show experimental (upwards) and fitted spectra (downwards). AMX_2 spin system [ppm, Hz]: $\delta_A = -245.7$ (1P), $\delta_M = -26.7$ (1P), $\delta_X = 53.2$ (2P); $^1J(P_AP_X) = -382.8$, $^1J(P_MP_X) = -227.3$, $^2J(P_AP_M) = -26.9$.

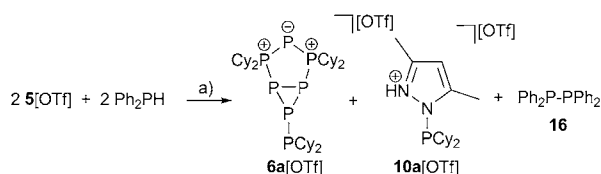
The formation of 5^+ can be understood mechanistically in terms of several subsequent substitution steps, followed by a base-induced reduction (Scheme 4). Step 1 most likely



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

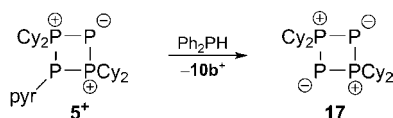
involves the formation of intermediates 12^+ and 13^{2+} . This step is a protolysis reaction, which is related to the reaction of 7^+ with water.^[9] Subsequently, monocation 12^+ may substitute one pyrazoliumyl substituent in dication 13^{2+} , forming dicationic intermediate 14^{2+} and 3,5-dimethylpyrazolium ion (9^+) after deprotonation (step 2). Similarly, an intramolecular substitution reaction of intermediate 14^{2+} 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-phosphanyldiazaphospholenes.^[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.

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_2PH or 1 equiv of Ph_2PH . The reaction of the latter with $5[OTf]$ yields $6a[OTf]$, $10a[OTf]$, 3,5-dimethylpyrazole (**11**), and remarkably diphosphane **16** (Scheme 5).^[12]



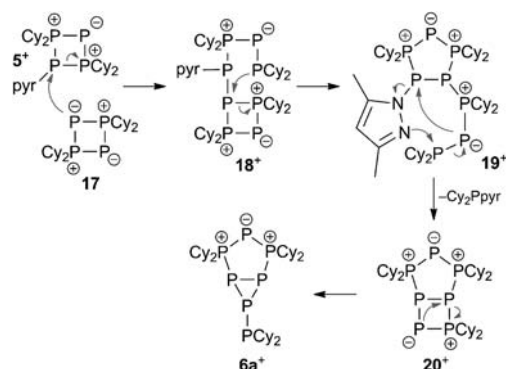
Scheme 5. Reaction of **5**[OTf] with Ph_2PH in a 1:1 ratio. a) –11, CH_2Cl_2 , 15 h, RT.

The $[\text{R}_2\text{P}]$ 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



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

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

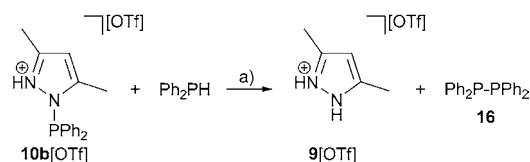


Scheme 7. Plausible mechanism of the formation of cation **6a**⁺.

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 thermo-

dynamically more favored owing to the presence of fused five- and three-membered rings.^[3b]

A side product of the synthesis of compound **6a**[OTf] is the pyrazolium-substituted phosphane **10a**⁺. This cation results from the protonation of the formed Cy_2Ppyr by $[\text{pyrH}][\text{OTf}]$ (**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 $\text{Cy}_2\text{P}-\text{PCy}_2$ 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] Furthermore, 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.

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