Phosphorus Chemistry

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Preparation of Ligand-Stabilized $[P_4O_4]^{2+}$ by Controlled Hydrolysis of a Janus Head Type Diphosphorus Trication**

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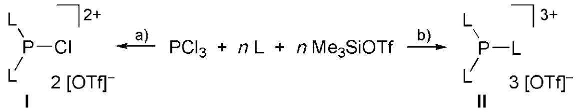
Introducing multiple cationic charges into inorganic or organic compounds dramatically influences their reactivities owing to a marked increase in electrophilicity and electron affinity.[1] In the realm of organic chemistry, the self-activated silyl-assisted poly-onio-substitution (SASAPOS) protocol[2] represents a powerful method for the preparation of spectacular polycationic frameworks, for example, a twentyfold cationic cluster with a porphyrin core.[2a] So far, the SASAPOS protocol has been predominantly applied to halogenated hydrocarbon-based systems. Applications in inorganic chemistry are extremely rare. In a pioneering study, Weiss and Engel showed that di- and tricationic phosphorus(III) compounds **I** and **II** may be generated by treating PCl_3 with an appropriate ligand (L; for example, 4-dimethylaminopyridine (DMAP)) and Me_3SiOTf (Scheme 1).[3] Cations **I** and **II** were proposed solely on the basis of spectroscopic and chemical analysis data and represent rare examples of di- or trications of trivalent phosphorus compounds.[3,4]

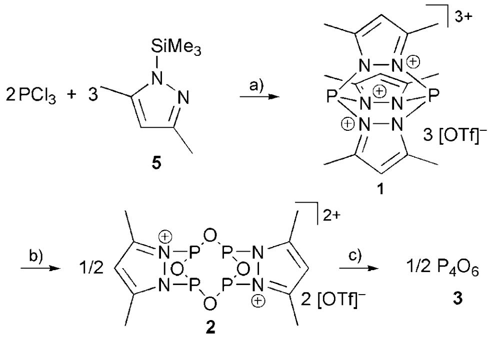


Scheme 1. Reaction of PCl_3 with L and Me_3SiOTf; a) $n = 2$, $-2\ Me_3SiCl$; b) $n = 3$, $-3\ Me_3SiCl$; L = DMAP.

Key to the success of this reaction is the sequestration of the by-product Cl^- as Me_3SiCl. Without the addition of Me_3SiOTf, monocationic phosphorus(I) derivatives are obtained.[3,5] We are particularly interested in per-onio substituted phosphorus(III) compounds as we anticipate unusual reactivity for the phosphorus center.[6] In this context and to prepare unprecedented inorganic ring systems, we devised a strategy that uses a labile tridentate ligand containing basic pyrazolyl moieties, which serve as suitable leaving groups.[7]

As a first proof of this concept, we now present the targeted, high-yield synthesis of the novel Janus head type diphosphorus trication **1** from commercially available starting materials (see Scheme 2).[8] Furthermore, we show that the unprecedented ligand-stabilized $[P_4O_4]^{2+}$ dication **2** can be prepared by controlled hydrolysis of **1**, en route to the targeted formation of the phosphorus suboxide P_4O_6 (**3**).

The reaction of PCl_3, 3,5-dimethyl-1-trimethylsilylpyrazole (**5**), and three equivalents of Me_3SiOTf in dichloromethane gave **1**$[OTf]_3$ as a colorless precipitate in almost quantitative yield (97%, Scheme 2). This reaction can be performed on a scale up to 60 g. Compound **1**$[OTf]_3$ is extremely moisture-sensitive, but appears to be indefinitely stable at ambient temperature in a dry Ar atmosphere. MeCN solutions of trication **1** are stable for at least several days. Together, these benevolent properties make **1**$[OTf]_3$ a very attractive precursor for further syntheses (see below).[8]



Scheme 2. Preparation of **1** and subsequent controlled hydrolysis reaction; a) 3 Me_3SiOTf, $-3\ Me_3SiCl$, CH_2Cl_2 (RT, 3 h); b) 2 H_2O, MeCN, −2 3,5-dimethylpyrazolium triflate (**4**[OTf]), (0 °C within ca. 1 h); c) H_2O, MeCN, −**4**[OTf], (RT, 10 min).

Multinuclear NMR studies indicated a D_{3h}-symmetrical structure for trication **1**. ^{31}P NMR characterization of **1**$[OTf]_3$ revealed a doublet (CD_3CN; $\delta = -2.8$ ppm, $^4J_{PH} = 4.1$ Hz), which is shifted to high field in comparison to the resonance of tris(3,5-dimethylpyrazol-1-yl)phosphane (**6**) ($CDCl_3$; $\delta = 71.9$ ppm).[9] The ^1H NMR spectrum showed a low-field resonance for the protons of the five-membered rings, which is split into a triplet of septets ($\delta = 6.89$ ppm, $^4J_{HH} = 0.6$ and

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$^5J_{PH} = 4.1$ Hz). A doublet for the protons of the methyl groups is observed at high field ($\delta = 2.94$ ppm, $^4J_{HH} = 0.6$ Hz). The deduced structure was confirmed by single-crystal X-ray diffraction. The compound **1**[OTf]$_3$ crystallizes as the MeCN solvate (**1**[OTf]$_3$·0.5 MeCN) in the triclinic space group $P\bar{1}$ with two independent formula units in the asymmetric unit (Figure 1). Interionic contacts in **1**[OTf]$_3$·0.5 MeCN appear to be negligible, since the distances between the phosphorus centers and the oxygen atoms of the triflate anions[10] are close to the sum of the respective van der Waals radii ($\Sigma r_W = 3.32$ Å).[11] The trication is composed of three pyrazolyl ligands bridging the two phosphorus(III) centers in a μ_2 mode. A ψ-tetrahedral geometry of the phosphorus atoms involving three nitrogen atoms (av. P–N bond length 1.740 Å; typical P–N single bonds $d_{cov(NP)} = 1.76$ Å; N-P-N angles range from 92.47(9) to 95.83(9)°[12]) and one lone pair of electrons are in agreement with a pronounced p character of the P–N bonds and predominately s character of the lone pair at the phosphorus atom.

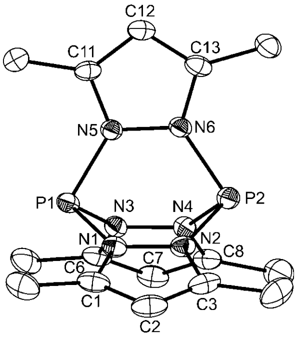


Figure 1. An ORTEP plot of the molecular structure of cation **1** in **1**[OTf]$_3$·0.5MeCN. Thermal ellipsoids with 50% probability (hydrogen atoms are omitted for clarity). Only one cation of the asymmetric unit is shown. Selected bond lengths [Å] and angles [°]: P1–N1 1.747(2), P1–N3 1.739(2), P1–N5 1.735(2), P2–N2 1.740(2), P2–N4 1.739(2), P2–N6 1.738(2), N1–N2 1.384(3), N3–N4 1.393(3), N5–N6 1.389(3); N1-P1-N3 95.26(9), N1-P1-N5 93.07(9), N3-P1-N5 94.50(9), N2-P2-N4 92.47(9), N2-P2-N6 94.92(9), N4-P2-N6 95.83(9).

To analyze the bonding situation in trication **1**, we performed natural bond orbital (NBO)[13] and molecular orbital (MO) analyses on the optimized molecular structure of **1**.[14] The pyrazol fragments represent delocalized 6π electron systems. Inspection of the NBOs shows that the P–N bonds are strongly polarized (N: 77%, P: 23%, sp$^{6.7}$ P-hybrid involved in bonding) and are essentially of σ character. The existence of a typical, localized, rather short single bond (av. 1.739 Å) between these atoms is in agreement with the calculated Wiberg bond index (WBI; av. 0.7277) and can be attributed to the high positive charge. The calculated natural atomic orbital population (NAO) net charges are +1.50 for phosphorus and 0.00 for the pyrazolyl moieties in **1** (Figure 2). This slight increase of positive charge on the phosphorus atom in **1** as compared to that of the phosphorus center in the neutral phosphane **6** (+1.44) is accounted for by Lewis representation **C** (and mirror image) and resembles typical features of a ligand-stabilized phosphenium cation.[15]

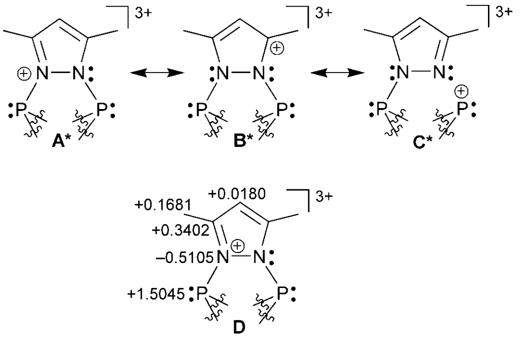


Figure 2. Lewis representations (**A–C**) and selected NAO charges (**D**, CH and CH$_3$ group charges are given) of trication **1** (*: mirror images not shown).

The total amount of charge transfer (Q_{CT}) in the trication **1**[14] computes to an increase of +0.48 for the pyrazolyl fragments in comparison to **6**.[14] This result is in accordance with the dominating Lewis representations **A** and **B**. A striking feature of **1** is that the molecular orbitals corresponding to the lone pairs (LPs) on the phosphorus centers are the HOMO−6 (−0.721 eV) and HOMO−7 (−0.722 eV) according to MO analysis. In contrast, the HOMO−1 (−0.235 eV) represents the LP on the phosphorus center in **6.**

Nucleophilic attack on the phosphorus center in **1** is expected to lead to the cleavage of a P–N bond. Hence, the pyrazolyl fragments in **1** can be regarded as leaving groups, which upon cleavage might act as bases in subsequent transformations. This special bonding situation should enable enhanced reactivity towards protic nucleophiles and is likely to result in an unusual phosphorus–element bond-formation reaction.[16]

To test this hypothesis, we carried out hydrolysis experiments. Upon treating **1**[OTf]$_3$ with two equivalents of water in MeCN, **2**[OTf]$_2$ was obtained as colorless crystals in 78% yield (CD$_3$CN; $\delta = 83.4$ ppm).[8,17] Solutions of **2**[OTf]$_2$ rapidly reacted with a further equivalent of water to quantitatively form adamantane-like P$_4$O$_6$ (**3**; ^{31}P NMR: $\delta = 112.5$ ppm)[18] in solution. In total, this reaction sequence consumes three molecules of water to form three equivalents of 3,5-dimethylpyrazolium triflate (**4**[OTf]; Scheme 2), which was confirmed by NMR spectroscopy and structural elucidations.[19]

2[OTf]$_2$ is extremely air- and moisture-sensitive, but is stable under Ar or N$_2$ atmosphere for at least six months. It crystallizes in the triclinic space group $P\bar{1}$ with half a dication and one triflate anion in the asymmetric unit (Figure 3). Dication **2** features an alternating [P$_4$O$_4$] core, in which the phosphorus atoms are bridged by two pyrazolyl fragments. This arrangement may be viewed as two [P$_2$O$_2$(pyr)]$^+$ units that are connected through the oxygen atoms O2 and O2^i in such a manner that the pyrazolyl units adopt a *transoid* arrangement.[17] The two oxygen atoms O1 and O1^i lie above and below the plane spanned by the remaining phosphorus and oxygen atoms. The P–O bond lengths (av. 1.629 Å) lie in the typical range for P–O single bonds (P–O bond length in P$_4$O$_6$: 1.653 Å).[20] The P1-O1-P2 angle (127.68(7)°) resembles the corresponding value in P$_4$O$_6$ (125.6°), whereas the P1-O2-P2^i angle (141.38(8)°) is typical for bridging oxygen atoms in

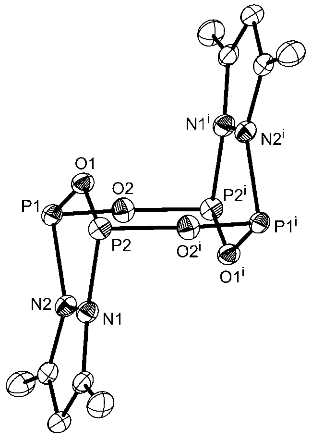
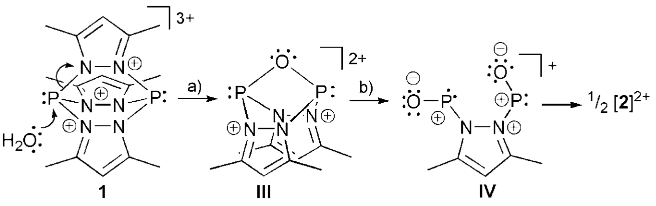


Figure 3. An ORTEP plot of the molecular structure of the cation **2** in **2**[OTf]$_2$. Thermal ellipsoids with 50% probability (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–N2 1.798(1), P2–N1 1.773(2), P1–O2 1.629(1), P1–O1 1.635(1), P2–O2^{i} 1.626(1), P2–O1 1.628(1), O2–P2^{i} 1.626(1), N1–N2 1.373(2); O2-P1-O1 102.51(6), O2-P1-N2 97.91(6), O1-P1-N2 89.26(6), O2^{i}-P2-O1 102.81(6), O2^{i}-P2-N1 99.24(7), O1-P2-N1 90.65(9), P2-O1-P1 127.68(7), P2^{i}-O2-P1 141.38(8); symmetry code i: $-x+1$, $-y+2$, $-z$.



Scheme 3. Suggested mechanism for the stepwise reaction of water with **1** to intermediate **III** and dication **2**; a) $-$**4**[OTf]; b) $+$H$_2$O, $-$**4**[OTf].

strain-free polyphosphates.[20b] The planar arrangement P1, P2^{i}, and O2 and the wide P1-O2-P2^{i} angle can be explained by hyperconjugation effects.[14] These effects also explain the pronounced high-field shift of the phosphorus signal of **2** in the ^{31}P NMR spectrum relative to that of P$_4$O$_6$ ($\Delta\delta = 29.1$ ppm).[21]

NBO analysis of optimized **2** indicates strongly polarized P–N (N: 79%, P: 21%, sp$^{8.8}$ P-hybrid involved in bonding) and P–O bonds (O: 82%, P: 18%, sp$^{8.0}$ P-hybrid involved in bonding) with essentially σ character.[14] The lone pairs of the nitrogen atoms occupy p-type orbitals and contribute to the π-electron system of the pyrazolyl fragment. The observed elongation of the P–N bonds in **2** (av. 1.786 Å) relative to **1** (av. 1.739 Å) may be explained by a significant intramolecular interaction (noncovalent effects)[13,14] of the p-type LP on the oxygen atom O1 with the adjacent P–N σ* bond (energy gain 9.4 kcal mol^{-1}) and the reduced positive charge. Increased s character of the sp$^{1.6}$ O hybrid in the O2-P1/P2^{i} bonding orbital explains the widened P1-O2-P2^{i} angle observed in the molecular structure.[14]

A possible, simplified mechanistic route for the formation of **2** is depicted in Scheme 3. Nucleophilic attack of water at one of the phosphorus centers of trication **1** initiates P–N bond cleavage leading to the formation of the assumed intermediate **III** and 3,5-dimethylpyrazolium triflate (Scheme 3a). Intermediate **III** reacts with a second equivalent of water in a similar way to form monomer **IV** and another equivalent of **4**[OTf] (Scheme 3b). DFT calculations suggest that all proposed intermediates are viable species. The subsequent dimerization of two molecules of **IV** to dication **2** is in agreement with the experimental results (calculated gas-phase Gibbs energy[11] for the dimerization: 2**IV**→**2**; $\Delta G^{298} = -2.04$ kcal mol^{-1}). However, attempts to isolate intermediate **III** by the reaction of **1**[OTf]$_3$ with one equivalent of water in MeCN, applying various reaction conditions such as low temperature, slow addition of water, or solvent combinations always led to the recovery of 0.5 equivalents of **1**[OTf]$_3$ and 0.25 equivalents of **2**[OTf]$_2$.

In summary, we have introduced the stepwise hydrolysis of Janus head type diphosphorus trication **1** representing an efficient method for the preparation of a ligand-stabilized [P$_4$O$_4$]$^{2+}$ dication **2**. This novel cationic [P$_4$O$_4$]$^{2+}$ framework, stabilized by bridging pyrazolyl ligands, is an interesting intermediate en route to the quantitative formation of the phosphorus suboxide P$_4$O$_6$. Our results will be helpful for further investigations of phosphorus suboxides and other puzzling aspects of the chemistry of mixed chalcogen–phosphorus compounds. Since the Janus head type trication **1** is accessible in high yield from cheap, commercially available starting materials, we expect that this compound will be an attractive precursor for a plethora of interesting protolysis reactions. Studies directed toward the construction of further novel cationic ring and cluster systems using **1**[OTf]$_3$ as a phosphorus building block are in progress.

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