Angewandte
Highlights

Phosphorus Chemistry

DOI: 10.1002/anie.201201600

Multiple-Charged P_1-Centered Cations: Perspectives in Synthesis**

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carbenes · cations · ligands · phosphorus · synthetic methods

Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday

"*p-Block elements play key roles in nearly all fields of chemistry.*"[1] Modern p-block chemistry has yielded intriguing compounds featuring fascinating properties and unprecedented bonding motifs.[1,2] Beyond the discovery of novel compounds, it is necessary to develop applications based on the in-depth understanding obtained from fundamental research. The increasing demand for economically and ecologically attractive synthetic methods provides additional impetus for the development of novel reagents for unprecedented chemical transformations.

Phosphorus-centered cations were long considered laboratory curiosities. However, a plethora of P-centered cations which show a large variety of bonding motifs involving the phosphorus atom became recently available.[3] Prominent phosphorus-based transformations such as the Wittig, Mitsunobu, Corey–Fuchs, and Michaelis–Arbuzov reactions proceed via monocationic intermediates.[4] Despite their often intriguing properties, the potential of phosphorus cations as powerful reagents in synthesis has largely remained neglected. It therefore seems that an investigation of multiple-charged P_1-centered cations as reagents in synthesis is long overdue.

Among the multitude of bonding motifs described for multiple-charged P_1-centered cations,[5] $[L_2PCl]^{2+}$ and $[L_3P]^{3+}$ frameworks are particularly intriguing (Figure 1). Such cations feature a trivalent P atom in the +III oxidation state in combination with either N- or C-based substituents (L_N, L_C). One of the pioneers of polyonio-substituted phosphorus chemistry was Weiss, who reported on the synthesis of peronio-substituted phosphorus compounds in the oxidation states +III (**1**$^{2+}$, **2**$^{3+}$; Figure 1)[6] and +V. Such Weiss-type compounds contain DMAP or QUIN as N-based substituents. Bertrand and co-workers reported on the synthesis of onio-, dionio-, and trionio-substituted phosphanes obtained from the reaction of DBN (1,5-diazabicyclo[4.3.0]non-5-ene) or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) with chlorophosphanes.[7]

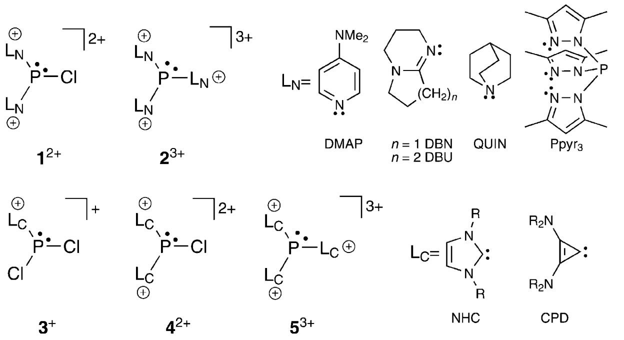

Figure 1. Examples of multiple-charged P^{III}-centered cations.

An important feature of multiple-charged P-centered cations is their propensity towards the reductive formation of P^I-species in the presence of a Lewis base. Thus, the chloride salt of dication **1**$^{2+}$ eliminates chlorine gas by an anion-induced redox reaction to yield the P^I-cation $[(DMAP)_2P]^+$.[6b] This remarkable reactivity is attributed to the optimal stabilization of the phosphide moiety in the P^I-cation $[(DMAP)_2P]^+$ by −I effects and through-space interactions[6] (field effects).[8] This kind of redox reaction can be prevented when a tridentate ligand such as $Ppyr_3$ (Figure 1) is reacted with PCl_3 in the presence of Me_3SiOTf. Key to the success of this reaction is the sequestration of the formed Cl^- anions into Me_3SiCl. Trication $[(Ppyr_3)P]^{3+}$ is obtained as a triflate salt. This compound represents the first example of a trication of type **2**$^{3+}$ which was structurally characterized.[9] Trication $[(Ppyr_3)P]^{3+}$ shows an unusual reactivity. The pyrazole moieties can act as leaving groups, thus making this cation a very promising reagent in synthesis as recently demonstrated by the use of $[(Ppyr_3)P]^{3+}$ in unprecedented P–O[9] and P–P[10] bond formations. Furthermore, the conversion of P–O into P–N bonds through chemoselective activation and subsequent substitution was described (Scheme 1).[11]

The formation of cations such as **4**$^{2+}$ (Figure 1) was initially impaired by the propensity of P-centered cations to reductively form P^I-species (see above). Thus, Macdonald and co-workers isolated the P^I-centered cation $[(NHC)_2P]^+$ from the reaction of a sterically less demanding NHC (N-heterocyclic carbene) with PCl_3.[12] To circumvent this reductive

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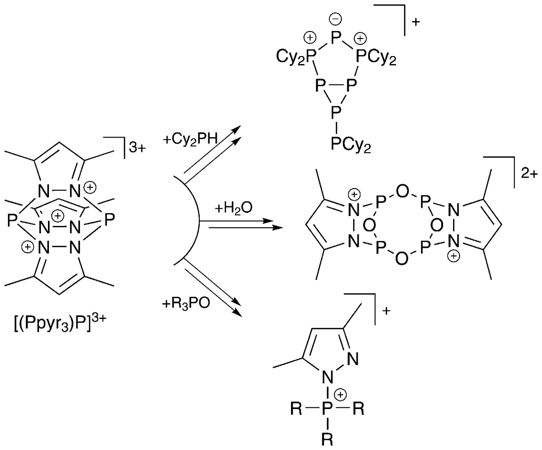
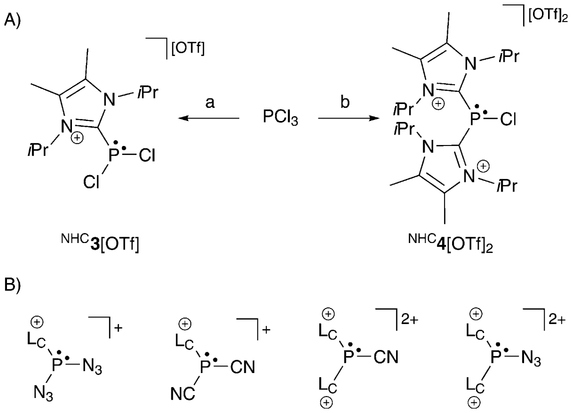
[**] This work was supported by the FCI (fellowship for K.-O.F.), the European Phosphorus Science Network (PhoSciNet CM0802), and the DFG (WE 4621/2-1).



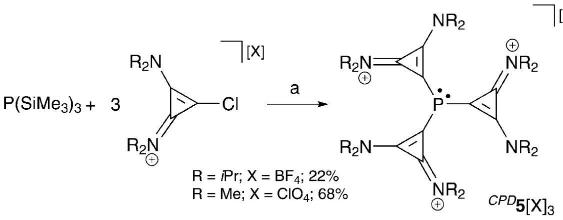
Scheme 1. Exemplary reactions demonstrating the reactivity of [(Ppyr$_3$)P]$^{3+}$.

pathway, a new approach based on Bertrand's "onio-substituent transfer" protocol[7b] was recently introduced by employing silylimidazolium salts [NHC-SiMe$_3$][OTf] as "imidazolium-transfer" reagents (Scheme 2).[13] This approach allows an efficient synthesis of the unique cations [(NHC)PCl$_2$]$^+$ ($^{NHC}\mathbf{3}^+$) and [(NHC)$_2$PCl]$^{2+}$ ($^{NHC}\mathbf{4}^{2+}$; Scheme 2). Trisubstituted cations [(NHC)$_3$P]$^{3+}$ ($^{NHC}\mathbf{5}^{3+}$; Figure 1) are also accessible by this route.[14] The isolation of a series of cyano- and azido-substituted cations derived from $^{NHC}\mathbf{3}^+$ and $^{NHC}\mathbf{4}^{2+}$ (Scheme 2) demonstrates that these cations are promising starting materials for subsequent functionalization.[13]



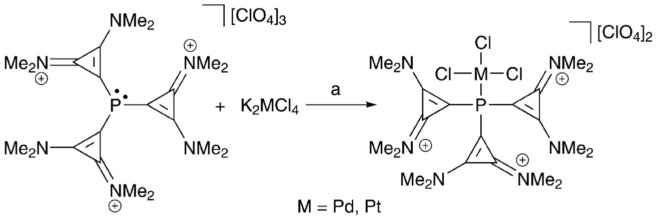
Scheme 2. A) Synthesis of cations $^{NHC}\mathbf{3}^+$ and $^{NHC}\mathbf{4}^{2+}$ as triflate salts. a) [NHC-SiMe$_3$][OTf], fluorobenzene, −Me$_3$SiCl; b) 2 [NHC-SiMe$_3$]-[OTf], fluorobenzene, −2 Me$_3$SiCl. B) Examples of cations derived from $^{NHC}\mathbf{3}^+$ and $^{NHC}\mathbf{4}^{2+}$. Tf = trifluoromethanesulfonate.

Very recently, Alcarazo and co-workers reported an alternative synthetic approach towards trications of type $\mathbf{5}^{3+}$ (Figure 1). Their clever synthetic strategy uses P(SiMe$_3$)$_3$ and 1-chloro-2,3-bis(dialkylamino)cyclopropenium salts to access the unprecedented trications [(CPD)$_3$P]$^{3+}$ ($^{CPD}\mathbf{5}^{3+}$; Scheme 3; CPD = cyclopropenylidene).[15] The reaction proceeds through sequential nucleophilic attack of the phosphane on the electron-deficient chloro-substituted carbon atom of the iminium salts accompanied by the formation of Me$_3$SiCl. The enhanced electrophilicity of the 1-chloro-2,3-bis(dialkylamino)cyclopropenium salts at the chloro-substituted carbon atom and the smaller steric demand of CPDs compared to NHCs are certainly beneficial for the formation of the cations [(CPD)$_3$P]$^{3+}$.



Scheme 3. Synthesis of CPD-derivatives [(CPD)$_3$P][X]$_3$ from P(SiMe$_3$)$_3$ and chlorocyclopropenium salts. a) fluorobenzene, 60 °C, overnight for R = *i*Pr, 3 d for R = Me, −3 Me$_3$SiCl.

Single-crystal X-ray diffraction analysis of cation [(^{Me}CPD)$_3$P][ClO$_4$]$_3$ shows that the degree of pyramidalization at the phosphorus atom (65.2 %) is comparable to that in phosphanes (e.g. 56.7 % for PPh$_3$). This observation indicates the presence of a lone pair of electrons on the central P atom. Quantum chemical calculations reveal the substantial lone-pair character of the HOMO despite the global charge of +3. Furthermore, it was anticipated that the low lying LUMO renders the trication a π acid. Hence, the electronic properties of the trications $^{CPD}\mathbf{5}^{3+}$ should allow for complex formation with electron-rich transition metal fragments. This is convincingly demonstrated by the reactions of $^{(Me)CPD}\mathbf{5}$[ClO$_4$]$_3$ with



Scheme 4. Synthesis of complexes [(^{Me}CPD)$_3$P-MCl$_3$][ClO$_4$]$_2$ (M = Pd, Pt). a) CH$_3$CN, overnight, −KCl, −KClO$_4$.

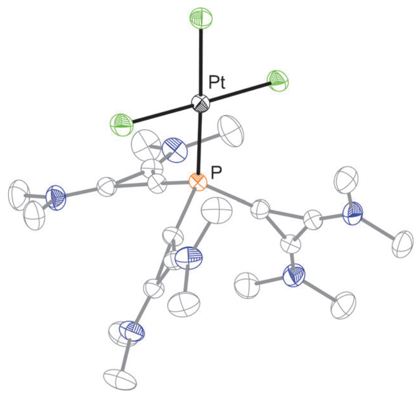


Figure 2. Molecular structure of complex [(^{Me}CPD)$_3$P-PtCl$_3$][ClO$_4$]$_2$ (perchlorate anions and hydrogen atoms are omitted for clarity).

K_2PdCl_4 and K_2PtCl_4, which yield the complexes $[(^{Me}CPD)_3P\text{-}MCl_3]^{2+}$ (M = Pd, Pt; Scheme 4 and Figure 2). The nature of the metal–ligand interaction is interpreted by means of a charge decomposition analysis. It was found that the stability of these complexes results from a substantial M→L π back-donation (0.43 *e*) and only secondarily from a L→M σ donation (0.31 *e*).

In summary, substantial progress was recently made in the developing field of multiple-charged P^{III}-centered cations. Based on improved synthesis, multiple-charged cations have been used as reagents for the preparation of unprecedented phosphorus compounds through conceptually new bond-forming and bond-activation processes. The preparation of transition-metal complexes featuring P^{III}-centered cations represents a remarkable extension of their chemistry. The ligand properties of these cations are related to those of neutral phosphanes. This discovery opens perspectives for the development of a new class of complexes which may find applications in homogenous catalysis.

Received: February 28, 2012

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