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Carbene-Stabilized Phosphorus(III)-Centered Cations $[LPX_2]^+$ and $[L_2PX]^{2+}$ (L = NHC; X = Cl, CN, N_3)

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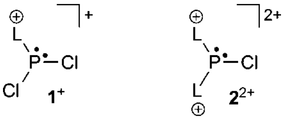
Abstract: A versatile, high-yielding synthesis of NHC-stabilized $[PCl_2]^+$ and $[PCl]^{2+}$ phosphorus synthons has been achieved by using an "onio-substituent transfer" reagent. Subsequent functionalization yields access to cationic cyano- and azido-substituted derivatives which represent first examples of a displacement reaction on NHC-stabilized phosphorus(III)-centered cations. The new salts have been fully characterized by NMR spectroscopy and X-ray crystallography.

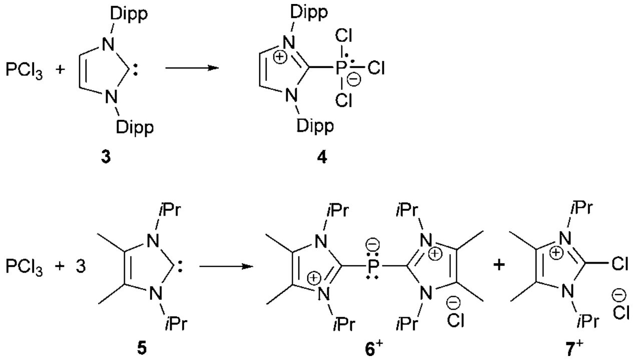
Main group element-centered cations can possess unusual reactivity and are, therefore, promising reagents for new synthetic procedures.[1] Developing viable methods for the preparation and an in-depth understanding of phosphorus cations is hence an important field of fundamental phosphorus chemistry. Several types of phosphorus-centered cations are known to date.[2] Most of them require stabilization *via* adduct formation with Lewis bases.[3] In addition to the phosphonium cation $[R_4P]^+$, one of the most prominent example is the carbene-analogous phosphenium cation $[R_2P]^+$.[4,3c,d] Multiply charged phosphorus-centered cations which incorporate trivalent P(III)-atoms and are suitable for further functionalization are not readily accessible.[5] For example, compounds **1**$^+$ and **2**$^{2+}$ are the only chlorine substituted derivatives (L = quinuclidine, 4-(dimethylamino)-pyridine).[5c,d] Herein we report the high-yielding synthesis of carbene-stabilized P(III)-centered cations $[LPCl_2]^+$ (**1**$^+$) and $[L_2PCl]^{2+}$ (**2**$^{2+}$) (L = NHC) by extending Bertrand's versatile "onio-substituent transfer" concept.[5a,b] Furthermore, we demonstrate that substitution reactions involving such multiply charged, base-stabilized P(III)-centered cations are a viable synthetic approach to novel classes of onio- and dionio-substituted phosphines.[6]



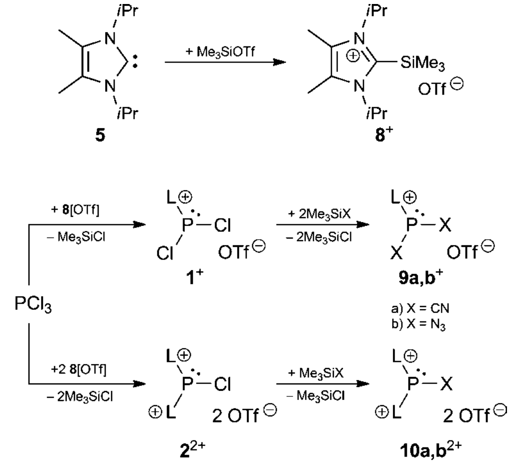
L = quinuclidine, 4-(dimethylamino)pyridine

Recently, new synthetic approaches for the stabilization of p-block-element compounds by NHCs[7] have been developed but have not been used for the stabilization of multiply charged P(III)-centered cations. Practical synthetic strategies giving access to NHC-stabilized derivatives of **1**$^+$ and **2**$^{2+}$, and allowing subsequent transformation, are yet to be established. It is known that the reaction of PCl_3 with NHCs (e.g., **3** or **5**) either gives adducts of the type NHC→PCl_3 (**4**, Scheme 1)[8] or triggers a redox reaction to yield P(I)-cation **6**$^+$ and cation **7**$^+$ (Scheme 1).[9]

Scheme 1



Scheme 2



To prevent these side reactions we transformed carbene **5** into the "onio-substituent transfer" reagent **8**[OTf] *via* adduct formation.[5b] Compound **8**[OTf] was prepared in nearly quantitative yield by the reaction of **5** with a slight excess of Me_3SiOTf in C_6H_5F.[10] The reaction of **8**[OTf] with an excess of PCl_3 (1.5 equiv, ultrasonic bath, 50 °C) yields after 10 h and workup **1**[OTf] quantitatively as moisture-sensitive, colorless crystals. The formation of cation **1**$^+$ is indicated by a ^{31}P NMR resonance shifted upfield

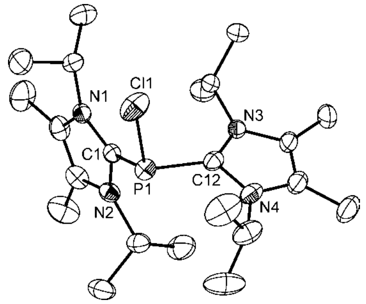


Figure 1. ORTEP plot of the molecular structure of the cation **2**$^{2+}$ in **2**$[OTf]_2$. Thermal ellipsoids at 50% probability (hydrogen atoms and counteranions omitted for clarity). Selected bond lengths (Å) and angles (deg): P1−Cl1 2.0356(9), C1−P1 1.850(2), C12−P1 1.827(2), N1−C1 1.353(3), N2−C1 1.355(3), N3−C12 1.378(3), N4−C12 1.360(3), C1−P1−C12 101.09(9), N1−C1−N2 107.6(2), N3−C12−N4 106.7(2).

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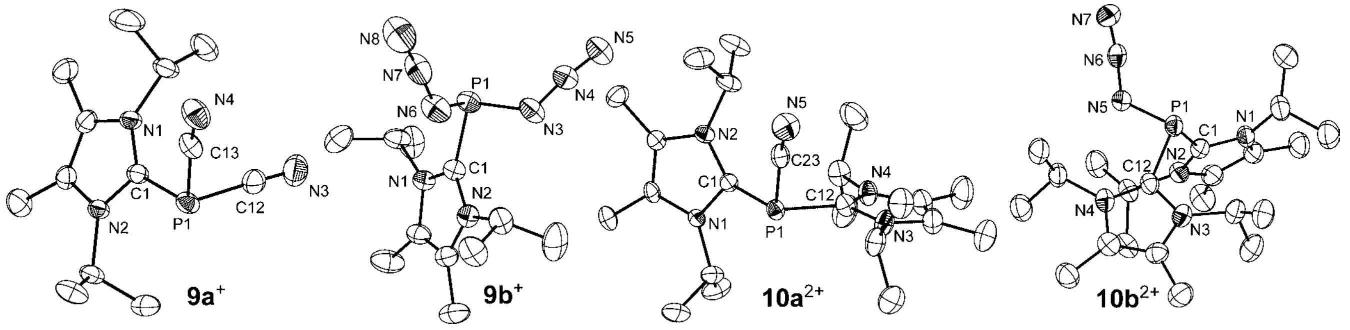

Figure 2. ORTEP plots of the molecular structures of the cations $\mathbf{9a}^{+}$, $\mathbf{9b}^{+}$, $\mathbf{10a}^{2+}$, and $\mathbf{10b}^{2+}$ of the corresponding triflate salts. Thermal ellipsoids at 50% probability (hydrogen atoms are omitted). Selected bond lengths (Å) and angles (deg) $\mathbf{9a}^{+}$: P1−C12 1.798(2), C12−N3 1.140(3), P1−C13 1.796(2), C13−N4 1.130(3), C1−P1 1.823(2), N1−C1 1.348(2), N2−C1 1.350(2), C12−P1−C13 94.62(9), N1−C1−N2 107.6(2); $\mathbf{9b}^{+}$: P1−N3 1.725(2), N3−N4 1.244(3), N4−N5 1.120(3), P1−N6 1.753(3), N6−N7 1.216(4), N7−N8 1.133(4), C1−P1 1.837(3), N1−C1 1.344(3), N2−C1 1.342(3); N3−P1−N6 97.6(1), N1−C1−N2 107.8(2), N3−N4−N5 172.0(3), N6−N7−N8 174.6(4); $\mathbf{10a}^{2+}$: P1−C23 1.792(5), C23−N5 1.141(6), C1−P1 1.834(4), C12−P1 1.858(4), N1−C1 1.347(5), N2−C1 1.358(5), N3−C12 1.360(5), N4−C12 1.342(5); C1−P1−C12 110.9(2), N1−C1−N2 107.6(3), N3−C12−N4 108.0(3); $\mathbf{10b}^{2+}$: P1−N5 1.713(3), N5−N6 1.245(5), N6−N7 1.126(5), C1−P1 1.849(3), C12−P1 1.867(4), N1−C1 1.355(5), N2−C1 1.342(5), N3−C12 1.356(5), N4−C12 1.346(5), C1−P1−C12 100.5(2), N1−C1−N2 108.0(3), N3−C12−N4 107.5(3), N5−N6−N7 172.4(4).

(δ = 109.1 ppm, CD_3CN) in comparison to PCl_3 (δ = 220.1 ppm).[11,12] The ^{31}P NMR spectrum of the reaction mixture of PCl_3 and 2 equiv of **8**[OTf] (ultrasonic bath, 50 °C) revealed the exclusive formation of dication $\mathbf{2}^{2+}$ after 24 h (δ = 19.9 ppm, CD_3CN).[12] The very air- and moisture-sensitive dication $\mathbf{2}^{2+}$ was isolated as the triflate salt in almost quantitative yield (98%).

The structure of $\mathbf{2}^{2+}$ was determined unambiguously by single crystal X-ray diffraction (Figure 1). Our approach represents a convenient method for the preparation of bottleable, crystalline materials **1**[OTf] and **2**$[OTf]_2$ in excellent yields.

We proceeded to investigate subsequent substitution reactions on these cations (Scheme 2) and gained access to the novel pseudohalogen substituted cations $[LPX_2]^+$ ($\mathbf{9a,b}^{+}$) and $[L_2PX]^{2+}$ ($\mathbf{10a,b}^{2+}$). In $\mathbf{1}^{+}$ and $\mathbf{2}^{2+}$ the chloro-substitutents are displaced quantitatively by CN- or N_3-groups when reacted with Me_3SiX (X = CN, N_3; Scheme 2).[12] These first examples of cyano substituted salts are isolated in good yields (**9a**[OTf], 65%; **10a**$[OTf]_2$, 64%). In the case of the azido substituted cations $\mathbf{9b}^{+}$[13] and $\mathbf{10b}^{2+}$, the salts are obtained in moderate yields (40−45%). To the best of our knowledge, $\mathbf{9b}^{+}$ is the first characterized diazidophosphenium cation and can be regarded as a stabilized seven-membered cationic pnictogen chain. $\mathbf{10b}^{2+}$ represents the first example of a dicationic phosphorus azide.[14] The structures of $\mathbf{9a,b}^{+}$ and $\mathbf{10a,b}^{2+}$ were determined unambiguously by single crystal X-ray diffraction (Figure 2). In all cases the pyramidalization of the phosphorus atom and the length of the C1/C12−P1 bonds (av. 1.844 Å) along with the opening of the internal angle at C1 of the carbene moiety (av. 107.8° vs ∼101° in NHCs)[15] is in agreement with the pronounced ability of the 2-imidazoline fragment to delocalize positive charge. Hence, the positive charge is siphoned away from the phosphorus atom accounting for the stability of these cations. The ^{31}P NMR data show the expected trends. The most upfield shift is observed for $\mathbf{9a}^{+}$ ($\delta = -120.2$ ppm) vs $\mathbf{10a}^{2+}$ ($\delta = -92.0$ ppm), and the opposite trend is observed for the azide derivatives ($\mathbf{10b}^{2+}$ δ = 26.9 ppm vs $\mathbf{9b}^{+}$ δ = 98.4) which can be nicely explained by the observed changes in bond angles[16] around the P(III) atom and the group electronegativity of the respective substituent.

In summary, an efficient synthesis of the unique NHC stabilized $[PCl_2]^+$ and $[PCl]^{2+}$ synthons has been introduced by using the "onio-substituent transfer" reagent **8**[OTf]. The subsequent functionalization of these cations is possible and has been demonstrated by the isolation of novel cyano- and azido-substituted cations $\mathbf{9a,b}^{+}$ and $\mathbf{10a,b}^{2+}$. Particularly appealing is the possibility of fine-tuning the properties of the $[PCl_2]^+$ and $[PCl]^{2+}$ synthons since various stable singlet carbenes are available. This approach very likely opens the way to the isolation of other very interesting pnictogen based multiply charged cations.

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Supporting Information Available: Full experimental and spectroscopic data of compounds **2**$[OTf]_2$, **9a,b**[OTf], and **10a,b**$[OTf]_2$ (CCDC numbers 782415−782419). This material is available free of charge via the Internet at http://pubs.acs.org.

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