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Phosphenium Dications

A Carbone-Stabilized Two-Coordinate Phosphorus(III)-Centered Dication**

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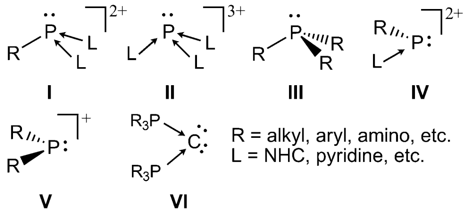
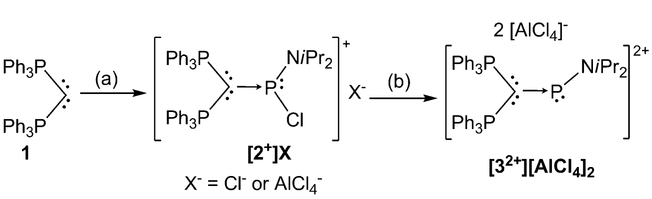
In recent years, the synthesis and structural elucidation of numerous mononuclear main-group polycations hase been achieved.[1–5] Electron-rich substituents, such as N-heterocyclic carbenes (NHCs),[4a,b] polyethers,[3c,d] pyridines,[2a,b] and diimines,[5a,b,d] were used to stabilize these highly reactive compounds. A majority of these polycations are either coordinatively saturated (for example, $[B(NC_5H_5)_4][Br]_3$[2a] and $[\{CH(CMe)_2(NC_6F_5)_2\}Al\ \{N(CH_2CH_2NMe_2)_3\}][OTf]_2$[2d]) or resemble classical Lewis bases ($[(NHC)_3Ge][OTf_2]$[3e]), rendering them inactive as Lewis acids. This certainly holds true with respect to the recently reported NHC-stabilized dicationic (**I**) and tricationic P^{III}-centered compounds (**II**; Scheme 1).[4a,b] Even though dication **I** (R = Cl; L = NHC) was subjected to chloride substitution[4b] and trication **II** (L = NHC) showed exciting coordination chemistry,[4a] they still resemble Lewis basic neutral phosphines (**III**). Therefore, our goal was to establish a ligand system that would stabilize a two-coordinate P^{III}-centered dication (**IV**) containing a formally vacant P3p orbital and potentially exhibiting reactivity associated with Lewis acids.[6] It is evident that the most stable two-coordinate P^{III}-centered monocations (**V**) that have been reported, also known as phosphenium cations, employed at least one, if not both, substituents R with strong π-donating capabilities, such as an amino group (NR'_2; R′ = alkyl, aryl).[7] It was subsequently proposed that the synthesis of the target dicationic compounds **IV** in the condensed phase would probably require both substituents R and L to be good π-donors.



Scheme 1. General structures of three- (**I**, **II** and **III**) and two-coordinate (**IV** and **V**) phosphorus compounds, and that of carbodiphosphoranes (**VI**).

The use of a dialkylamino group as the R substituent was already predetermined,[7c] but we needed to identify a suitable neutral ligand for L. It was then recognized that carbodiphosphoranes (**VI**), also known as carbones, fit the criteria for L, as computational and experimental studies showed that **VI** contains two lone electron pairs with σ and π symmetry that are available for bonding.[8] Additionally, the stability of an electron-deficient dihydridoborenium cation was attributed to π-donor capabilities of the carbone ligand.[9] Therefore, we set out to explore the synthesis of the target dicationic species using carbobis(triphenyl)phosphorane (**1**) as L.

The synthesis of the dication is shown in Scheme 2. First, **1** was added to a benzene solution containing excess iPr_2NPCl_2. Chloride displacement and the formation of [**2**$^+$][Cl] was elucidated from ES-MS and $^{31}P\{^1H\}$ NMR experiments. The ES-MS experiment showed a peak at *m*/*z* 702.2339 (calcd for **2**$^+$: 702.2370) with the correct isotopic pattern predicted for **2**$^+$ (see the Supporting Information). The room-temperature $^{31}P\{^1H\}$ NMR spectrum showed two second-order signals at $\delta_P = 25.9$ (d) and 133.4 ppm (t), which were resolved into three doublets of doublets at −90 °C, consistent with the carbone-for-chloride exchange and the formation of carbone-stabilized phosphenium cation **2**$^+$.



Scheme 2. Key reagents/conditions: a) iPr_2NPCl_2 (excess), benzene for $X = Cl^-$, addition of $AlCl_3$ (1.0 equiv), CH_2Cl_2 for $X = AlCl_4^-$; b) 1.0 equiv of $AlCl_3$ for $X = AlCl_4^-$ and 2.0 equiv of $AlCl_3$ if $X = Cl^-$ in CH_2Cl_2.

The unambiguous identity of **2**$^+$, as a tetrachloroaluminate ($AlCl_4^-$) salt, was confirmed by single-crystal X-ray diffraction;[13b] one of the two independent cationic molecules is shown in Figure 1. The average P–N (1.656(5) Å) bond length, which is comparable to the average P–N (1.663(4) Å) bond length observed for $[(iPr_2N)_2P(DBN)]^+$ (DBN = 1,5-diazabicyclo[4.3.0]-non-5-ene),[10] is consistent with the established bond order of 1.5 for similar systems.[11] The average $P_{central}$–$C_{carbone}$ bond distance of 1.814(6) Å is slightly shorter than the average P–C bond distance (1.838(6) Å) observed

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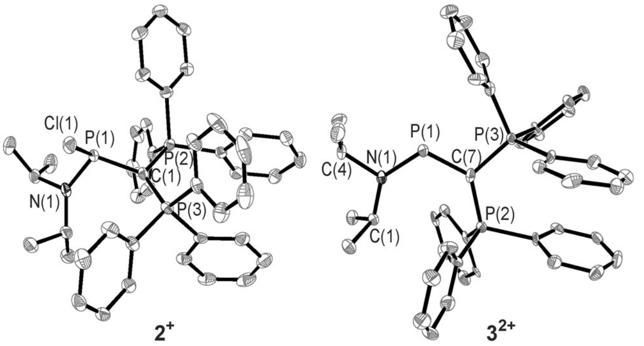

Figure 1. Molecular view of $\mathbf{2}^+$ and $\mathbf{3}^{2+}$ (ellipsoids set at 50% probability). For clarity, only one of the two asymmetric units is shown for both structures, and the counterions $[AlCl_4^-]$ together with hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] (values in the parenthesis are of the second asymmetric unit): $\mathbf{2}^+$: P1–C1, 1.812(5) (1.815(6)), P1–N1, 1.660(4) (1.652(5)), P1–Cl1, 2.173(2) (2.178(2)); N1-P1-C1, 111.6(2) (110.8(2)), N1-P1-Cl1, 106.58(18) (107.06(18)), C1-P1-Cl1, 100.84(18) (100.9(2)). $\mathbf{3}^{2+}$: P1–C1, 1.741(6) (1.79(7)), P1–N1, 1.623(6) (1.622(6)); N1-P1-C1, 118.1(3) (117.3(3)).

for carbene-stabilized mono- and dicationic three-coordinate P^{III}-centered compounds, but is within the values expected for a P–C single bond.[4b] Pyramidal geometry for $\mathbf{2}^+$ is confirmed by the value of 318.9(2)° for the sum of bond angles around the $P_{central}$.

The formation of dication $\mathbf{3}^{2+}$ from $[\mathbf{2}^+][Cl]$ was achieved by halide abstraction using 2.0 equiv of $AlCl_3$ (Scheme 2). The most indicative piece of evidence for the heterolytic P–Cl bond cleavage in $\mathbf{2}^+$ and the formation of dication $\mathbf{3}^{2+}$ originated from the appearance of a signal shifted downfield at $\delta_P = 355.7$ ppm, which is within the range of 200–500 ppm established for the known two-coordinate phosphenium cations.[7b–e] Furthermore, depleted electron density at the dication was also evident from the ^{13}C NMR spectrum, as the $C_{carbone}$ signal ($\delta_C = 67.8$ ppm) was found at about 50 ppm shifted downfield with the respect to the same signal for $\mathbf{2}^+$ ($\delta_C = 19.5$ ppm). This observation also suggested an increase in electron donation from the carbone lone pair with π symmetry to the newly created and formally vacant P 3p orbital.

Indeed, the molecular structure of $\mathbf{3}^{2+}$ (one of the two asymmetric units is shown in Figure 1)[13b] exhibits planarity along the C_2NPCP_2 fragment, placing not only the amino but also the carbone π symmetry lone pair in an ideal position to interact with the formally vacant P 3p orbital. This $N \rightarrow P \leftarrow C$ π-interaction is manifested by shortening of the average $P_{central}$–N (1.623(6) Å for $\mathbf{3}^{2+}$ vs. 1.656(5) for $\mathbf{2}^+$) and $P_{central}$–$C_{carbone}$ bonds (1.745(7) Å for $\mathbf{3}^{2+}$ vs. 1.813(6) Å for $\mathbf{2}^+$) with the respect to the precursor. Taking into account that 1) the accepted description of the P–N bond is somewhere between a single and double bond, and 2) the average P–C bond for $\mathbf{3}^{2+}$ is very similar to the P–C bond (1.7376(14) Å) observed for a phosphaalkene,[12] it is, therefore, reasonable to assume that the NPC fragment for $\mathbf{3}^{2+}$ is allene-like, providing the necessary thermodynamic stabilization for the dication.

At this point it is worth noting that the interion interactions, manifested by P···Cl contacts (3.527(8) and 3.585(9) Å, respectively, for the two independent molecules), are at the extreme end of the sum of van der Waal's radii for P and Cl (3.55 Å).[13a] As similar close contacts have been observed for analogous phosphenium salts,[14] it is generally accepted that these contacts have little or no effect on the structural features of the cation(s) and the anion(s)[14a] unless hydrogen bonding is involved.[15]

To gain more insight into the structural/electronic features of dication $\mathbf{3}^{2+}$, a series of density function theory (DFT) calculations were performed (see the Supporting Information). The optimized structural parameters for $\mathbf{3}^{2+}$, including the C_2NPCP_2 fragment, are in good agreement with the experimental values. The delocalized nature of the HOMO orbital for $\mathbf{3}^{2+}$ (Figure 2 b) along the N–P–C fragment seems to be very different from the HOMO for $[P(NMe_2)_2]^+$, which is similar to filled N 2p atomic orbitals.[11] The molecular orbital that resembles the lone pair located on the central P atom for $\mathbf{3}^{2+}$ (HOMO−12,[16] −12.737 eV; see the Supporting Information) is quite destabilized with respect to the analogous orbital for $[P(NMe_2)_2]^+$ (−13.518 eV), hinting at $\mathbf{3}^{2+}$ being a better σ-donor than the phosphenium cation.

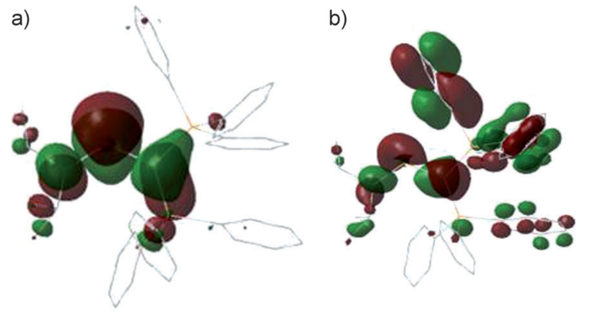

Figure 2. Selected molecular orbitals for $\mathbf{3}^{2+}$. a) LUMO, b) HOMO.

Interestingly, the most bonding π-orbital, HOMO−14[16] (−13.810 eV; see the Supporting Information) for $\mathbf{3}^{2+}$ is more stabilized than the same orbital for $[P(NMe_2)_2]^+$ (−13.450 eV) implying a more effective π interaction along the N 2p–P 3p–C $2p_\pi$ fragment for $\mathbf{3}^{2+}$ with respect to the analogous N 2p–P 3p–N 2p fragment for $[P(NMe_2)_2]^+$.[11] Nonetheless, the LUMO (π^*, Figure 2 a) detected at −7.638 eV for $\mathbf{3}^{2+}$ is still more stabilized relative to the LUMO (−6.910 eV) for $[P(NMe_2)_2]^+$, which is presumably due to a greater positive charge at the former compound. Thus, this particular observation indicates that $\mathbf{3}^{2+}$ should also be a better Lewis acid (e^- acceptor) than $[P(NMe_2)_2]^+$.

Lewis acidic properties of the dication were explored by the addition of either 1 or 2 equiv of PMe_3 into a dichloromethane solution containing $[\mathbf{3}^{2+}][AlCl_4]_2$ (see the Supporting Information for details). It was immediately evident that a simple Lewis acid–base adduct formation did not occur, but a more complex reaction mixture was developing. Variable-temperature ^{31}P NMR studies showed the formation of not only $\mathbf{3}^{2+}\cdot PMe_3$ ($\delta_P = 40.7$ ppm) adduct but also $\mathbf{2}^+$ precursor, suggesting the existence of a dynamic equilibrium system (Scheme 3). On the other hand, the reaction between $[\mathbf{3}^{2+}]$-$[AlCl_4]_2$ and DMAP (dimethylaminopyridine) resulted in the

$$[\mathbf{3}^{2+}\cdot\mathrm{PMe_3}][\mathrm{AlCl_4}]_2 \xrightleftharpoons{+\,\mathrm{PMe_3}} [\mathbf{3}^{2+}][\mathrm{AlCl_4}]_2 \xrightleftharpoons{+\,\mathrm{PMe_3}} [\mathbf{2}^{+}][\mathrm{AlCl_4}] + \mathrm{Me_3P\cdot AlCl_3}$$

Scheme 3. Proposed equilibria.

formation of [$\mathbf{2}^{+}$][$AlCl_4$] and DMAP·$AlCl_3$, an observation which is consistent with the HSAB concept regarding PMe_3 and DMAP.[7b]

To eliminate counterion interference with respect to the dication reactivity with DMAP, [$\mathbf{3}^{2+}$][BAr^f_4]$_2$ ($Ar^f = 3,5\text{-}(CF_3)_2\text{-}C_6H_3$) was synthesized (see the Supporting Information). Indeed, introducing 1.0 equiv of DMAP in a solution containing [$\mathbf{3}^{2+}$][BAr^f_4]$_2$ resulted in the formation of the target adduct [$\mathbf{3}^{2+}$·DMAP] ($\delta_P = 131.2$ ppm).

Therefore, the unprecedented equilibrium system (Scheme 3), especially the equilibrium involving a heterolytic P–P bond formation/cleavage,[17] for phosphenium chemistry revealed that PMe_3 has a higher preference to interact with $AlCl_4^-$ than with the cation but that the preference can be altered with a decrease in temperature. Lastly, the presence of a (partially) vacant P 3p orbital on $\mathbf{3}^{2+}$ and, hence, the Lewis acidic nature of this dication was confirmed with the observed formation of $\mathbf{3}^{2+}$·PMe_3 and $\mathbf{3}^{2+}$·DMAP.

In conclusion, we have succeeded in utilizing the unique electron-donor properties of **1** to stabilize the very first example of coordinatively unsaturated P^{III}-centered dication $\mathbf{3}^{2+}$. Electronic (based on DFT) and reactivity properties (based on the reactions with PMe_3 and DMAP) promise an exciting chemistry for this polycation. In fact, we hope that $\mathbf{3}^{2+}$ could be to phosphenium chemistry as cyclic (alkyl) (amino) carbenes (CAACs) are to carbene chemistry.[18] Reactivity investigations of this interesting polycationic molecule, especially involving transition-metal chemistry, are ongoing and will be reported in due course.

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