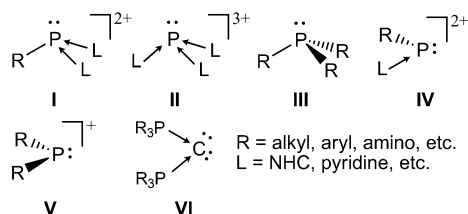


A Carbene-Stabilized Two-Coordinate Phosphorus(III)-Centered Dication**

Madelyn Qin Yi Tay, Yunpeng Lu, Rakesh Ganguly, and Dragoslav Vidović*

In recent years, the synthesis and structural elucidation of numerous mononuclear main-group polycations have 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, $[\text{B}(\text{NC}_5\text{H}_5)_4][\text{Br}]_3^{2+}$ and $[\{\text{CH}(\text{CMe})_2(\text{NC}_6\text{F}_5)_2\}\text{Al}\{\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_3\}][\text{OTf}]_2^{2+}$) or resemble classical Lewis bases ($[(\text{NHC})_3\text{Ge}][\text{OTf}]_2^{3+}$), 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** ($\text{R} = \text{Cl}$; $\text{L} = \text{NHC}$)



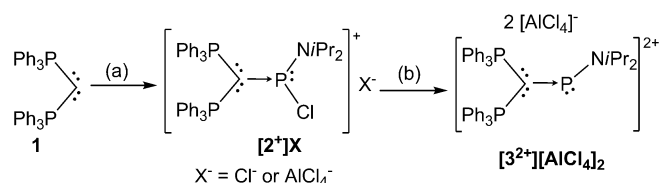
Scheme 1. General structures of three- (**I**, **II** and **III**) and two-coordinate (**IV** and **V**) phosphorus compounds, and that of carbodiphosphoranes (**VI**).

was subjected to chloride substitution^[4b] and trication **II** ($\text{L} = \text{NHC}$) 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 $\text{P}3\text{p}$ 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 ; $\text{R}' = \text{alkyl, aryl}$).^[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.

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 carbenes, 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 dihydridoborenum cation was attributed to π -donor capabilities of the carbene 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 $i\text{Pr}_2\text{N}(\text{P}(\text{Cl})\text{Cl}_2)_2$. Chloride displacement and the formation of **[2⁺]**



Scheme 2. Key reagents/conditions: a) $i\text{Pr}_2\text{N}(\text{P}(\text{Cl})\text{Cl}_2)_2$ (excess), benzene for $\text{X} = \text{Cl}^-$, addition of AlCl_3 (1.0 equiv), CH_2Cl_2 for $\text{X} = \text{AlCl}_4^-$; b) 1.0 equiv of AlCl_3 for $\text{X} = \text{AlCl}_4^-$ and 2.0 equiv of AlCl_3 if $\text{X} = \text{Cl}^-$ in CH_2Cl_2 .

$[\text{Cl}]$ was elucidated from ES-MS and $^{31}\text{P}\{^1\text{H}\}$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two second-order signals at $\delta_{\text{P}} = 25.9$ (d) and 133.4 ppm (t), which were resolved into three doublets of doublets at -90°C , consistent with the carbene-for-chloride exchange and the formation of carbene-stabilized phosphenium cation 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 $\text{P}-\text{N}$ (1.656(5) Å) bond length, which is comparable to the average $\text{P}-\text{N}$ (1.663(4) Å) bond length observed for $[(i\text{Pr}_2\text{N})_2\text{P}(\text{DBN})]^+$ (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 $\text{P}_{\text{central}}-\text{C}_{\text{carbene}}$ bond distance of 1.814(6) Å is slightly shorter than the average $\text{P}-\text{C}$ bond distance (1.838(6) Å) observed

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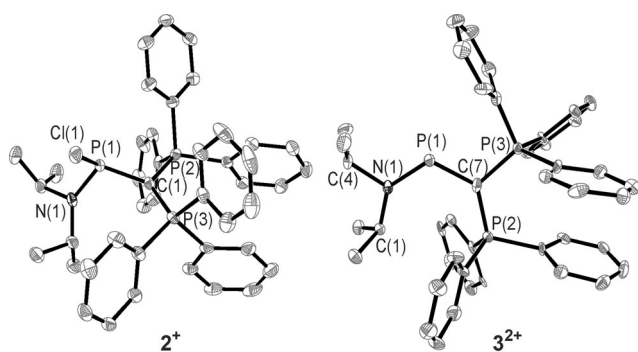


Figure 1. Molecular view of 2^+ and 3^{2+} (ellipsoids set at 50% probability). For clarity, only one of the two asymmetric units is shown for both structures, and the counterions $[\text{AlCl}_4]^-$ together with hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [°] (values in the parenthesis are of the second asymmetric unit): 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)). 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 2^+ is confirmed by the value of $318.9(2)^\circ$ for the sum of bond angles around the $\text{P}_{\text{central}}$.

The formation of dication 3^{2+} from $[2^+][\text{Cl}]$ 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 2^+ and the formation of dication 3^{2+} originated from the appearance of a signal shifted downfield at $\delta_{\text{P}} = 355.7$ ppm, which is within the range of 200–500 ppm established for the known two-coordinate phosphonium cations.^[7b–e] Furthermore, depleted electron density at the dication was also evident from the ^{13}C NMR spectrum, as the $\text{C}_{\text{carbene}}$ signal ($\delta_{\text{C}} = 67.8$ ppm) was found at about 50 ppm shifted downfield with the respect to the same signal for 2^+ ($\delta_{\text{C}} = 19.5$ ppm). This observation also suggested an increase in electron donation from the carbene lone pair with π symmetry to the newly created and formally vacant $\text{P}3\text{p}$ orbital.

Indeed, the molecular structure of 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 carbene π symmetry lone pair in an ideal position to interact with the formally vacant $\text{P}3\text{p}$ orbital. This $\text{N} \rightarrow \text{P} \leftarrow \text{C}$ π -interaction is manifested by shortening of the average $\text{P}_{\text{central}}\text{--N}$ (1.623(6) Å for 3^{2+} vs. 1.656(5) for 2^+) and $\text{P}_{\text{central}}\text{--C}_{\text{carbene}}$ bonds (1.745(7) Å for 3^{2+} vs. 1.813(6) Å for 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 3^{2+} is very similar to the P–C bond (1.7376(14) Å) observed for a phosphalkene,^[12] it is, therefore, reasonable to assume that the NPC fragment for 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 $\text{P} \cdots \text{Cl}$ 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 Waals radii for P and Cl (3.55 Å).^[13a] As similar close contacts have been observed for analogous phosphonium 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 3^{2+} , a series of density function theory (DFT) calculations were performed (see the Supporting Information). The optimized structural parameters for 3^{2+} , including the C_2NPCP_2 fragment, are in good agreement with the experimental values. The delocalized nature of the HOMO orbital for 3^{2+} (Figure 2b) along the N–P–C fragment seems

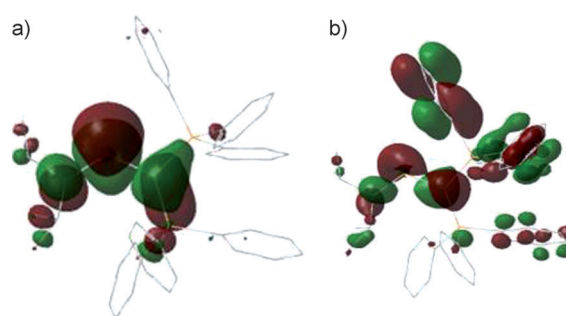


Figure 2. Selected molecular orbitals for 3^{2+} . a) LUMO, b) HOMO.

to be very different from the HOMO for $[\text{P}(\text{NMe}_2)_2]^+$, which is similar to filled $\text{N}2\text{p}$ atomic orbitals.^[11] The molecular orbital that resembles the lone pair located on the central P atom for 3^{2+} (HOMO–12,^[16] –12.737 eV; see the Supporting Information) is quite destabilized with respect to the analogous orbital for $[\text{P}(\text{NMe}_2)_2]^+$ (–13.518 eV), hinting at 3^{2+} being a better σ -donor than the phosphonium cation.

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

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 $[3^{2+}][\text{AlCl}_4]_2$ (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 $3^{2+}\cdot\text{PMe}_3$ ($\delta_{\text{P}} = 40.7$ ppm) adduct but also 2^+ precursor, suggesting the existence of a dynamic equilibrium system (Scheme 3). On the other hand, the reaction between $[3^{2+}][\text{AlCl}_4]_2$ and DMAP (dimethylaminopyridine) resulted in the



Scheme 3. Proposed equilibria.

formation of $[2^+][\text{AlCl}_4]$ and $\text{DMP}\cdot\text{AlCl}_3$, an observation which is consistent with the HSAB concept regarding PMe_3 and DMP .^[7b]

To eliminate counterion interference with respect to the dication reactivity with DMP , $[3^{2+}][\text{BAr}^f_4]_2$ ($\text{Ar}^f = 3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$) was synthesized (see the Supporting Information). Indeed, introducing 1.0 equiv of DMP in a solution containing $[3^{2+}][\text{BAr}^f_4]_2$ resulted in the formation of the target adduct $[3^{2+}\cdot\text{DMP}]$ ($\delta_{\text{P}} = 131.2$ ppm).

Therefore, the unprecedented equilibrium system (Scheme 3), especially the equilibrium involving a heterolytic P–P bond formation/cleavage,^[17] for phosphonium 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 3^{2+} and, hence, the Lewis acidic nature of this dication was confirmed with the observed formation of $3^{2+}\cdot\text{PMe}_3$ and $3^{2+}\cdot\text{DMP}$.

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 3^{2+} . Electronic (based on DFT) and reactivity properties (based on the reactions with PMe_3 and DMP) promise an exciting chemistry for this polycation. In fact, we hope that 3^{2+} could be to phosphonium 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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