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COMMUNICATION

Synthesis, Characterization, and Reactivity of an Acyclic Alkyl-Imino-Phosphenium Cation

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Lucas C. Torres,[a,c] Casey A. Lenart,[a] Avik Bhattacharjee,[a] Michael Seidl,[c] Pawel Löwe,[b] Fabian Dielmann,*[c] and Christopher B. Caputo*[a]

An acyclic alkyl-imino phosphenium cation stabilized by an N-heterocyclic imine is reported, revealing how scaffold modification unlocks reactivity inaccessible to classical phosphenium platforms. The cation displays pronounced Lewis acidity, ambiphilic cycloaddition reactivity, and N–H bond oxidative addition-like reactivity that is unprecedented for acyclic phosphenium platforms. These findings demonstrate that strategic modification of the phosphenium scaffold enables new modes of bond activation, expanding on the reactivity of acyclic phosphenium cations.

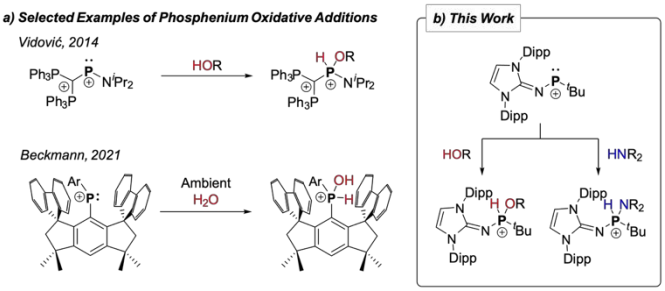
Phosphorus analogues of classical carbon-based reactive species have attracted sustained interest due to the distinct, yet related, electronic properties of these two elements.[1] Among the most prominent examples are phosphenium cations, two-coordinate phosphorus species that are isoelectronic with carbenes, and in fact, were isolated well before their carbon congeners.[2] These cations have demonstrated rich reactivity in coordination chemistry,[3] bond activation,[4] chelotropic cycloadditions,[5] and catalysis,[6] to name a few.

Like carbenes, phosphenium cations often require heteroatom stabilization, with N-heterocyclic phosphenium (NHP) frameworks representing a robust and widely studied platform.[7] Modifications to the supporting framework, particularly when moving beyond heterocyclic to acyclic systems, can result in markedly different electronic structures and reactivity, again mirroring trends observed in carbene chemistry.[8]

Recent reports have shown that carefully designed acyclic systems can access oxidative addition-like chemistry. Vidović and co-workers described a dicationic phosphenium species stabilized by a π-electron-rich carbodiphosphorane and an amido group, which undergoes oxidative addition of water or methanol to yield phosphonium dications.[9] Similarly, Beckmann and co-workers reported diaryl phosphenium cations stabilized by a sterically demanding fluorenyl substituent that also oxidatively adds water (Figure 1).[10] While certain cyclic or geometrically constrained phosphenium cations have enhanced the ability for oxidative addition-like behaviour, facilitating Si-H, N-H and H-H bond activations,[11] oxidative addition-like chemistry at acyclic phosphenium cations has primarily explored O-H bonds, with dications showing a wider scope.[4c]

We questioned whether donor/steric design could expand the scope of oxidative addition for acyclic phosphenium cations. N-heterocyclic imines (NHIs) are strong π donors that have enabled the isolation of numerous reactive phosphorus compounds in our groups and others.[12] We therefore sought to employ an NHI substituent to stabilize an acyclic, alkyl-imino-phosphenium cation and to probe whether this platform could unlock new bond-activation pathways. Herein, we report the synthesis and reactivity of a *tert*-butyl/NHI-substituted acyclic phosphenium cation, finding that it cannot only perform oxidative addition with O-H bonds, but with N-H bonds as well.

Figure 1 – a) Selected examples of phosphenium cations undergoing oxidative addition with hydroxyl groups. b) This work. Anions omitted for clarity.



[a] Department of Chemistry, York University, 4700 Keele St, Toronto, ON M3J 1P3, Canada
[b] Institute of Inorganic and Analytical Chemistry, Westfälische Wilhelms-Universität Münster, 48149, Corrensstrasse 30 48149, Münster, Germany
[c] Institute of General, Inorganic and Theoretical Chemistry, Universität Innsbruck, Innrain 80–82, Innsbruck 6020, Austria
† Footnotes relating to the title and/or authors should appear here.
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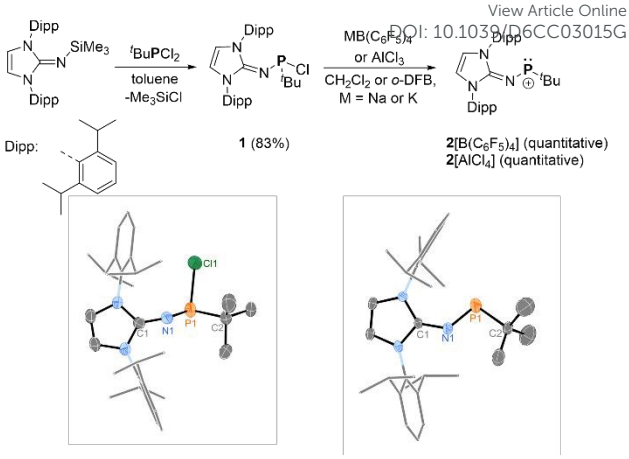
Following a recently reported procedure, the alkyl-imino-chlorophosphine (**1**) was prepared by adding one equivalent of a Dipp-substituted silyl NHI to a solution of $tBuPCl_2$ in toluene at -78 °C (Scheme 1).[13] The reaction was stirred for 30 minutes and allowed to react at room temperature for 16 hours. The volatiles were removed in vacuo, and the product was isolated as an off-white powder in 83% yield. The ^{31}P NMR chemical shift was diagnostic of product formation, with a decet resonance at δ: 157.6 ppm. Single crystals of this product were obtained from a concentrated hexanes solution at -40 °C, and confirmed the formation of the expected product. The solid-state structure was highly disordered, as the phosphine is racemic and co-crystallizes as enantiomers, with an elongated P–Cl bond (av. 2.13 Å) and compressed P–N bond (av. 1.60 Å), which could be attributed to π-donation from the NHI substituent into the P–Cl σ* orbital(Scheme 1).

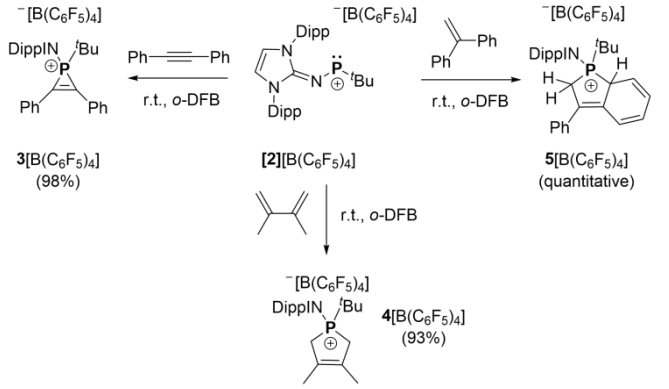
To access the corresponding phosphenium cation, **1** was added to a stirring suspension of $NaB(C_6F_5)_4$ or $KB(C_6F_5)_4$ in either CH_2Cl_2 or 1,2-difluorobenzene (*o*-DFB). This resulted in an instant colour change from light yellow to dark red. The phosphenium species **2**$[B(C_6F_5)_4]$ was isolated as a bright red-pink solid in quantitative yields and exhibited a distinctly downfield chemical shift in the ^{31}P NMR spectrum at δ: 596 ppm, over 400 ppm units apart from the starting material. The ^{11}B and ^{19}F NMR spectra presented resonances consistent with that of the $B(C_6F_5)_4$ anion. Comparable acyclic phosphenium cations exhibit similarly downfield ^{31}P NMR chemical shifts. This includes a structurally related amino-alkyl phosphenium $[tBuP(NMe_2)]^+$ (δ: 513 ppm) prepared by Cowley,[14] and the diarylphosphenium cations recently reported by Beckmann (δ: 542 ppm and 573 ppm), the latter being the phosphenium cation with the most downfield chemical shift.[10] With a resonance more than 20 ppm further downfield, **2**$[B(C_6F_5)_4]$ is, to the best of our knowledge, the new record holder for this moniker. Unfortunately, all attempts to confirm the solid-state structure of **2**$[B(C_6F_5)_4]$ failed owing to the tendency to form oils. Nevertheless, the structure of the phosphenium cation was unambiguously identified when using $AlCl_3$ as a chloride abstracting reagent and **2**$[AlCl_4]$ was successfully isolated in quantitative yield, resulting in a near identical ^{31}P NMR chemical shift of 594.4 ppm, indicating its ionic behaviour in the solution state. **2**$[AlCl_4]$ exhibited no signs of decomposition in CD_2Cl_2 at room temperature, even after a week, with decomposition only observed upon heating to 60 °C. Red block single crystals suitable for X-ray diffraction were obtained, and interestingly, the P-N bond length is shorter (1.576(6) Å) relative to the phosphine precursor **1**, indicating some multiple bond character for **2**$[AlCl_4]$ arising from π-donation from the exocyclic imine nitrogen atom to phosphorus (Scheme 1). The P-C2 bond length of 1.826(7) Å is consistent with a P–C single bond with a N1–P–C2 bond angle of 103.4(3)° is more acute compared to other acyclic amino alkyl phosphenium cations.[15]



Scheme 1 – Synthesis of phosphenium cation 2^+. *o*-DFB = 1,2-difluorobenzene(top). Bottom, solid state structures of **1** and **2**$[AlCl_4]$. In all cases, ellipsoids are shown at 50% probability, with hydrogen atoms omitted for clarity.

The electronic structure of **2** was examined using DFT calculations at the B3LYP-D3BJ/def2-TZVP level of theory.[16] The HOMO has contributions from the π-system of the imidazole ring, as well as from the lone pair on the exocyclic nitrogen atom and the phosphorus atom. In contrast, the LUMO is predominantly comprised of the empty p-orbital on phosphorus (ESI, Figure S83). The HOMO-LUMO gap of 3.31 eV is similar to that of a related silylene reported by Inoue (3.22 eV).[17] Mayer bond orders indicate significant π-bonding character within the C=N-P fragment (P-N1: 1.6, C1-N1: 1.4) and Natural Bond Orbital (NBO) analysis confirm the phosphorus atom being the most electrophilic site on the molecule as indicated with a +1.14 charge situated on the atom. The Hirshfeld charge analysis also confirms that the phosphorus is the most positively charged atom (Figure S84). This electrophilicity was experimentally corroborated as **2**$[B(C_6F_5)_4]$ readily reacted with various Lewis bases. For example, addition of DMAP to the phosphenium cation led to the immediate dissipation of the cation's characteristic red colour and a diagnostic ^{31}P NMR chemical shift change from δ: 596 ppm to δ: 136.6 ppm, indicating the formation of an adduct. Finally, the effective Lewis acidity was determined using the Gutmann-Beckett method,[18] with a ^{31}P NMR chemical shift of δ: 85.3 ppm for the Et_3PO probe after coordination to **2**$[B(C_6F_5)_4]$, corresponding to an acceptor number of 98. Interestingly, this exceeds the ubiquitous borane Lewis acid, $B(C_6F_5)_3$ (AN 82) but is lower than other reported acyclic phosphenium cations and P(V) cations bearing NHI substituents (ESI, Figure S17).[10,12a,18b,19]

We probed the ambiphilic reactivity of **2**$[B(C_6F_5)_4]$ through chelotropic cycloaddition reactions (Scheme 2). The reaction of diphenylacetylene with **2**$[B(C_6F_5)_4]$ afforded the P(V) phosphirenium salt **3**$[B(C_6F_5)_4]$ via a [2+1] cycloaddition in 98 % yield, with a distinctive ^{31}P NMR resonance at δ: -82.5 ppm. Similarly, combining 2,3-dimethyl-1,3-butadiene with **2**$[B(C_6F_5)_4]$ cleanly affords the cyclic P(V) phospholenium

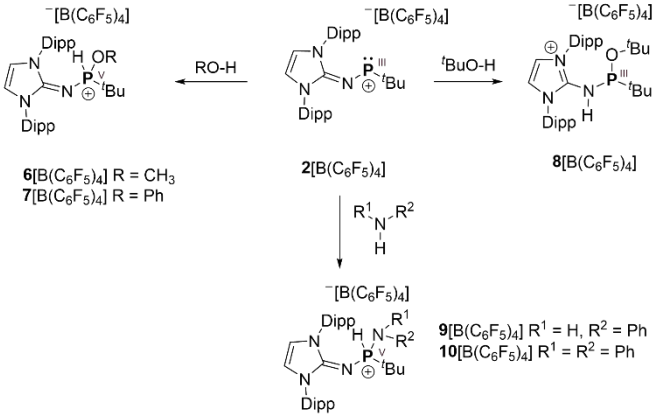


Scheme 2 – Ambiphilic chelotropic cycloaddition reactions with **2**[B(C$_6$F$_5$)$_4$].

4[B(C$_6$F$_5$)$_4$] in 93 % yield via a [4+1]cycloaddition, with a new ^{31}P NMR chemical shift of δ: 43.9 ppm. Both chemical shifts closely agree with reported literature compounds.[5a,b] Interestingly, employing 1,1-diphenylethylene afforded a cyclic phospholenium cation **5**[B(C$_6$F$_5$)$_4$] resulting from arene dearomatization. This analysis was supported by 2D NMR spectroscopic methods, along with the ^{1}H NMR spectrum showing environments indicative of a cyclohexabutadiene fragment (ESI, Figure S38). The ^{31}P NMR resonance of **5**[B(C$_6$F$_5$)$_4$] is shifted to low field frequency (δ: 63.4 ppm) relative to the phosphenium cation.

Looking beyond chelotropic reactions, we focused our attention on more challenging oxidative addition reactions, exploring both alcohols and amine functional groups. First, **2**[B(C$_6$F$_5$)$_4$] was reacted with a stoichiometric amount of methanol at room temperature, which resulted in the formation of a single, new product. Multinuclear NMR experiments revealed that the product was the result of O–H bond activation at phosphorus, evident by $^1J_{HP}$ coupling (514 Hz) in the ^{1}H and ^{31}P NMR Spectra. Furthermore, the ^{31}P NMR chemical shift (δ: 35.2 ppm) suggests a tetrahedral environment at the phosphorus centre and additional $^3J_{HP}$ = 13 Hz can be observed with the -OC*H*$_3$ moiety. Taken together, these data suggest both P–H and P–O bond formation events occur, with a change in oxidation state from P(III) to P(V), giving the phosphonium cation **6**[B(C$_6$F$_5$)$_4$] (Scheme 3). Similarly, reaction with phenol resulted in oxidative addition to the product **7**[B(C$_6$F$_5$)$_4$] akin to MeOH, with spectroscopic features consistent with an addition across the O–H bond (^{31}P NMR δ: 27.5 ppm, $^1J_{HP}$ = 522 Hz). Surprisingly, when **2**[B(C$_6$F$_5$)$_4$] was reacted with *tert*-butanol, it was immediately apparent that P–H bond formation had not occurred given the absence of $^1J_{HP}$ coupling features in either the ^{1}H or ^{31}P NMR spectra. The ^{31}P NMR spectrum instead showed one resonance at δ: 125.5 ppm, which is shifted slightly downfield from the phosphine **1**, indicating that activation likely leads to a compound with a tricoordinate P(III) centre. Correlations in the ^{1}H/^{13}C HMBC spectrum were used to identify this species as a cationic phosphonamidite **8**[B(C$_6$F$_5$)$_4$] where both P–O and N–H bond formation occurs. This observation suggests that the basicity of the P and N atoms in the corresponding neutral phosphine must be very similar. It has previously been shown that phosphines bearing NHI and alkyl substituents are typically protonated at P,[20] while the introduction of electron-withdrawing alkoxygroups on the phosphorus renders the exocyclic NHI nitrogen atom more basic.[21] This product may be formed to accommodate the steric crowding around the phosphorus centre, as the phosphonamidite may better fit the bulky -NHIDipp, - *t*Bu, and – O*t*Bu substituents in a trigonal pyramidal rather than tetrahedral geometry. While some geometrically constrained P(III) species,[22] or highly reactive P(V) systems,[12a,23] have shown this cooperative activation between phosphorus and substituent, to the best of our knowledge, this is the first discreet example with a phosphenium cation. It should be noted that all attempts to force the reductive elimination of the alcohols from **6**–**8**[B(C$_6$F$_5$)$_4$] failed as these compounds show extreme stability even at elevated temperatures and reduced pressures.

To push the boundaries, we explored the reactivity of **2**[B(C$_6$F$_5$)$_4$] with amines, and gratifyingly, it was found to react with both primary and secondary aryl amines to give P(V) oxidative addition products through the N-H bond. Equimolar amounts of aniline and **2**[B(C$_6$F$_5$)$_4$] instantly afforded the new product **9**[B(C$_6$F$_5$)$_4$] in qualitative yield (Scheme 3). The oxidative addition of the N-H bond was evidenced by the appearance of a doublet of doublet of decets centred at δ: 13.7 ppm ($^1J_{HP}$ = 490 Hz, $^2J_{HP}$ = 5.9 Hz) in the ^{31}P NMR spectrum. Further, ^{1}H/^{13}C HMBC experiments confirmed the location of the proton as aniline bound and not bound to the exocyclic nitrogen atom of the NIDipp substituent. The reaction of **2**[B(C$_6$F$_5$)$_4$] with the bulkier *N,N*-diphenylamine proceeded much slower. Spectroscopically, it appears an initial Lewis acid-base adduct occurs between **2**[B(C$_6$F$_5$)$_4$] and the bulkier amine, with dissipation of the red colour and the intermediate singlet ^{31}P NMR chemical shift of δ: 72.7 ppm featuring no obvious multiplicity that would otherwise indicate P-H bond formation (ESI, Figure S76). Nevertheless, heating this reaction mixture at 70 °C for 20 days drove the reaction to the oxidative addition product **10**[B(C$_6$F$_5$)$_4$] with a ^{31}P NMR chemical shift of 21.4 ppm ($^1J_{HP}$ = 504 Hz). To the best of our knowledge, these would be the first example of N–H oxidative addition at a non-cyclic or geometrically constrained phosphenium species.



Scheme 3 – Oxidative addition-like reactivity of **2**[B(C$_6$F$_5$)$_4$] with various alcohols and amines.

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In conclusion, the synthesis of an acyclic alkyl imino substituted phosphenium cation supported by an N-heterocyclic imine substituent was described. Together, these features imparted unique and multifaceted reactivity at the phosphorus centre. The electrophilic character of **2**[$B(C_6F_5)_4$] was experimentally demonstrated through the formation of Lewis acid-base adducts with DMAP and Et_3PO, with the latter enabling a quantitative assessment of Lewis acidity via the Gutmann-Beckett method. Furthermore, **2**[$B(C_6F_5)_4$] displays ambiphilic behaviours, engaging in cheletropic cycloaddition reactions with various unsaturated hydrocarbon substrates.

Notably, **2**[$B(C_6F_5)_3$] was found to participate in oxidative addition-like activation of E-H bonds across the phosphenium centre with both amines and alcohols. These results collectively highlight how modification of the phosphenium scaffold can unlock unprecedented bond-activation pathways, establishing acyclic phosphenium cations as versatile platforms for main-group reactivity.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data is available in the Supplementary Information PDF file associated with this manuscript. This includes general methods, synthetic procedures, spectroscopic characterization, control experiments, and computational details. Crystallographic data have been deposited to the CCDC: 2530874, 2562678.

Notes and references

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Data Availability Statement

All data is available in the Supplementary Information PDF file associated with this manuscript. This includes general methods, synthetic procedures, spectroscopic characterization, control experiments, and computational details. Crystallographic data have been deposited to the CCDC: 2530874, 2562678.