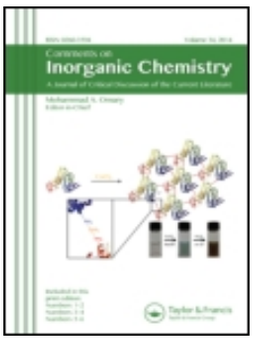

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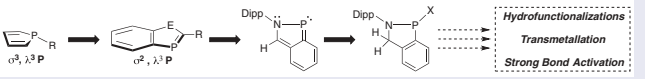
1,2-(Benz)Azaphospholes: A Slow Beginning to a Bright Future

Matthew F. Cain

Department of Chemistry, University of Hawai'i at Mānoa, Honolulu, Hawaii, USA

ABSTRACT

While initially laboratory curiosities, the chemistry of phospholes evolved as a better understanding of their structure, reactivity, and electronic properties was established. With their potential as building blocks for new electronic materials emerging, researchers started to investigate phospholes that maximized π-conjugation. Subsequently, numerous heteroatom-substituted derivatives with a σ^2,λ^3 P-center were reported, but one particular analog, 1,2-(benz)azaphospholes was noticeably absent, likely due to unusual/impractical synthetic methods. A serendipitous synthetic discovery in 2016 provided straightforward access to these highly aromatic 6π-electron (10π if the fused benzene ring is included) heterocycles. Early reactivity studies have shown that the functionalized products of these rare heterocycles have unusual structures and may find application as catalysts for hydrofunctionalization, as new types of transmetallation agents, or as reactive centers for strong bond activation.



KEYWORDS

Benzazaphospholes; aromaticity; pnictogens; phospheniums; main group

1. Introduction and background – Pre 2016

σ^3, λ^3-Phospholes,[1] a class of heterocycles containing a five-membered ring with a three-coordinate P-center were initially viewed as laboratory curiosities,[2] but have found application as ligands in transition metal chemistry,[3] as building blocks for electronic materials,[4] and as enzyme inhibitors in medicine.[5] Much of the early investigation into these heterocycles focused on aromaticity[6] since phospholes exhibited lower barriers to inversion than their saturated phospholane counterparts,[7] the P-center was pyramidal,[8] and bond length equalization in the solid state was not observed.[9] However, new synthetic avenues, particularly the Fagan-Nugent method[10] and related strategies involving the metallation of a halogenated

CONTACT Matthew F. Cain mfcain@hawaii.edu Department of Chemistry, University of Hawai'i at Mānoa, 2545 McCarthy Mall, Honolulu, HI 96822, USA

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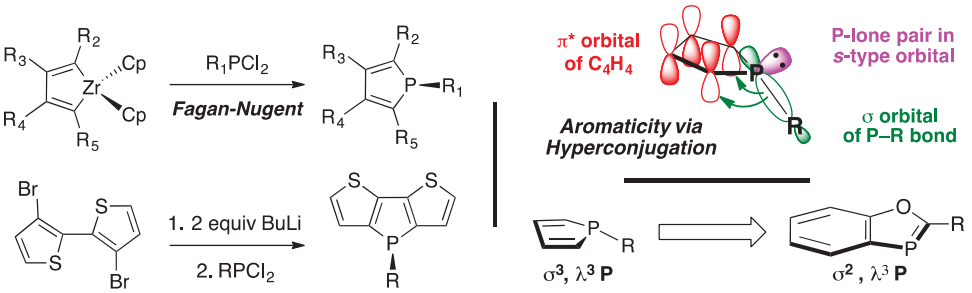
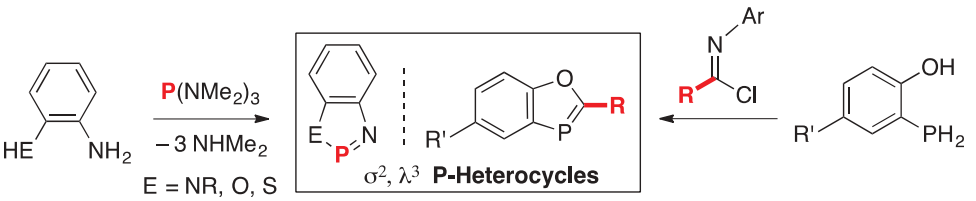
organic framework followed by quenching with readily accessible $RPCl_2$ derivatives[11] provided access to phospholes with limitless substitution patterns, resulting in a better fundamental understanding of their structure,[12] reactivity,[13] and electronic properties[14] (Scheme 1, left). Today, phospholes are generally considered to be weakly aromatic due to positive hyperconjugation between the π*-system of the butadiene unit and the σ orbital of the P–R bond (Scheme 1, upper right),[15] but depending on the substituents can range from anti-aromatic[16] to highly aromatic[17]; a recent computational paper tacked on additional complexity, suggesting that negative hyperconjugation, specifically, π (butadiene) → σ* (P–C) donation may contribute more stabilization to the heterocycle than previously assumed.[18] Motivated by developing more conjugated organic platforms for use in next-generation organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and other optical materials,[19] researchers turned to directly incorporating the P-center into π-bonds (Scheme 1, lower right). To this end, a series of σ^2,λ^3-1,3-benzoxaphospholes were synthesized and exhibited fluorescence and reversible electrochemical behavior,[20] highly desirable properties for new electronic materials.

Reports of phosphorus engaging in π-bonding are not new[21]; shortly after the initial reports of σ^3-phospholes were disclosed, countless heterocycles incorporating a σ^2, λ^3 P-center were synthesized.[22] The general synthetic strategy, also used in the preparation of 1,3-benzoxaphospholes,[20] involves employing an unsaturated 1,2-disubstituted organic building block (olefin, benzene, heteroaromatic) and anellating the five-membered ring via condensation utilizing a reagent that serves as an equivalent of P(III) or CR (Scheme 2).[23]

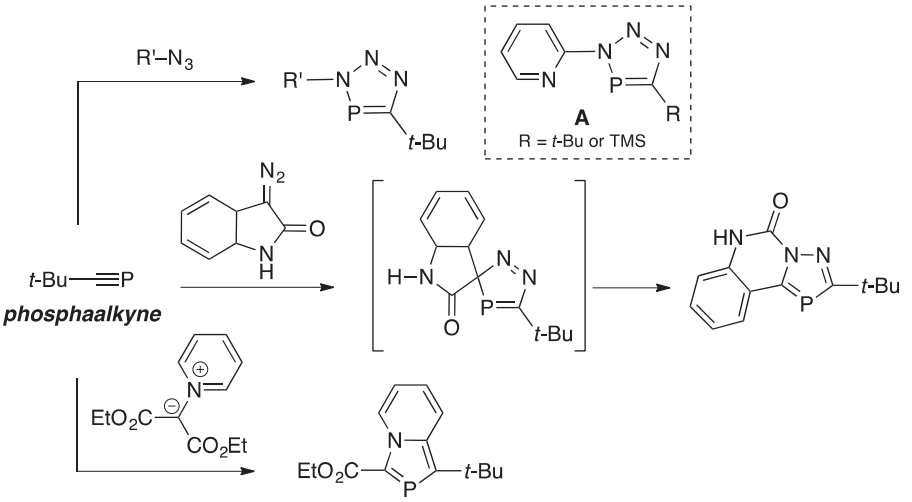
A common alternative approach is to form the phosphole-derived ring via cycloaddition.[23] Specifically, acting as dienophiles, phosphaalkynes or phosphaalkenes react with dienes or other 1,3-dipoles like diazo compounds and azomethine ylides to produce a diverse group of nitrogen-containing P-heterocycles containing a wide range of functional groups.[24] A particularly prevalent heterocycle is 1,2,3,4-triazaphospholes like **A**,[25] which are easily



Scheme 1. Synthesis and origin of aromaticity in σ^3, λ^3-Phospholes and the structure of σ^2, λ^3-heterophospholes.



Scheme 2. Synthesis of σ^2, λ^3 phosphorus-containing heterocycles via condensation.



Scheme 3. Synthesis of σ^2, λ^3 phosphorus-containing heterocycles via cycloaddition.

constructed from phosphaalkynes and readily accessible organic azides (Scheme 3).[26]

Solid-state structures of these diverse σ^2, λ^3-heterophospholes have shown that these rings are planar with bond lengths intermediate between normal single and double P–C, C–N, and C–C bonds,[27] properties consistent with aromatic molecules. However, unlike most hydrocarbon scaffolds in which all the carbon atoms are sp^2-hybridized, the phosphorus centers in these molecules are not. The angle at P generally ranges from about 88 to 100 deg,[27,28] reflecting the high *p*-character in the P–C bonds, while the lone pair is predominantly *s*[29]; some selected structural parameters of 1,3-benzazaphospholes summarized by Heinicke are highlighted in Chart 1.[27] Although "flat" molecules are often targeted for their light-emitting properties[30] and 1,3-benzoxaphospholes were known to exhibit blue fluorescence as early as 1985,[31] only recently have 1,3-azaphospholes[32] and 1,2,3,4-triazaphospholes (**A**)[25] emerged as viable candidates for numerous electronic applications, particularly as *n*-type materials.[4]

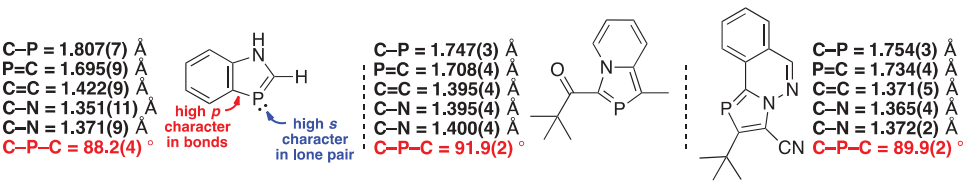
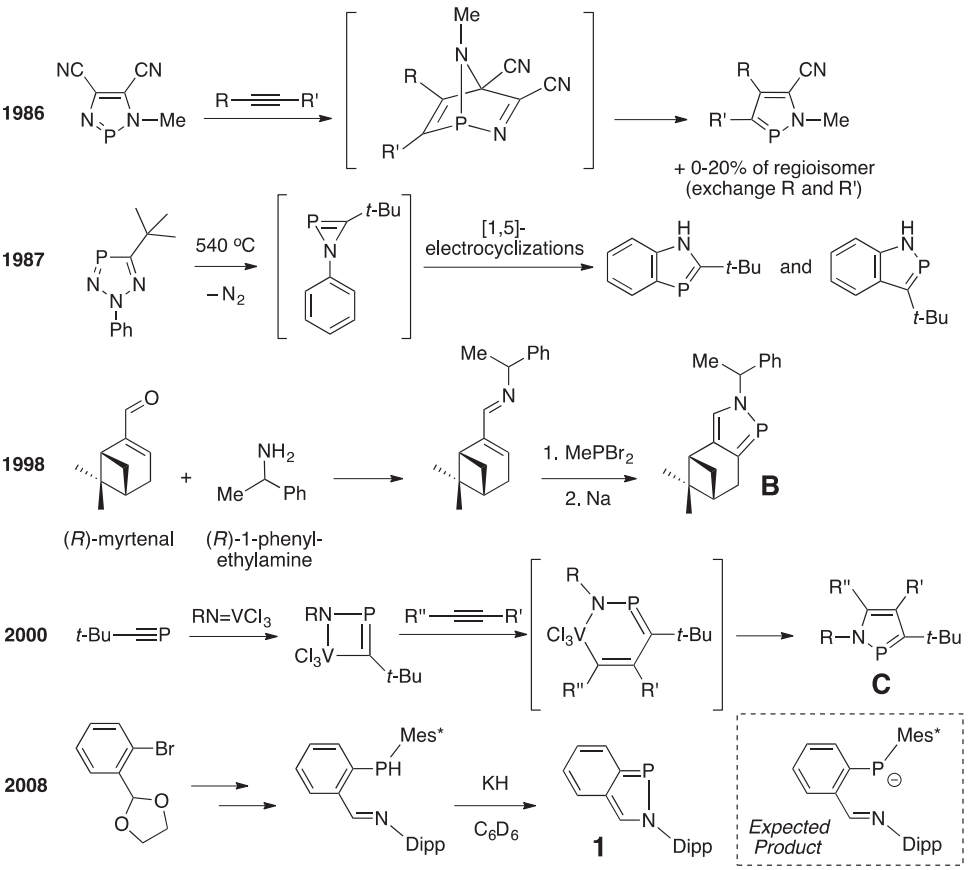


Chart 1. Selected bond lengths (Å) and angles (°) in some 1,3-benzazaphosphole derivatives.

Given the long history and potential applications of these PN heterocycles, it is surprising that the related isomeric analogs, 1,2-benzazaphospholes, the focus of this perspective, are noticeably absent in the literature. In fact, an exhaustive search of the literature revealed that only five examples of 1,2-(benz)azaphospholes were reported before 2016, likely due to their unusual/impractical syntheses. The first reported synthesis[33] relied on initially generating 4,5-dinitrile-functionalized 1,3,2-diazaphospholes (1,3,2-diazaphosphole-4,5-dicarbonitriles), followed by exposure to functionalized acetylenes, resulting in a Diels-Alder (DA) cycloadduct, which subsequently underwent a retro DA process to give 1,2-azaphospholes featuring a –CN group at the five-position. In a similar fashion, Regitz accessed well-known 1,2,3,4-triazaphospholes, then subjected two selected ones to flash vacuum pyrolysis,[34] leading to nitrogen extrusion and unselective [1,5]-electrocyclizations[35] to give a separable mixture of 1,3- and 1,2-benzazaphospholes. Alternatively, most reminiscent to our streamlined synthesis (*vide infra*), but in a highly stepwise fashion requiring difficult purifications, two chiral reagents, (–)-myrtenal and (*R*)-1-phenylethylamine were condensed to form an *E*/*Z* mixture of functionalized imines, enriched in the *E*-isomer. This product mixture was treated with $MePBr_2$ and reduced with Na, affording myrtenal-supported azaphosphole **B**.[36] Transition-metal mediated processes were also employed[37]; a [2 + 2] cycloaddition between a V(V) imido complex and a phosphaalkyne produced an intermediate metallacyclobutene that upon exposure to substituted acetylenes furnished a hydrocarbon-substituted collection of 1,2-azaphospholes (**C**). Lastly, while attempting to prepare a PN analog of a nacnac ligand,[38] Tokitoh discovered that the final deprotonation of the proligand with KH led to unexpected P–C bond cleavage and formation of benzazaphosphole **1** (Scheme 4).[39]

2. Post-2016 – Fate of Pincer-supported E(I) species

Our foray into these azaphosphole scaffolds, specifically, 1,2-benzazaphospholes was serendipitous[40] but resulted in the discovery of a convenient synthetic method.[41] Independently,[41,42] our group and the Nikonov laboratory were intrigued by a report by Dostál[43] in which hypervalent Sb(I) and Bi(I) complexes (**2** and **3**, respectively) were stabilized within an NCN pincer. A recent publication from the Cornella laboratory in which H_2



Scheme 4. Previous syntheses of 1,2-(benz)azaphospholes (Mes* = 2,4,6-tri-*tert*-butylbenzene, Dipp = 2,6-diisopropylbenzene).

was loaded onto **3** using ammonia-borane and then transferred to azobenzenes to generate hydrazines further piqued our interest.[44] Motivated to investigate similar catalytic Main Group chemistry, we were curious if a related and likely much more reactive P(I) species[45] could be supported within a similar scaffold (Chart 2).[46]

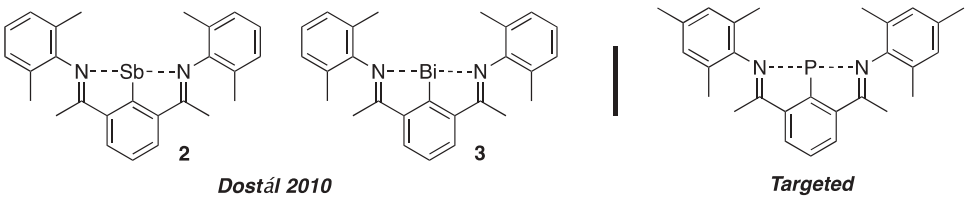
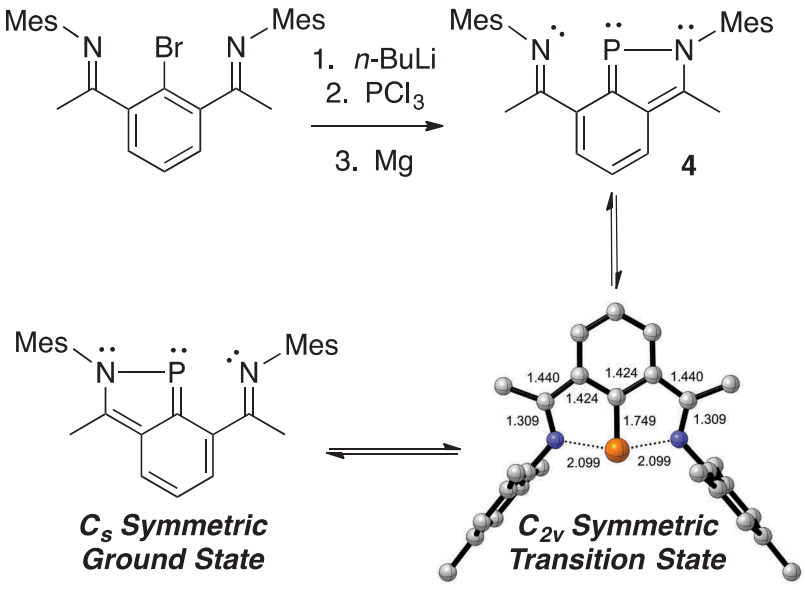


Chart 2. Isolated 10–Sb–3 and 10–Bi–3 species and a targeted P analog.

To probe this, lithiation of a brominated NCN pincer, followed by quenching with PCl_3 and reduction with Mg generated a phosphorus-containing product that displayed C_{2v} symmetry in solution by ^1H NMR spectroscopy with a single signal in the $^{31}P\{^1H\}$ NMR spectrum (δ 150.6).[40] However, the solid-state structure revealed only one nitrogen was bound to phosphorus, and the product was C_s symmetric 1,2-benzazaphosphole **4** featuring a second P—N contact at 2.676 Å. The NMR spectra were consistent with rapid bond switching via a "bell-clapper"[47] process between N_1–P_1 and P_1–N_2, proceeding through a C_{2v} symmetrical transition state that lay only 4.0 kcal/mol above the ground state and could not be frozen out by routine VT NMR spectroscopy (Scheme 5).

Careful analysis of the solid-state structure revealed the previously exocyclic sp^2-sp^2 C–C bond (1.403(4) Å) that was now part of the five-membered ring, the sp^2-sp^2 C–C bond (1.436(3) Å) at the ring junction, and the P–C bond (1.744(3) Å) were all intermediate between localized single and double bonds (Figure 1, left).[48] Furthermore, the C–N bond (1.350(4) Å) of the azaphosphole ring had lengthened considerably compared with its tethered imine counterpart (1.287(4) Å), and although the P–N bond (1.757(2) Å) was slightly longer than normal[49] with a WBI[50] value of 0.76,[41] the ring structure was planar, leading us to speculate that this 1,2-benzazaphosphole was a five-membered 6π-electron (10π if the fused benzene ring is counted) aromatic system. The analogous "bell-clapper" (**5**) reported by Nikonov exhibited similar NMR dynamics and solid-state structural characteristics (Figure 1, right).[42]



Scheme 5. Synthesis and dynamic behavior of 1,2-benzazaphosphole 4 (Mes = 2,4,6-trimethylbenzene).

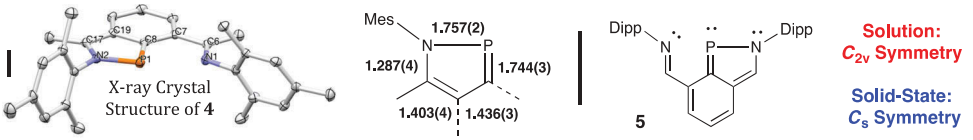
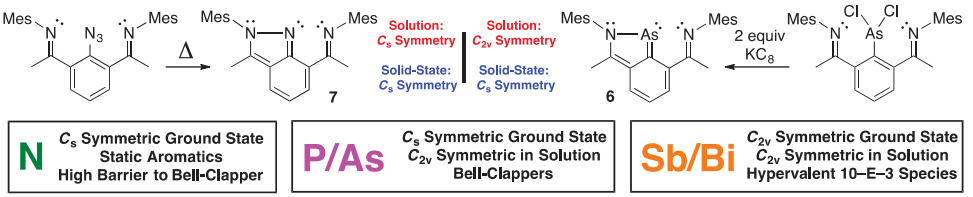


Figure 1. X-ray crystal structure of 4 with selected bond lengths of the five-membered PN ring and bell-clapper 5.



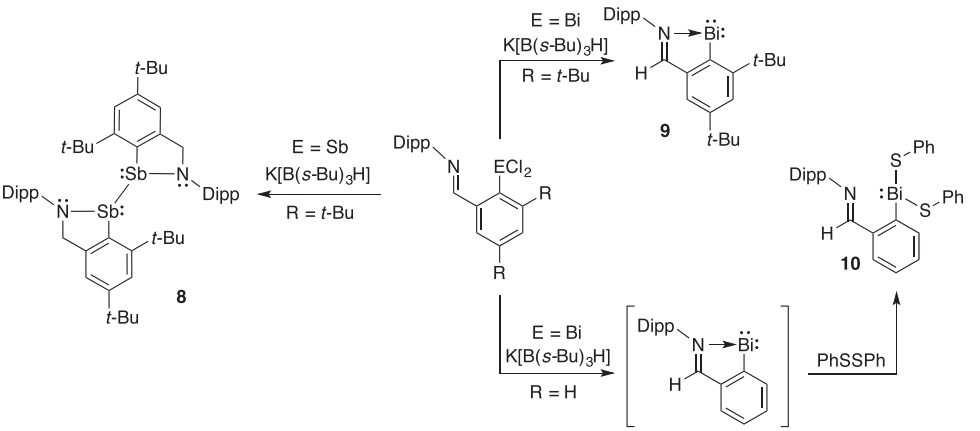
Scheme 6. Synthesis of 1,2-benzazaarsole 6 and indazole 7 and a summary of pnictinidene generation within NCN pincers.

With the fate of P(I), Sb(I), and Bi(I) species generated within analogous NCN ligands known (**4/5, 2**, and **3**),[40–43] the corresponding nitrogen and arsenic derivatives were synthesized. As predicted by DFT calculations,[40] the formation of an arseninidene within the pincer (by reduction of $LAsCl_2$, L = NCN pincer) resulted in redistribution of electron density and isolation of C_s-symmetric benzaazaarsole **6**; like its phosphorus counterpart (**4**), in solution, rapid bond switching between N_1–As_1 and As_1–N_2 was observed, resulting in an apparent C_{2v} symmetric structure (Scheme 6, right).[41,51] On the other hand, nitrogen extrusion from an NCN-supported azide formed indazole **7** (Scheme 6, left), a known aromatic heterocycle,[52] which featured a large calculated barrier to bell-clapper-type behavior (39.4 kcal/mole).[41] With the pnictogen series completed, the obvious question for the P- and As-derivatives was: is the secondary N—E contact observed in the solid state for **4** and **6** (P—N = 2.676 Å; As—N = 2.504 Å) necessary for stabilization?

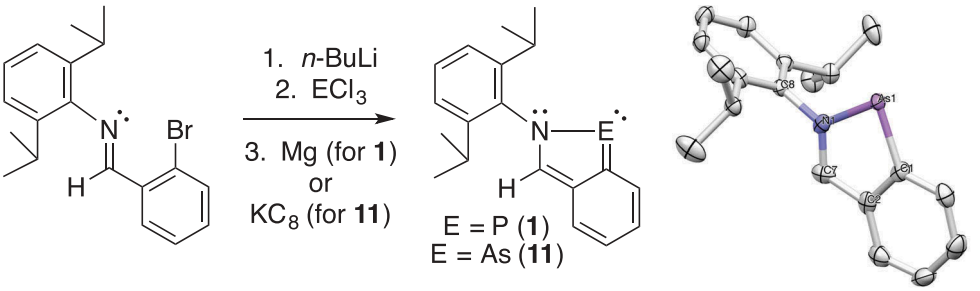
3. NC-chelated E(I) analogs

For the heavier analogs, specifically, simpler NC-chelated Sb(I) and Bi(I) complexes,[53] Dostál found that reduction of the $SbCl_2$ intermediate with [K][B(*s*-Bu)$_3$H] resulted in dimerization to **8**.[54] On the contrary, analogous Bi derivative **9** was a monomer and isolable,[55] but without the flanking *t*-Bu groups, decomposition was observed unless the generated bismuthinidene was trapped by diphenyldichalcogenides to give Bi(III) species **10** (Scheme 7).[56]

Utilizing the same *N*-Dipp substituted *o*-brominated imine scaffold, lithiation followed by quenching with PCl_3/$AsCl_3$ and reduction afforded unsupported (by steric bulk or electron donation) benzazaphosphole and -arsole scaffolds **1** and **11**



Scheme 7. Synthesis of NC-chelated derivatives 8–10 (E = Sb, Bi).



Scheme 8. Synthesis of 1,2-benzazaheteroles 1 and 11 with the X-ray structure of 11.

(Scheme 8).[41] Despite being supported by a bidentate NC chelate, generation of these E(I) species like their "bell-clapper" counterparts **4–6**, resulted in a similar redistribution of electrons within the fused ring system.

In fact, the E = C bond lengths of **1** and **4** and **11** and **6** were the same within error with subtle changes in C–N and C–C bonds observed,[41] but the most noticeable difference was in the E–N bond lengths (Figure 2, left). Unlike the bell-clapper analogs in which donation of the second nitrogen lone pair into the E–N σ* orbital weakens and elongates that bond significantly, benzazaphosphole **1** (P–N = 1.702(10) Å) and arsole **11** (As–N = 1.883(6) Å) feature E–N bonds within the normal range.[41] In addition to the stronger P/As–N bond, WBI values (Figure 2,

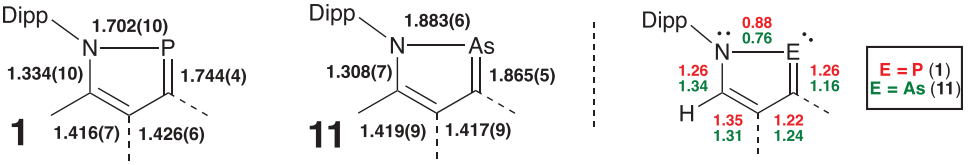


Figure 2. Selected bond lengths of 1 and 11 and their WBI values.

right) corroborated the widespread delocalization of electron density and intermediacy of single and double bonds within the five-membered rings. NICS calculations (GIAO/M06/cc-pVTZ(-PP) level)[57] confirmed that these five-membered rings are strongly aromatic. In fact, the NICS(1)$_{zz}$, the best indicator of aromaticity,[57] showed that both NC-chelated derivatives **1** (−31.9 ppm) and **11** (−29.4 ppm) are significantly more aromatic than their bell-clapper analogs **4** (−26.8 ppm) and **6** (−20.7 ppm) with their aromaticity rivaling that of known heterocycles like indazole **7** (−34.4 ppm) and benzene (−29.8 ppm). This reduced aromaticity of the bell-clappers (**4/6**) relative to their single-arm analogs (**1/11**) is likely to due decreased *s* character in the E–N bond (resulting from donation of the second N_{LP} into the E–N σ* orbital), which ultimately minimizes the amount of *p* character available for π-conjugation, leading to less significant bond length equalization compared with **1/11**.[41]

4. Reactivity of (benz)azaphospholes – Cycloadditions

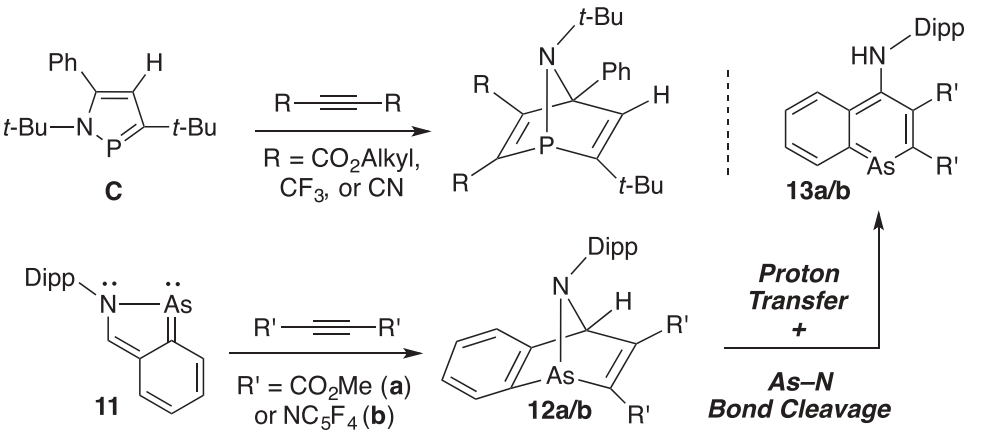
From a simplistic organic perspective, aromatics, unlike alkenes or other unsaturated molecules have a propensity to engage in substitution (sulfonation, nitration, etc.) rather than addition reactions.[58] Although the planar structure of 1,2-azaphospholes of Type **C** suggested that heterocycle was aromatic, initial reactivity studies demonstrated its reactivity was more consistent with a diene.[37] For example, exposure of **C** to electron-poor acetylenes led to Diels-Alder adducts with nitrogen at the bridge position.[37] In the presence of electron-withdrawing alkynes, benzazaarsole **11** behaves similarly undergoing a [4 + 2] cycloaddition to give bicyclic intermediates **12a/b**.[59] However, these intermediates are unstable and rearrange via CH to NH proton transfer accompanied by As–N bond cleavage/rearomatization to form extremely rare examples of 1-arsanaphthalenes (**13a/b**, Scheme 9).[60]

5. Protonation and subsequent nucleophilic substitution

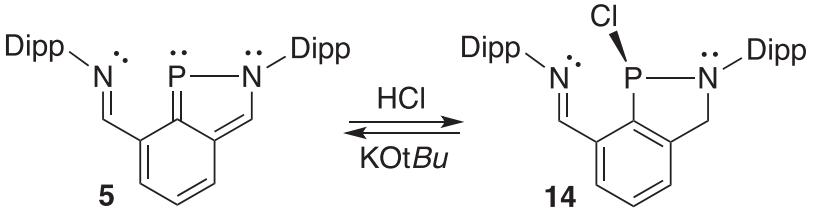
Although no reactivity studies of benzazaphosphole **1** have been reported, the Nikonov laboratory investigated the reactivity of bell-clapper **5**. Treatment of **5** with HCl afforded *P*-chloro derivative **14**, resulting in the formal dearomatization of the PN ring and rearomatization of the benzene unit (Scheme 10).[42]

At first glance (this reversible) protonation of the carbon atom adjacent to nitrogen may seem odd, but it is consistent with the structure and bonding of **5** for several reasons:

(1) The lone pair on phosphorus is not appreciably basic, containing a significant degree of *s* character (the P_{LP} in **1** is 71% *s*)[41]
(2) The nitrogen lone pair is part of the 6π-electron system and



Scheme 9. Diene-type reactivity observed for 1,2-(benz)azaheteroles.

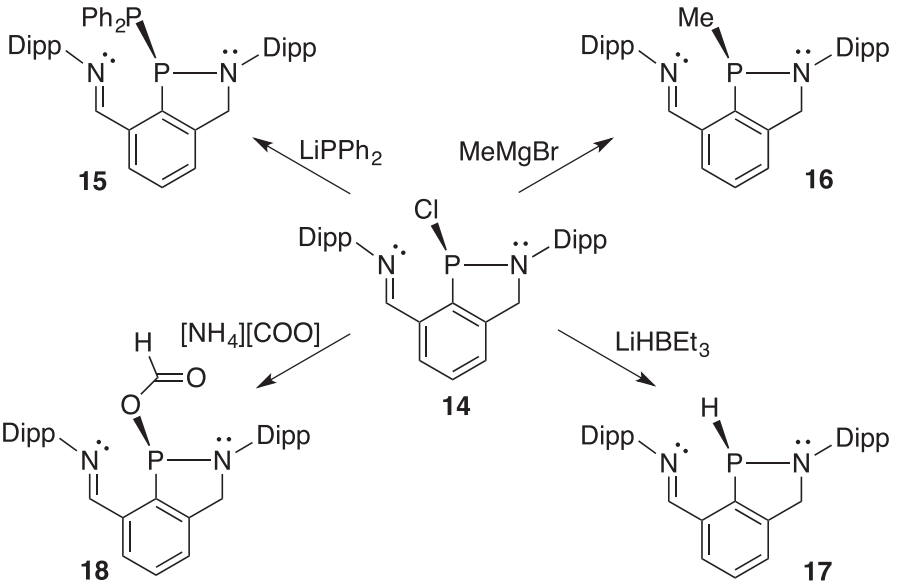


Scheme 10. Protonation of bell-clapper 5.

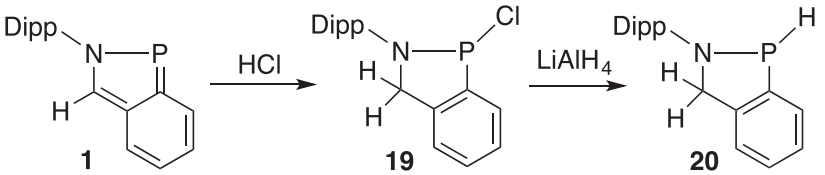
(3) Protonation at either ring junction carbon, despite the enamine-type $R_2N–CH = CR_2$ functional group in which a resonance structure can be drawn with a formal negative charge on the sp^2-hybridized Cβ atom and the polarized (δ+)P = C(δ–) bond, would destroy the aromaticity of the entire heterocyclic scaffold.

Chlorophosphine **14** serves as an excellent intermediate for substitution by reactive nucleophiles such as Ph_2P^-, Me^-, H^-, and $HCOO^-$. These novel compounds (**15–18**) were characterized by NMR spectroscopy, elemental analysis, and mass spectrometry (Scheme 11).[42]

Although currently unpublished,[61] we performed a similar proton plus hydride delivery on **1**, utilizing HCl and $LiAlH_4$ in a sequential fashion. The structure of P–Cl intermediate **19** and P–H product **20** was confirmed by X-ray crystallography, revealing that the P–Cl (2.1649(8) Å) and P–H (1.52(4) Å, J_{PH} = 150 Hz) bonds were significantly elongated (Scheme 12). Related bond elongations were observed with diazaphospholenes[62] (NHPs, *vide infra*) and originate from donation from the N_{LPs} into the σ* orbital of the P–X bond.[63] Given the N-atoms in **19** and **20** are sp^2-hybridized (Σ of angles = 359.91 and 359.86 deg, respectively), we hypothesize that a similar



Scheme 11. Nucleophilic substitution of P–Cl derivative 14.

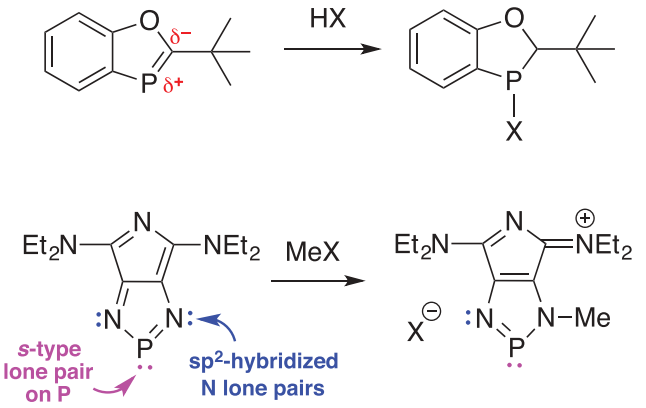


Scheme 12. Sequential H^+/H^- delivery to 1.

frontier orbital environment is present in these "singly nitrogenated" functionalized benzazaphospholes. In the **Outlook and Future Directions Section**, we will describe potential research avenues that will exploit these weak and highly polarized P–X bonds.

6. Functionalization at P by electrophiles/metallation

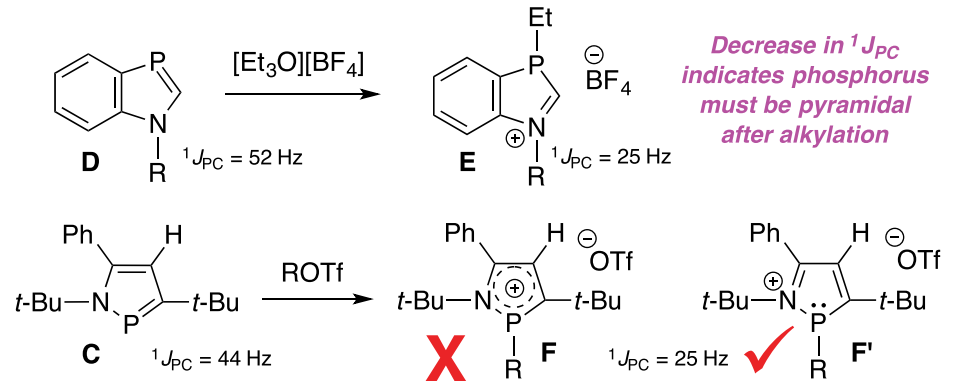
Phosphorus-based heterocycles featuring a σ^2, λ^3 P-center have polarized (δ+) P = C(δ–) bonds with a lone pair localized in a low-lying orbital (due to the high degree of *s* character[28]) and a HOMO largely centered on the P = C π bond, restricting functionalization at the P-center by electrophiles,[64] especially in the presence of a significantly more basic/nucleophilic nitrogen atom. This phenomenon was observed for 1,3-benzoxaphospholes as acids protonate at carbon with the counterion quenching the developing positive charge on phosphorus,[65] while in 1,3,2-analogues, alkylation by MeI/Me_2SO_4 occurs at the sp^2-hybridized nitrogen (Scheme 13).[23]



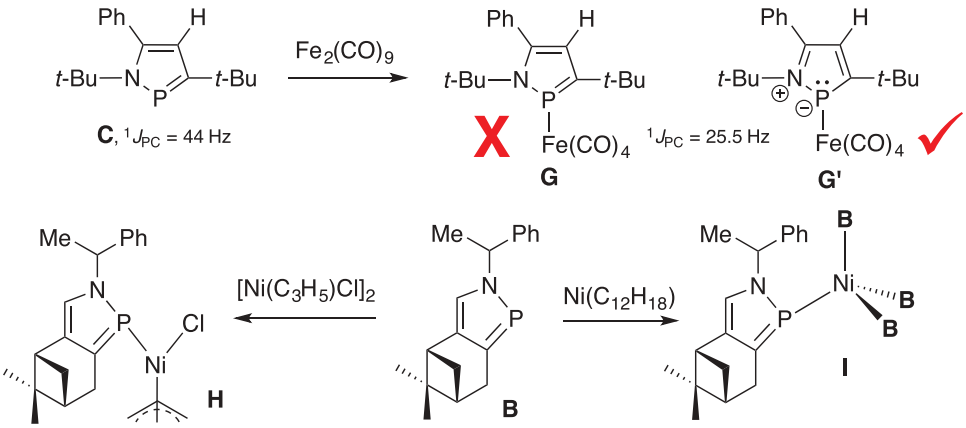
Scheme 13. Protonation and methylation of σ², λ³-heterophospholes.

However, alkylation at P of both 1,3- and 1,2-analogues can be achieved with Meerwein-type reagents[66] or alkyl trifluoromethanesulfonates.[37] For example, treatment of **D** with $[Et_3O][BF_4]$ afforded P–Et derivative **E** (Scheme 14, top)[66]; likewise, Regitz reported that P-alkylation of **C** utilizing Me- or EtOTf gave **F**.[37] Although the atom connectivity in **F** is correct, we believe that some structural subtleties were overlooked. Specifically, the product must contain a pyramidal phosphorus atom with an adjacent iminium-type center. In the free azaphosphole, the carbon atom adjacent to phosphorus features a $^1J_{PC}$ coupling constant of 44 Hz, alkylation results in a significant decrease to ~25 Hz.[37] If the P-center remained planar and therefore, sp²-hybridized (after alkylation), the increased *s* character in the bonds would result in increased $^1J_{PC}$ values.[29] The fact that the coupling constant drops considerably reflects the P-center reorganizes to a pyramidal geometry with bonds high in *p* character and an *s*-type lone pair, and therefore, the correct structure is more likely **F′** (Scheme 14, bottom). For comparison, 1,3-benzazaphosphole **D** had a $^1J_{PC}$ of 52 Hz, and alkylation gave **E** featuring a significantly reduced $^1J_{PC}$ = 25 Hz.[66]

In principle, metallation could also alter the geometry at phosphorus. Treatment of **C** with $Fe_2(CO)_9$ reportedly gave **G**,[37] but given the drastic decrease in the $^1J_{PC}$ coupling constant, we speculate complexation to Fe triggers a similar geometric rearrangement at P from planar to pyramidal affording **G′** (Scheme 15, top). Despite the apparent propensity for phosphorus to adopt a pyramidal geometry, a planar structure can be maintained. Exposure of myrtenal-derived 1,2-azaphosphole **B** to $[Ni(\eta^3\text{-}C_3H_5)Cl]_2$ or $Ni(C_{12}H_{18})$ ($C_{12}H_{18}$ = cyclododecatriene) produced two metal complexes (**H** and **I**) in which the phosphorus center remained planar, adopting sp²-hybridization as confirmed by X-ray crystallography (Scheme 15, bottom).[36] Unfortunately, ^{13}C NMR spectra were not obtained so the change in $^1J_{PC}$ could not be analyzed.

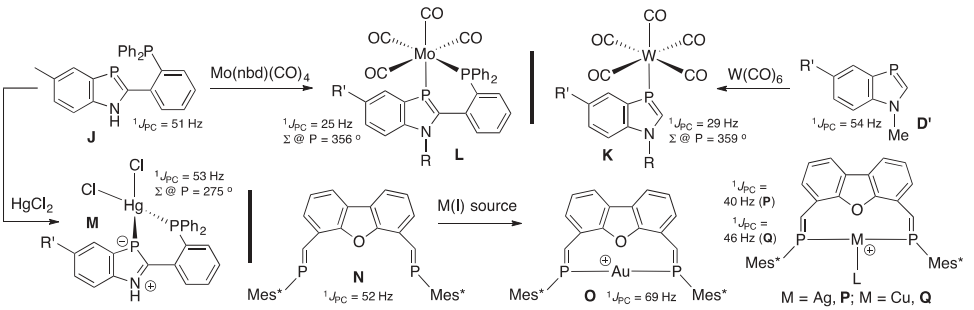


Scheme 14. Σ^2, λ^3-heterophospholes can be alkylated at P.



Scheme 15. Initial metallation studies with 1,2-azaphospholes.

Ultimately, a comment by a reviewer led to a more thorough examination of the geometry/coordination chemistry of σ^2, λ^3 P-based species and their corresponding $^1J_{PC}$ values. The reviewer questioned if analogous compounds featuring P = C bonds undergo a related geometric change on binding to the commonly employed $W(CO)_5$ fragment[67] or a Au(I) source.[68] As discussed above, if a compound featuring a σ^2, λ^3 phosphorus atom coordinates to a metal center through the P-lone pair and remains planar, phosphorus will hybridize to ~sp^2 with the expectation that the $^1J_{PC}$ will increase and the sum of the angles at phosphorus will approach 360 deg.[29] Yet, when 1,3-azaphosphole **D** (R′ = Me)[69] and its bidentate counterpart **J**[70] coordinate to W(0) and Mo(0), the corresponding metal complexes **K** and **L** feature sp^2 hybridized P-centers with reduced $^1J_{PC}$ coupling (!); at the same time, the PPh_2 unit in **J** exhibits normal behavior as its $^1J_{PC}$ values increase on binding (15 Hz in **J** to 33 Hz in **L**) as phosphorus adopts sp^3 hybridization (Scheme 16, top).[70] On the other hand, complexation of **J** to $HgCl_2$ results in a pyramidalized P donor in **M** with an unexpectedly larger $^1J_{PC}$ (!).[71]



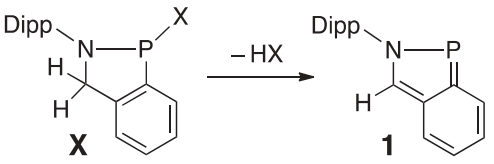
Scheme 16. Coordination chemistry of related σ^2, λ^3 phosphorus ligands and their corresponding $^1J_{PC}$ values.

Additional related and contradictory structural and NMR spectroscopic data can be extracted by analyzing the coordination chemistry of dibenzofuran-supported bis(phosphaalkene)-based ligand **N** with Cu(I), Ag(I), and Au(I) (Scheme 16, bottom).[72] In each case, binding of **N** to the d^{10} metal center gave a planarized P atom (Σ @ P ~ 360 deg); two-coordinate Au(I) complex **O** had an increased $^1J_{PC}$ (as expected for increased *s* character), while tricoordinate Ag(I) and Cu(I) species **P** (L = H_2O) and **Q** (L = CH_3CN) contained decreased $^1J_{PC}$ values (!).[72] At the moment, we are perplexed by these scattered, almost seemingly random $^1J_{PC}$ coupling constants and their relationship to the geometry at phosphorus, but speculate the origin of this behavior may be linked to both the coordination number and geometry of the transition metal complex and the ability of the σ^2, λ^3-derived P-donor to accept electron density from the metal center (backbonding). We believe as the number of transition metal complexes featuring donors with P = C bonds increases that more concrete trends and understanding of structure and bonding of these currently rare species will be established.

7. Outlook and future directions

Preliminary reactivity studies combined with the newly discovered straightforward access to these 1,2-benzazaphospholes have opened up a number of interesting potential applications. Unlike 1,3-benz(oxa/aza)phospholes, which have shown promise as new electronic materials,[20] we anticipate that functionalized derivatives of these heterocycles will enable interesting bond forming and breaking processes due to the unique structural features embedded in these molecules. For example, if we consider the generic structure **X**, which could represent **19** or **20**, several features are eye-catching:

(1) An extremely long and polarized P–X bond
(2) Acidic, benzylic-type protons and
(3) Shifting aromaticity (6π to 10π electron) back to **1**



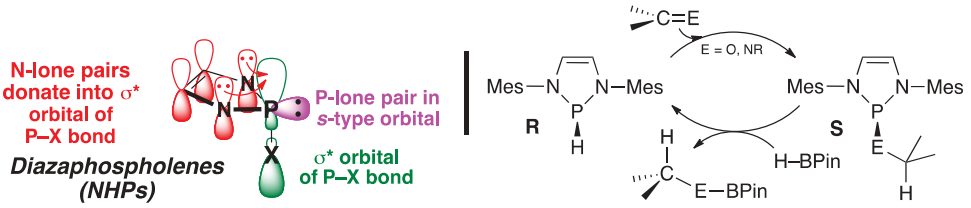
We speculate that any or all of these three features can be exploited for hydrofunctionalization processes, σ-bond metathesis/transmetallation, and bond activation by phosphenium ions.

8. Hydrofunctionalization processes

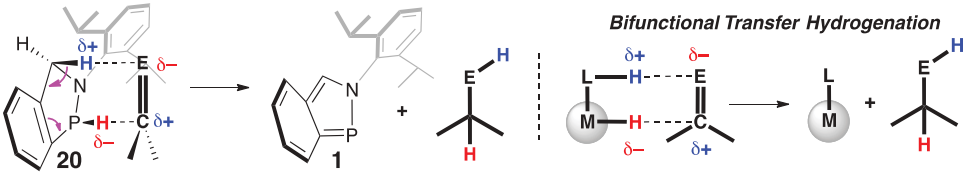
Approximately 20 years ago, Gudat published a seminal paper on diazaphospholenes or NHPs (**R**), which were five-membered C_2N_2P heterocycles with an unsaturated C–C backbone and two sp^2-hybridized nitrogen atoms adjacent to a σ^3, λ^3 P-center.[62,63] As aforementioned, the lone pairs on nitrogen donated electron-density into the σ* orbital of the P–X bond, resulting in an elongated and highly polarized bond (Scheme 17, left). In fact, if X = H, the P–H bond was no longer *acidic*, but rather *hydridic* and was able to add to carbonyls, affording functionalized derivatives (**S**, E = O) with a P–O bond.[73] Recently, Kinjo[74] and Speed (with imines)[75] demonstrated that σ-bond metathesis between insertion product **S** and H–Bpin was possible, leading to a new catalytic metal-free hydroboration process (Scheme 17, right).

Given that the O–BPin product is hydrolyzed to an alcohol on workup, a more atom efficient and practical solution would be the direct hydrogenation of carbonyls/imines. If the process shown in Scheme 12 is considered, sequential H^+ plus H^- addition to **1** is the equivalent of formally loading H_2 onto the benzazaphosphole scaffold (in Generic Structure **X**, X = H). Since the P–H bond is hydridic and the benzylic position is acidic, can an equivalent of hydrogen be delivered to a carbonyl via a bifunctional process resembling Ru-catalyzed[76] transfer hydrogenation (Scheme 18)?[77]

Clearly, HCl and LAH are incompatible in the same pot, but if any "masked" hydrogen source, such as ammonia-borane,[78] Hantzsch esters,[79] dihydrophenanthridine,[80] or diimides[81] can add an hydrogen equivalent to **1**



Scheme 17. Electronic environment and reactivity of NHPs.

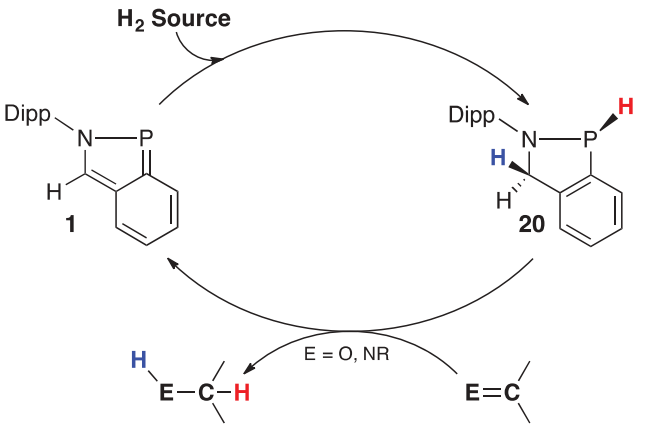


Scheme 18. Transfer hydrogenation with 20 and its transition metal precedent.

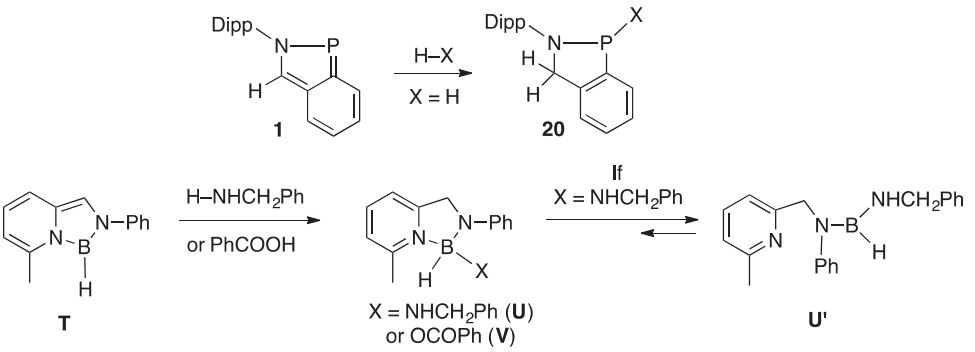
and it can be transferred by **20** to an unsaturated organic substrate, then a new metal-free transfer hydrogenation process could be realized (Scheme 19).

For now, we will restrict our discussion to transfer hydrogenation, but many H–X functionalizations such as hydroamination and hydrophosphination may be possible with these heterocycles. However, there are some unknowns/questions/obstacles that warrant consideration:

(1) Is the barrier to rearomatization too high? Bond activations driven by aromatization/dearomatization are common in TM chemistry,[82] but extending this concept to metal-free systems is much rarer.[83,84] In a system analogous to **1/20**, Milstein demonstrated 10π-electron heterocycle **T** could shuttle aromaticity back to the pyridine unit by N–H and O–H activation to give **U/U′** and **V** (Scheme 20).[83] ***The concern is: is this a dead end?*** DFT calculations showed that these bond activations were highly concerted in nature affording H–X functionalized products that were significantly thermodynamically downhill relative to their starting point. Therefore, any process that released H–X (in a concerted fashion) would have to climb a significant activation barrier to re-generate the starting 10π electron system. In fact, no transfer of H–X to an organic substrate or "dehydrofunctionalization" of **U/U′** or **V** has been reported, suggesting that this may be the limiting factor.



Scheme 19. Hypothetical transfer hydrogenation catalyzed by 1.

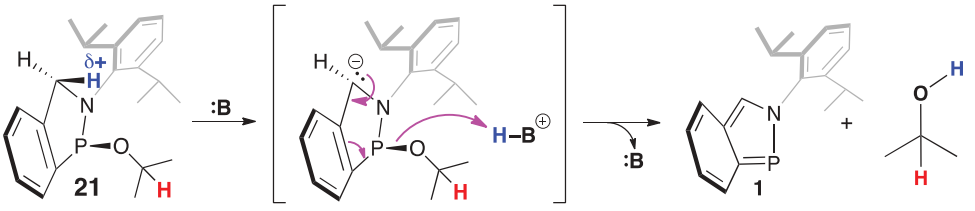


Scheme 20. HX-functionalization of 1 and T.

(2) If transfer hydrogenation occurs in a stepwise fashion, a likely first step is insertion of the P–H bond into an unsaturated organic functionality. Considering carbonyls as a model substrate, the resulting intermediate would be a P–O derivative of Type **21**, similar to those reported by Gudat,[62,63,73] Kinjo,[74] and Speed.[75] The most desirable carbonyl would **both** rapidly insert and be basic enough to deprotonate the benzylic proton; the problem is carbonyls that are likely to undergo facile insertion are electron-deficient (example: trifluoroacetophenone) and therefore, the resulting P–O intermediate would then be weakly basic and unable to intramolecularly deprotonate the benzylic arm. T*he question then is: is there an external base that can assist in the proton transfer event (Scheme 21)?* Depending on the exact pKa of the benzylic position: bases such as proton sponge, KO*t*Bu, Verkade's base, etc., could be used to shuttle the proton to the P–O unit assisting in the eventual rearomatization of the heterocyclic scaffold and turning over of a catalytic cycle like in Scheme 19.

9. R^- transfer/σ-bond metathesis

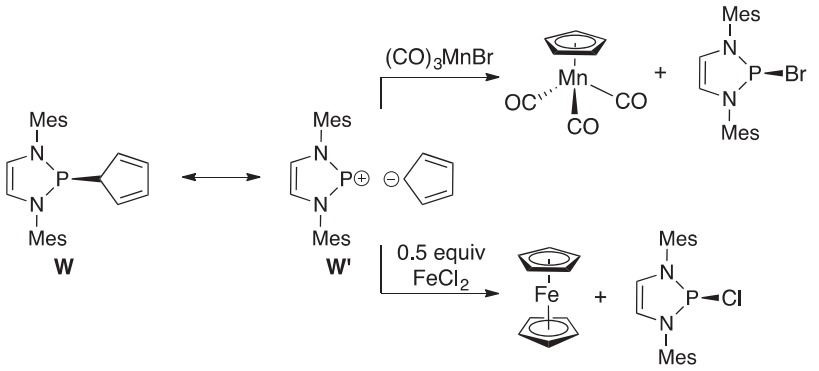
Reactions that proceed via σ-bond metathesis like the hydroborations discussed above, have significantly more precedent than reactions driven by



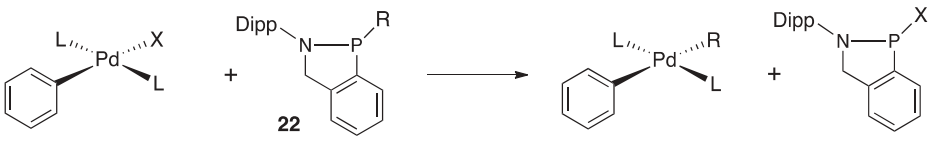
Scheme 21. Base-assisted transfer hydrogenation.

shifting aromaticity.[83,84] By taking advantage of the enhanced stability of phosphenium (PR_2^+) ions in the presence of adjacent π-donors (like sp^2-hybridized nitrogen donors)[85] and delocalized carbanions, Gudat demonstrated that P–Cp/M–Halogen (M = Mn, Fe) σ-bond metathesis,[86] reactivity consistent with "bond/no-bond" resonance structure **W′** could be promoted with NHPs (Scheme 22).

1,2-Benzazaphosphole scaffolds like **22** (R = hydrocarbyl group) feature a similar structural skeleton to the NHP platform, specifically, an adjacent sp^2-hybridized nitrogen donor and elongated P–R bonds, and although the importance of transferring Cp^- with NHPs is limited, the installation of carbon-based groups on metal centers is a central focus in chemistry. Pd-catalyzed cross-coupling,[87] arguably the most important method of forming C–C bonds, has evolved to such an extent that most of the problems with oxidative addition[88] and reductive elimination[89] have been solved through ligand design. Now, the most difficult step is often transmetallation,[90] the metathesis-esque process by which the second hydrocarbyl functionality is installed on Pd. If benzazaphosphole scaffolds like **22** featuring exocyclic P–R bonds, in which R is a stabilized carbanion like Cp, Ph, or CCPh can be accessed,[91] can these P–R units undergo σ-bond metathesis with Pd-Halogen species? A potential model reaction of study is shown in Scheme 23. If successful, this would lead to the possibility of developing new phosphorus-based transmetallating agents.



Scheme 22. Reactions driven by σ-bond metathesis using NHPs.



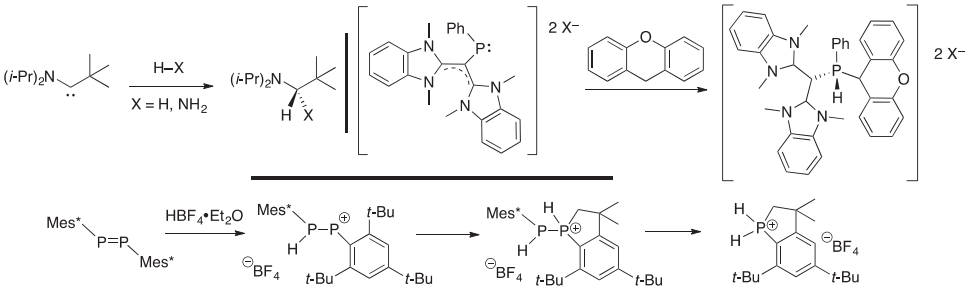
Scheme 23. A model reaction for transmetallation with P-based reagent 22.

10. Strong bond activation with phosphenium ions

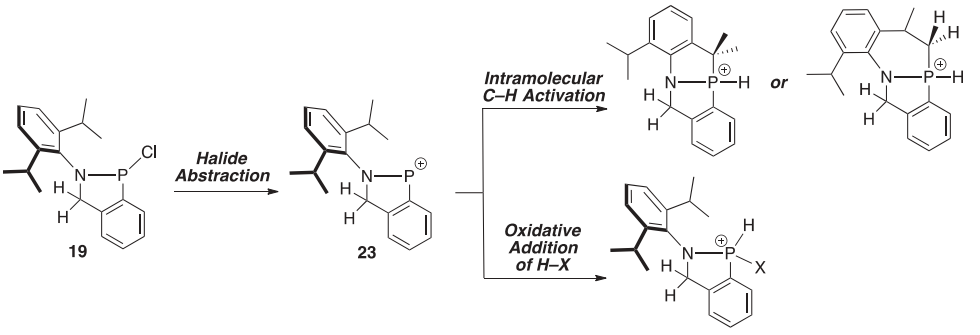
Phosphenium ions, heavier cationic analogs of carbenes, are singlets with a filled low-lying *s*-orbital and a vacant *p*-type orbital.[85] This frontier orbital environment possesses donor-acceptor capabilities analogous to transition metal centers that permit oxidative addition of small molecules.[92] In fact, certain carbenes can promote H_2 and NH_3 activation (Scheme 24, left),[93] while phospheniums ions can intramolecularly activate strong C–H bonds[94] (Scheme 24, bottom panel) and cleave weakened C–H bonds in a intermolecular fashion (Scheme 24, right).[95,96]

Halide abstraction from **19** will generate phosphenium **23**, permitting a gauge of both its inherent stability and reactivity toward strong bonds. Phosphenium ions usually have a significantly downfield shifted ^{31}P NMR signal[85] so its stability in solution should be readily apparent; however, there are C–H bonds in close proximity that could be activated to form five- or six-membered rings. If **23** is persistent, the oxidative addition of small molecules could be readily tested (Scheme 25).

These potential applications represent only a few possible avenues of exploration for 1,2-benzazaphospholes and their functionalized derivatives. We anticipate that this once under-recognized class of heterocycles will greatly increase in popularity in the near future.



Scheme 24. Known examples of strong bond activation by carbenes and phosphenium ions.



Scheme 25. Potential reactivity with targeted phosphenium ion 23.

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Declaration of interest statement

The authors declare no competing financial interest.

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