

Introducing *N*-Heterocyclic Iminophosphoranes (NHIPs): Synthesis by [3+2] Cycloaddition of Azophosphines with Alkynes and Reactivity Studies

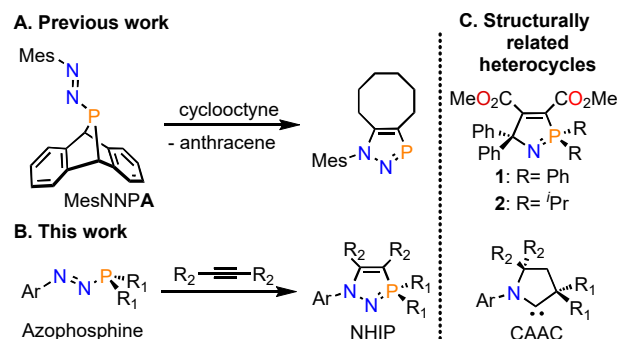
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Abstract: Azophosphines (Ar-N=N-PR_2) were prepared from *N*-aryl-*N'*-trimethylsilyldiazenes (Ar-N=N-SiMe_3) and R_2PCl by Me_3SiCl elimination or oxidation of phosphinohydrazines (Ar-NH-NH-PR_2) by 2,5-dialkyl-1,4-benzoquinones (2,5-dialkylBQ). Azophosphines underwent 1,3-dipolar cycloaddition with cyclooctyne and dimethylacetylene dicarboxylate (DMAD) to give *N*-heterocyclic iminophosphoranes (NHIPs), which are structurally similar to cyclic alkyl amino carbenes (CAACs). The cycloaddition reaction is compatible with various P-atom substituents including phenyl (**NHIP-1,4,6**), isopropyl (**NHIP-2**), cyclohexyl (**NHIP-3**) and dimethylamino (**NHIP-5**) groups. The $\text{p}K_{\text{BH}^+}$ values of the NHIPs in acetonitrile range from 13.13 to 23.14. Based on the Huynh electronic parameter (HEP), **NHIP-1** and **NHIP-2** have comparable σ -donor strength with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). **NHIP-1** underwent facile 1,2-addition with pentafluoropyridine to form a rare fluorophosphorane. The treatment of **NHIP-1** with triphenylsilane resulted in P–N bond cleavage, accompanied by reduction of P(V) to P(III). A homoleptic, cationic copper(I)-**NHIP-1** complex was also prepared. The potential utility of π -donating NHIPs was demonstrated by the stabilization of a reactive iminoborane ($\text{Cl-B}\equiv\text{N-SiMe}_3$). The facile scalable synthesis, tunability of steric demands, and basicity of NHIPs suggest that this new heterocycle class may find a wide range of applications in synthetic chemistry.

Iminophosphoranes ($\text{R}_3\text{P=NR}$) are not only versatile intermediates for functional group manipulations,^{1–4} but also used as ligands^{5–7} and organocatalysts⁸ due to the basic nitrogen center, which can be rationalized by the resonance structures ($\text{R}_3\text{P=NR} \leftrightarrow \text{R}_3\text{P}^+-\text{N}^-\text{R}$).^{9,10} Cyclic iminophosphoranes,¹¹ where all the substituents are bonded to phosphorus atoms through nitrogen atoms, have been prepared by condensing amines with PCl_5 and subsequent deprotonation. The rigid cyclic structure enabled selective anion recognition via hydrogen-bonding, which was essential for achieving high enantioselectivity.^{12–15} A rigid cyclic structure is also advantageous for the stabilization of reactive main group or metal species by preventing decomposition by steric shielding. In this context, cyclic iminophosphoranes (**1,2**; Scheme 1C), having geminal aromatic substitutions α to the basic nitrogen, were prepared by 1,3-dipolar cycloaddition of phosphinoimine ($\text{Ph}_2\text{C=N-PR}_2$) and DMAD.^{16–18} The resulting cyclic iminophosphorane **1** was used as a ligand for Au(I),¹⁹ but further reactivity studies have not been pursued presumably because of the extreme steric crowding at the basic nitrogen atom. Recently, cycloaddition of



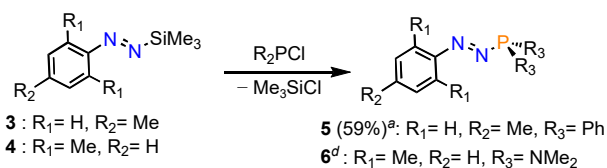
Scheme 1. 1,3-dipolar cycloaddition of azophosphine and alkynes. NHIP = *N*-heterocyclic iminophosphorane.

MesNNPA (**A** = anthracene) and cyclooctyne was disclosed, where a nucleophilic phosphorus center and an electrophilic N=N π^* component enabled MesNNPA to react as a 1,3-dipole (Scheme 1A).²⁰ This result motivated us to investigate the cycloaddition reaction of alkynes and azophosphines which do not have an anthracene leaving group (Scheme 1B). This cycloaddition reaction provides a new class of heterocycles, *N*-heterocyclic iminophosphoranes (NHIPs), which are structurally similar to CAACs (Scheme 1C).^{21,22} The less sterically blocked basic nitrogen center and enhanced stability due to the more delocalized π electrons involving an additional nitrogen atom in the ring system lead to the expectation that the new heterocycles could find a wide range of applications. Here, we describe new protocols for the synthesis of azophosphines and their cycloaddition reactivity with alkynes. The basicity, electronic properties, reactivity, and coordination chemistry of the resulting NHIPs are also investigated.

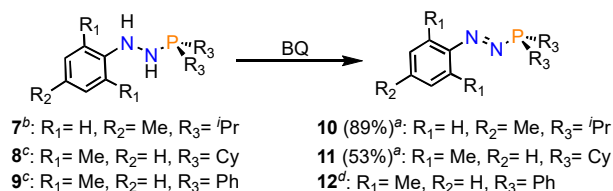
Our investigation began with the synthesis of azophosphines. Azophosphines, having a general formula of $\text{R-N=N-PR}'_2$ have scarcely been mentioned in the literature.^{23–25} Although detailed synthetic protocols for azophosphines are unavailable, the reaction of Ph_2PCl with Ph-N=N-SiMe_3 in DCM at -30°C (5 h) is reported to give Ph-N=N-PPh_2 as a red solid in 30% yield.²³ Thus we decided to try similar reaction conditions for preparing azophosphines.

The reaction of Tol-N=N-SiMe_3 ²⁶ with Ph_2PCl in pentane at 21°C under atmospheric pressure gave a mixture of products;²⁷ however, when the same reaction was repeated under vacuum (1 Torr), the reaction mixture solidified within 10 min to afford the desired product in moderate purity based on the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The crude azophosphine was purified by crystallization from diethyl ether/pentane at -20°C to afford **5**, as a red solid, in 59%

A. Me₃SiCl elimination route



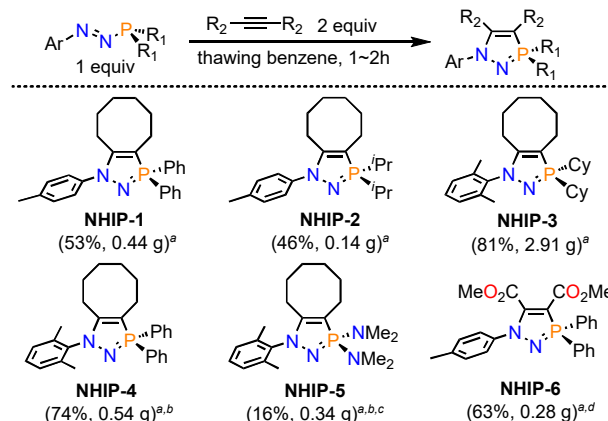
B. oxidation route



Scheme 2. Preparation of azophosphines. Reaction conditions for Me₃SiCl elimination route (**A**): azophosphine (1 equiv), R₂PCl (1 equiv), neat, −20 °C to 21 °C. Reaction conditions for oxidation route (**B**): phosphinohydrazine (1 equiv), BQ (1 equiv), benzene, 21 °C, 1 h. ^aisolated yield. ^b2,5-di-*tert*-butylBQ was used. ^c2,5-dimethylBQ was used. ^dthe product could not be purified.

yield (2.7 g, Scheme 2A). Using the same protocol, **6** was generated. However, attempts to purify this compound via crystallization were unsuccessful and, as a result, the crude material was used in the next step without further purification. However, this Me₃SiCl elimination route was not applicable to sterically hindered chlorophosphines, including *i*Pr₂PCl.²⁸ Indeed, the P-atom substituents in reported azophosphines are limited to methyl and phenyl groups.^{23–25}

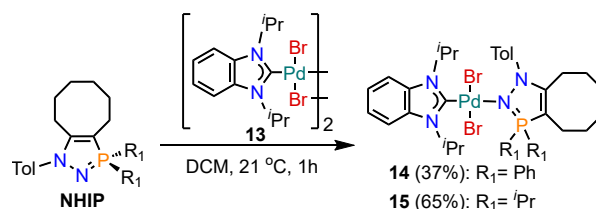
To access a wider range of azophosphines, we targeted selective oxidation of phosphinohydrazines (Ar–NH–NH–P^{*i*}Pr₂, Scheme 2B). Given that Me–NH–NH–P^{*i*}Pr₂ has been prepared using *i*Pr₂PCl,²⁹ N–P bond formation appears to be less sensitive to steric hindrance. Inspired by a recent study on oxidation of Ar–NH–NH–SiR₃ to Ar–N=N–SiR₃,²⁶ we screened several oxidants, including di-*tert*-butylazodicarboxylate (DBAD) and BQ derivatives. A major challenge of this targeted route is posed by the potential side reactions of electron-rich and nucleophilic phosphorus centers with oxidants. Indeed, the reactivity of PPh₃ towards select oxidants has been well studied. For example, DBAD is known to react with PPh₃ to form a betaine, a key intermediate for the Mitsunobu reaction.³⁰ Also, in benzene, *p*-chloranil forms P–O bonds with PPh₃ via cationic phosphorus radicals, which are formed by single electron transfer between *p*-chloranil and PPh₃.^{31–33} By contrast, non-substituted BQ, a weaker oxidant than *p*-chloranil in benzene, resulted in the formation of a P–C bond with PPh₃ by conjugate addition.³³ Bearing in mind these facts, oxidation conditions were screened using **7** as the model substrate. Of all the oxidants screened, 2,5-dimethylBQ and 2,5-di-*tert*-butylBQ showed the best results, where only product and starting material were observed in the crude reaction mixtures with good conversions (~70%) based on ³¹P{¹H} NMR spectra.³⁴ Encouraged by these results, 2,5-di-*tert*-butylBQ was chosen for further screening of the reaction conditions, as *tert*-butyl substituents should more effectively suppress side reactions relative to methyl substituents. To our delight, phosphinohydrazine **7** fully converted to azophosphine **10** using more concentrated reaction media, and the product was easily purified by silica gel column chromatography to afford a red oil in 89% (0.21 g) isolated yield. Although less sterically hindered 2,5-dimethylBQ had to be used, the same protocol afforded **11** in 53% (0.44 g) yield as a dark-



Scheme 3. Scope of 1,3-dipolar cycloaddition. Reaction conditions: Azophosphine (1 equiv), cyclooctyne (2 equiv), thawing benzene, 1 or 2 h. ^aisolated yield. ^bcrude azophosphine was used. ^coverall yield from Ar–N=N–SiMe₃. ^dDMAD (1 equiv) was used.

orange solid. The reaction also worked for the preparation of **12**; however, a small amount of unreacted starting material **9** and a side product (2,6-Me₂C₆H₃)PPh₂ could not be removed.³⁵ Given that BQ with various substitution patterns have been synthesized, the yield could be further improved by choosing proper substituents for optimal reduction potential and steric protection.³⁶

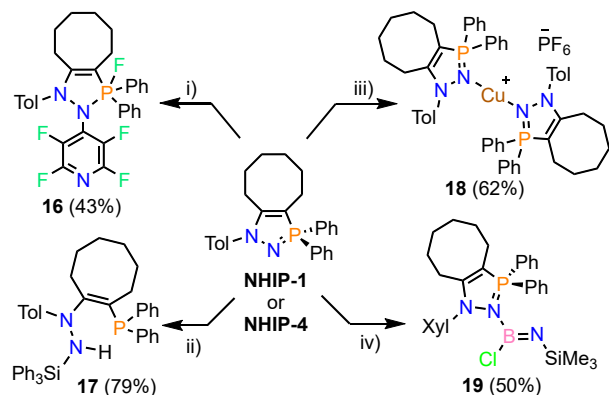
With azophosphines in hand, 1,3-dipolar cycloaddition was investigated (Scheme 3). Addition of cyclooctyne to a thawing solution of azophosphine **5** in benzene resulted in a color change from deep red to orange. The crude material was purified by crystallization from DCM/diethyl ether at −20 °C to afford orange crystals (**NHIP-1**³⁷) in 53% yield. As expected, crystallographic analysis revealed a 5-membered heterocycle, with all the ring atoms in the same plane. The cycloaddition was not sensitive to the steric demands of our azophosphines and **NHIP-2** and **NHIP-3** were obtained as white solids. The crystalline nature of NHIPs allowed us to use crude azophosphines for the synthesis of **NHIP-4** and **NHIP-5**,³⁸ which were purified by crystallization to give orange and pale yellow crystals, respectively. DMAD was also a good dipolarophile, giving **NHIP-6**³⁹ as a yellow solid.⁴⁰ Structural comparison between **1** (Scheme 1C) and **NHIP-6** revealed that the C=C (1.400(2) Å) and P=N (1.6326(15) Å) bonds of NHIP are longer than the C=C (1.331(2) Å) and P=N (1.5749(15) Å) bonds of **1**, a finding consistent with the more delocalized nature of the 6π system of NHIP than the 4π system of **1** and the smaller atomic radius of nitrogen as compared with carbon.⁴¹ The p*K*_{BH+} values for **NHIP-2**, **NHIP-4**, **NHIP-5**, and **NHIP-6** in MeCN were determined to be 23.14, 19.86, 22.02, and 13.13 respectively.^{42–44}



Scheme 4. Preparation of Pd-complexes for HEP analysis. Reaction conditions: NHIP (2 equiv), **13** (1 equiv), DCM, 21 °C, 1 h.

Next, we investigated the σ-donor strength of the NHIPs, using Huynh electronic parameter (HEP) analysis, which

covers a wide variety of σ donors including labile ligands such as pyridines and acetonitrile.^{45,46} For the HEP analysis, the target palladium complex **14** was prepared by combining **NHIP-1** with **13** in DCM⁴⁷ (Scheme 4),⁴⁷ and crystal structure analysis revealed that **NHIP-1** binds *trans* to the carbene ligand.⁴⁸ The $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shift of the carbene carbon is 166.33 ppm, suggesting that the NHIP's σ -donor strength is comparable with that of DBU, whose Pd-complex's carbene carbon $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shift is 166.32 ppm.⁴⁵



Scheme 5. Functionalization of NHIPs. Reaction conditions: (i): **NHIP-1** (1 equiv), pentafluoropyridine (2 equiv), THF, 21 °C, 1 h; (ii): **NHIP-1** (1 equiv), Ph_3SiH (1 equiv), benzene, 80 °C, 14 h; (iii): **NHIP-1** (2 equiv), $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ (1 equiv), THF, 21 °C, 30 min; (iv): **NHIP-4** (1 equiv), $(\text{Me}_3\text{Si})_2\text{NBCl}_2$ (1.05 equiv), benzene, 21 °C, 4 h.

Finally, reactivity of NHIPs with common organic synthesis reagents was investigated. When a THF solution of **NHIP-1** was combined with pentafluoropyridine, the orange color of NHIP dissipated. $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of the crude reaction mixture showed complete consumption of NHIP and clean conversion to **16**, which exhibits a resonance at δ -34.76 ($^1J_{\text{PF}} = 618.7$ Hz) ppm. The crystal structure revealed pyramidal nitrogen N2 and trigonal bipyramidal geometry at phosphorus.⁴⁹ A P-F bond length of 1.6785(7) Å was found, consistent with those of recently reported fluorophosphoranes.^{50,51}

Next we investigated the reactivity of **NHIP-1** with Ph_3SiH . Complete consumption of the **NHIP-1** and a single new resonance at δ -10.58 ppm was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum upon heating **NHIP-1** and Ph_3SiH in benzene at 80 °C for 14 h. Crystallographic analysis revealed selective P-N bond cleavage and reduction of P(V) to P(III).⁵²

Inspired by recently developed cationic iminophosphorane-ligated copper complexes for catalytic azide-alkyne cycloaddition,⁵³ corresponding NHIP-ligated copper complexes were targeted. The target product was easily prepared by treating **NHIP-1** with $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ in THF. Crystallographic analysis revealed a cationic, homoleptic copper complex, in which the Cu-N bond length (1.8544(13) Å) is comparable to those reported for copper iminophosphorane complexes (1.865(4) to 1.8902(18) Å),⁵³ indicating the potential catalytic activity of **18** for azide-alkyne cycloaddition.

As NHIPs are both σ and π donating due to the filled p orbital, we wondered whether NHIPs may be used to stabilize low-coordinate boron centers via π donation into the empty p orbital of boron. The resulting NHIP adducts should exhibit markedly different structural properties from corre-

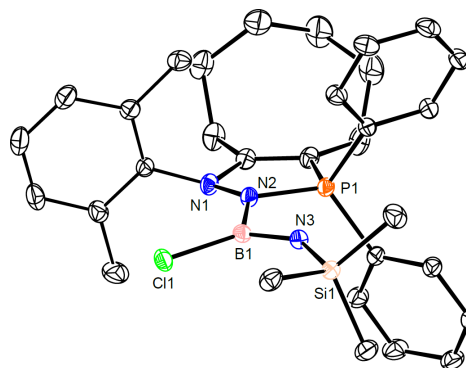


Figure 1. Solid-state structure of **19** drawn using 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Select bond lengths (Å): B1-N2, 1.477(2); B1-N3, 1.346(2).

sponding compounds stabilized by CAACs, which are only σ donors due to the empty p orbitals at the coordinating carbon center. To compare the structures of NHIP- and CAAC-stabilized boron species, $\text{Cl-B}\equiv\text{N-SiMe}_3$, whose CAAC-adduct has been prepared,⁵⁴ was targeted. When **NHIP-4** was treated with $(\text{Me}_3\text{Si})_2\text{NBCl}_2$ in benzene, a new resonance at δ 21.7 ppm was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. ^1H NMR analysis showed the loss of one - SiMe_3 group, and a new resonance at δ 21.1 ppm in the ^{11}B NMR spectrum was observed, indicating the formation of a 3-coordinate boron center. Single crystal X-ray diffraction revealed that the NHIP's ring and B=N bond are nearly in the same plane (torsion angle = 8.83°) due to the NHIP's π donation, while the corresponding CAAC-adduct showed that B=N and CAAC's ring are perpendicular to each other (torsion angle = 106.4°),^{54,55} as expected.

In conclusion, scarcely known azophosphine compounds have been prepared and shown to act as facile 1,3-dipoles for cycloaddition reactions with activated alkynes. The resulting NHIPs represent a robust and modular new class of strongly basic heterocycles with potential applications as ligands in d- and p-block element chemistry and catalysis.

Acknowledgments

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Supplementary Information

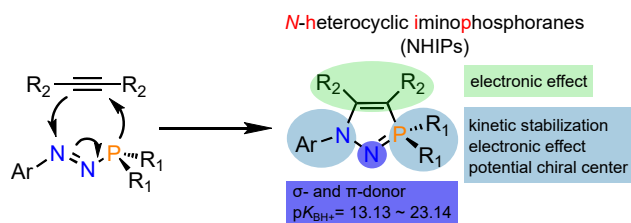
Crystallographic data are available from the Cambridge Structural Database under refcodes 2158532, 2158533, 2158534, 2158543, 2158542, 2158544, 2158545, 2158965, 2159472, and 2159100. Experimental details, characterization data, and computational details are provided in the Supporting Information document. Coordinates of optimized structures are provided in the xyz file format.

References

- (1) Köhn, M.; Breinbauer, R. The Staudinger Ligation-A Gift to Chemical Biology. *Angew. Chem. Int. Ed.* **2004**, *43*, 3106–3116.
- (2) Steiner, A.; Zacchini, S.; Richards, P. I. Iminophosphoranes: Useful Building Blocks for the Preparation of Nitrogen-Containing Heterocycles. *Synthesis* **1994**, *12*, 1197–1218.

- (3) Wamhoff, H.; Richardt, G.; Stölben, S. Iminophosphoranes: Versatile Tools in Heterocyclic Synthesis. *Adv. Heterocycl. Chem.* **1995**, *64*, 159–249.
- (4) Fresneda, P. M.; Molina, P. Application of Iminophosphorane-Based Methodologies for the Synthesis of Natural Products. *Synlett* **2004**, *1*, 1–17.
- (5) García-Álvarez, J.; García-Garrido, S. E.; Cadierno, V. Iminophosphorane-phosphines: Versatile ligands for homogeneous catalysis. *J. Organomet. Chem.* **2014**, *751*, 792–808.
- (6) García-Garrido, S. E.; Soto, A. S.; García-Álvarez, J. Iminophosphoranes ($R_3P=NR'$): From terminal to multidentate ligands in organometallic chemistry. *Adv. Organomet. Chem.* **2022**, *77*, 105–168.
- (7) Steiner, A.; Zacchini, S.; Richards, P. I. From neutral iminophosphoranes to multianionic phosphazenes. The coordination chemistry of imino-aza-P(V) ligands. *Coord. Chem. Rev.* **2002**, *227*, 193–216.
- (8) Núñez, M. G.; Farley, A. J. M.; Dixon, D. J. Bifunctional Iminophosphorane Organocatalysts for Enantioselective Synthesis: Application to the Ketimine Nitro-Mannich Reaction. *J. Am. Chem. Soc.* **2013**, *135*, 16348–16351.
- (9) Ishikawa, T. Superbases for Organic Synthesis: Guanidines, Amidines, Phosphazenes and Related Organocatalysts. *John Wiley & Sons, Ltd* **2009**.
- (10) Puleo, T. R.; Sujansky, S. J.; Wright, S. E.; Bandar, J. S. Organic Superbases in Recent Synthetic Methodology Research. *Chem. Eur. J.* **2021**, *27*, 4216–4229.
- (11) Sleiman, H. F.; Mercer, S.; McElwee-White, L. Synthesis and Reactivity of Cyclic 6-Membered Six- π - and Four-Membered Four- π Electron Ylides. *J. Am. Chem. Soc.* **1994**, *116*, 8087–8094.
- (12) Uraguchi, S.; Sakai, O.; Ooi, T. Chiral Tetraaminophosphonium Salt-Mediated Asymmetric Direct Henry Reaction. *J. Am. Chem. Soc.* **2007**, *129*, 12392–12393.
- (13) Krawczyk, H.; Dziegielewska, M.; Deredas, D.; Albrecht, A.; Albrecht, L. Chiral Iminophosphoranes-An Emerging Class of Superbase Organocatalysts. *Chem. Eur. J.* **2015**, *21*, 10268–10277.
- (14) Weitkamp, R. F.; Neumann, B.; Stämmler, H.-G.; Hoge, B. Phosphorus-Containing Superbases: Recent Progress in the Chemistry of Electron-Abundant Phosphines and Phosphazenes. *Chem. Eur. J.* **2021**, *27*, 10807–10825.
- (15) Wang, Y.-H.; Cao, Z.-H.; Li, Q.-H.; Lin, G.-Q.; Zhou, J.; Tian, P. Activating Pronucleophiles with High pK_a Values: Chiral Organo-Superbases. *Angew. Chem. Int. Ed.* **2020**, *59*, 8004–8014.
- (16) Schmidpeter, A.; Zeiss, W. A Novel Type of 1,3-Dipolar Cycloaddition: 1,2-Aza-P^V-phosphol-1-ines from Methyleneiminophosphanes. *Angew. Chem. Int. Ed.* **1971**, *10*, 396–397.
- (17) Schmidpeter, A.; von Criegern, T. Vier- und fünfgliedrige Phosphorheterocyclen, 36¹ 1,3-Dipolare Cycloadditionen an Azaphosphole und Azaphospholine. *Chem. Ber.* **1979**, *112*, 3472–3479.
- (18) Schmidpeter, A.; von Criegern, T. [2 + 2] Cycloadducts from isocyanates and azaphospholes. *J. Chem. Soc., Chem. Commun.* **1978**, *11*, 470–471.
- (19) Brown, C. C.; Glotzbach, C.; Stephan, D. W. Ag(I) and Au(I) complexes of sterically crowded cyclic phosphinimine ligands. *Dalton Trans.* **2010**, *39*, 9626–9632.
- (20) Riu, M.-L. Y.; Transue, W. J.; Rall, J. M.; Cummins, C. C. An Azophosphine Synthetic Equivalent of Mesitylphosphazide and Its 1,3-Dipolar Cycloaddition Reactions. *J. Am. Chem. Soc.* **2021**, *143*, 7635–7640.
- (21) Soleihavoup, M.; Bertrand, G. Cyclic (Alkyl)(Amino)Carbenes (CAACs): Stable Carbenes on the Rise. *Acc. Chem. Res.* **2015**, *8*, 256–266.
- (22) Melaimi, M.; Jazzar, R.; Soleihavoup, M.; G., B. Cyclic (Alkyl) (amino) carbenes (CAACs): Recent Developments. *Angew. Chem. Int. Ed.* **2017**, *56*, 10046–10068.
- (23) Wiberg, N. Silyl, Germyl, and Stannyl Derivatives of Azenes, N_nH_n : Part I. Derivatives of Diazene, N_2H_2 . *Adv. Organomet. Chem.* **1984**, *23*, 131–191.
- (24) Kroner, J.; Schneid, W.; Wiberg, N.; Wrackmeyer, B.; Ziegler, G. ^{13}C , ^{14}N and ^{29}Si Nuclear magnetic resonance and photoelectron spectra of azo compounds. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1909–1919.
- (25) Attanasi, O. A.; Filippone, P.; Guerra, P.; Serra-zanetti, F. Conjugated Azoalkenes Part III. Synthesis of Some Phosphorous Azoalkenes. *Synth. Commun.* **1987**, *17*, 555–561.
- (26) Chauvier, C.; Finck, L.; Hecht, S.; Oestreich, M. General Synthesis and Optical Properties of *N*-Aryl-*N'*-Silyldiazenes. *Organometallics* **2019**, *38*, 4679–4686.
- (27) See the Supporting Information, S1.3.4.
- (28) See the Supporting Information, S1.3.3.
- (29) Kornev, A. N.; Belina, N. V.; Sushev, V. V.; Fukin, G. K.; Baranov, E. V.; Kurskiy, Y. A.; Poddelskii, A. I.; Abakumov, G. A.; Lönnecke, P.; Hey-Hawkins, E. The First Structurally Characterized Metal (κ^2N,P)-Phosphinohydrazides: The Key to Understanding the Intramolecular Rearrangement $R_2P-NR'-NR'-M \rightarrow R'N=PR_2-NR'-M$. Metalloderivatives of Diisopropylphosphinohydrazides: Synthesis and Properties. *Inorg. Chem.* **2009**, *48*, 5574–5583.
- (30) Swamy, K. C. K.; Kumar, N. N. B.; Balaraman, E.; P., K. K. V. P. Mitsunobu and Related Reactions: Advances and Applications. *Chem. Rev.* **2009**, *109*, 2551–2651.
- (31) Lucken, E. A. C.; Ramirez, F.; Catto, C. P., V. Smith Radical Ions in the Reactions of *p*-Chloranil with triphenylphosphine and with Triethylphosphine. *Tetrahedron* **1965**, *22*, 1941–1959.
- (32) Ramirez, F.; Rhum, D.; Smith, C. P. Reaction of Diethylphenylphosphine with Chloranil. *Tetrahedron* **1965**, *21*, 1941–1959.
- (33) Ramirez, F.; Dershowitz, S. The Structure of Quinone-Donor Adducts. I. The Action of Triphenylphosphine on *p*-Benzoquinone, 2,5-Dichloro-*p*-benzoquinone and Chloranil. *J. Am. Chem. Soc.* **1956**, *78*, 5614–5622.
- (34) See the Supporting Information, S1.5.1.
- (35) See the Supporting Information, S1.5.4.
- (36) Huynh, M. T.; Anson, C. W.; Cavell, A. C.; Stahl, S. S.; Hammes-Schiffer, S. Quinone 1 e^- and 2 $e^-/2 H^+$ Reduction Potentials: Identification and Analysis of Deviations from Systematic Scaling Relationships. *J. Am. Chem. Soc.* **2016**, *138*, 15903–15910.
- (37) The treatment of **NHIP-1** with water (10 equiv) in THF resulted in rapid hydrolysis, as is typical behavior for iminophosphoranes. See the Supporting Information, S1.10.1.
- (38) **NHIP-5** did not decompose in the solid state after it was exposed to air at 21 °C for 2 d. **NHIP-5** showed negligible hydrolysis in the presence of water (10 equiv) in THF even after 2 h at 21 °C, consistent with the known water stability of tris(amino)iminophosphoranes. See the supporting information, S1.10.3.
- (39) **NHIP-6** underwent hydrolysis at one of the ester groups, while keeping the ring system intact. See the supporting information, S1.10.2.
- (40) The scope of dipolarophile is limited to activated alkynes at this stage.
- (41) Pykkö, P. Additive Covalent Radii for Single-, Double-, and Triple-Bonded Molecules and Tetrahedrally Bonded Crystals: A Summary. *J. Phys. Chem. A* **2015**, *119*, 2326–2337.
- (42) Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. Acid-Base Equilibria in Nonpolar Media. 2¹ Self-Consistent Basicity Scale in THF Solution Ranging from 2-Methoxypyridine to EtP₁(pyrr) Phosphazene. *J. Org. Chem.* **2002**, *67*, 1873–1881.
- (43) Rodima, T.; Mäemets, V.; Koppel, I. Synthesis of *N*-aryl-substituted iminophosphoranes and NMR spectroscopic investigation of their acid-base properties in acetonitrile. *J. Chem. Soc., Perkin Trans. 1* **2000**, *16*, 2637–2644.
- (44) See the Supporting Information, S1.8.
- (45) Teng, Q.; Ng, P. S.; Leung, J. N.; Huynh, H. V. Donor Strengths Determination of Pnictogen and Chalcogen Ligands by the Huynh Electronic Parameter and Its Correlation to Sigma Hammett Constants. *Chem. Eur. J.* **2019**, *25*, 13956–13963.
- (46) Teng, Q.; Huynh, H. V. A unified ligand electronic parameter based on ^{13}C NMR spectroscopy of *N*-heterocyclic carbene complexes. *Dalton Trans.* **2017**, *46*, 614–627.
- (47) Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. Palladium(II) Complexes of a Sterically Bulky, Benzannulated *N*-Heterocyclic Carbene with Unusual Intramolecular C–H $\cdots$ Pd and Ccarbene $\cdots$ Br Interactions and Their Catalytic Activities. *Organometallics* **2006**, *25*, 3267–3274.
- (48) See the Figure S179 in the supporting information.
- (49) See the Figure S180 in the supporting information.
- (50) Fujimoto, H.; Kusano, M.; Kodama, T.; Tobisu, M. Aryne-Induced S_NAr /Dearylation Strategy for the Synthesis of Fluorinated Dibenzophospholes from Triarylphosphines via a P(V) Intermediate. *Org. Lett.* **2020**, *22*, 2293–2297.
- (51) Ponce-de León, J.; Infante, P. R. Espinet Easy wide scope access to luminescent fluorophosphoranes. *Chem. Commun.* **2021**, *57*, 5458–5461.
- (52) Lin, Y.-C.; Gilhula, J. C.; Radosevich, A. T. Nontrigonal constraint enhances 1,2-addition reactivity of phosphazenes. *Chem. Sci.* **2018**, *9*, 4338–4347.
- (53) Venderbosch, B.; Oudsen, J.-P. H.; van der Vlugt, J. I.; Kosterjanje, T. J.; Tromp, M. Cationic Copper Iminophosphorane Complexes as CuAAC Catalysts: A Mechanistic Study. *Organometallics* **2020**, *39*, 3480–3489.
- (54) Dahcheh, F.; Martin, D.; Stephan, D. W.; Bertrand, G. Synthesis and Reactivity of a CAAC-Aminoborylene Adduct: A Hetero-Allene or an Organoboron Isoelectronic with Singlet Carbenes. *Angew. Chem. Int. Ed.* **2014**, *53*, 13159–13163.
- (55) Dahcheh, F.; Stephan, D. W.; Bertrand, G. Oxidative Addition at a Carbene Center: Synthesis of an Iminoboryl-CAAC Adduct. *Chem. Eur. J.* **2015**, *21*, 199–204.

TOC graphic:



TOC Synopsis New protocols for the synthesis of azophosphines and their cycloaddition reactivity with alkynes are described. The basicity, electronic properties, reactivity, and coordination chemistry of the resulting NHIPs (*N*-heterocyclic iminophosphoranes) are also investigated. The potential utility of π -donating NHIPs was demonstrated by the stabilization of a reactive iminoborane ($\text{Cl}-\text{B}\equiv\text{N}-\text{SiMe}_3$).