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海 外 特 別 研 究 員 最 終 報 告 書

独立行政法人日本学術振興会 理事長　殿

採 用 年 度　令和 2 年度
受 付 番 号　202060609
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海外特別研究員としての派遣期間を終了しましたので、下記のとおり報告いたします。
なお、下記及び別紙記載の内容については相違ありません。

記

1. 用務地（派遣先国名）用務地：　マサチューセッツ州　（国名：　アメリカ合衆国　）

2. 研究課題名（和文）※研究課題名は申請時のものと違わないように記載すること。
ホスフィニデントランスファーによる炭素―水素結合の触媒的ホスフィン化反応の開発

3. 派遣期間：令和　２年　　４月　　１日　～　令和　　４年　　３月　　３１日（　730 日間）

4. 受入機関名及び部局名
受入機関名：　マサチューセッツ工科大学
部局名：　化学科

5. 所期の目的の遂行状況及び成果…書式任意　**書式任意（A4 判相当 3 ページ以上、英語で記入も可）**

【記載事項】
- 研究・調査実施状況及びその成果の発表・関係学会への参加状況等
- 新型コロナウイルス感染症の影響にかかる特例措置のうち、国内採用開始・採用期間延長・翌年度渡航のいずれかの適用を受けた場合は、当該措置の適用による影響等

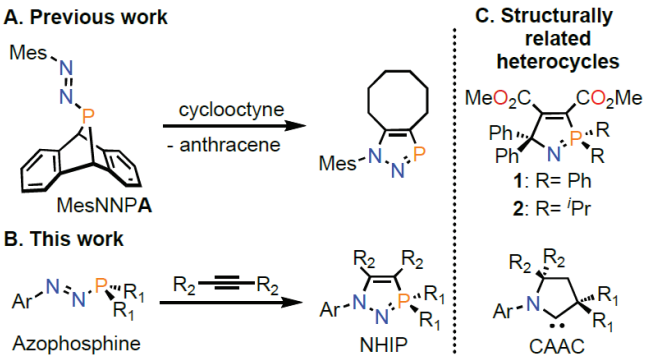
（注）「6. 研究発表」以降については様式 10－別紙 1～4 に記入の上、併せて提出すること。

< research purpose>

The reactivity of the catalysts largely depends on the ligands, and design and generation of new class of ligands in of paramount importance. We aimed to develop a new heterocycle class, and investigate the basicity, electronic properties, reactivity, and coordination chemistry for their application in catalytic reactions including C–H activation.

<results>

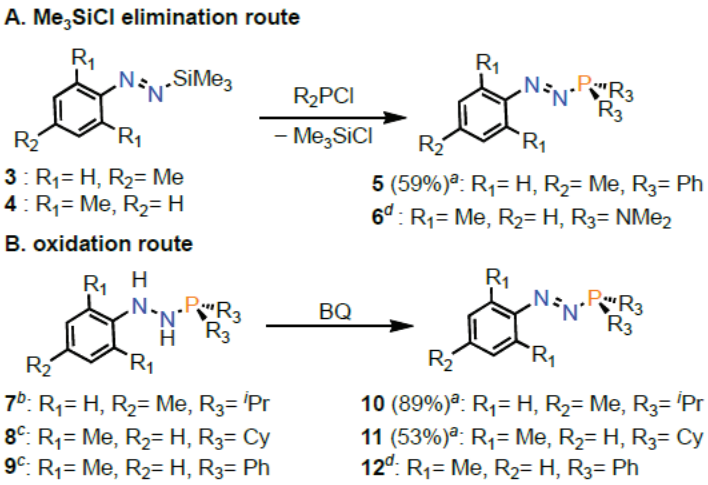
Iminophosphoranes ($R_3P{=}NR$) are not only versatile intermediates for functional group manipulations, but also used as ligands and organocatalysts due to the basic nitrogen center, which can be rationalized by the resonance structures ($R_3P{=}NR \leftrightarrow R_3P^+–N^-R$). Cyclic iminophosphoranes, 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. 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 at *α* to basic nitrogen, were prepared by 1,3-dipolar cycloaddition of phosphinoimine ($Ph_2C{=}N–PR_2$) and dimethylacetylene dicarboxylate (DMAD). The resulting cyclic iminophosphorane **1** was used as a ligand for Au(I), but further reactivity studies have not been pursued presumably because of the extreme steric crowding at the basic nitrogen atom. Recently cycloaddition of MesNNP**A** (**A** = anthracene) and cyclooctyne was disclosed, where a nucleophilic phosphorus center and an electrophilic N=N *π** component enabled MesNNP**A** to react as a 1,3-dipole (Scheme 1A). This result motivated us to investigate the cycloaddition reaction of alkynes and azophosphines which do not have anthracene leaving groups (Scheme 1B). This cycloaddition reaction provides a new class of heterocycles, *N*-heterocyclic iminophosphoranes (NHIPs), which are structurally similar to cyclic alkyl amino carbene (CAAC) ligands (Scheme 1C). 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.



Scheme 1. 1,3-dipolar cycloaddition of azophosphine and alkynes. NHIP = *N*-heterocyclic iminophosphorane, CAAC = cyclic alkyl amino carbene.

Our investigation began with the synthesis of azophos-phines. Azophosphines, having a general formula of R–N=N–PR'$_2$ have scarcely been mentioned in the literature. Encouraged by our recent success in the synthesis of MesNNP**A** by treating $[Na(Et_2O)_2][Ph_3BPA]$ with mesityl diazonium triflate, we attempted the synthesis of Mes–N=N–PCy_2 by the reaction of lithium dicyclohexyl phosphide with the same diazonium salt. However, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture showed a major product at δ −21.2 ppm, corresponding to $Cy_2P–PCy_2$.

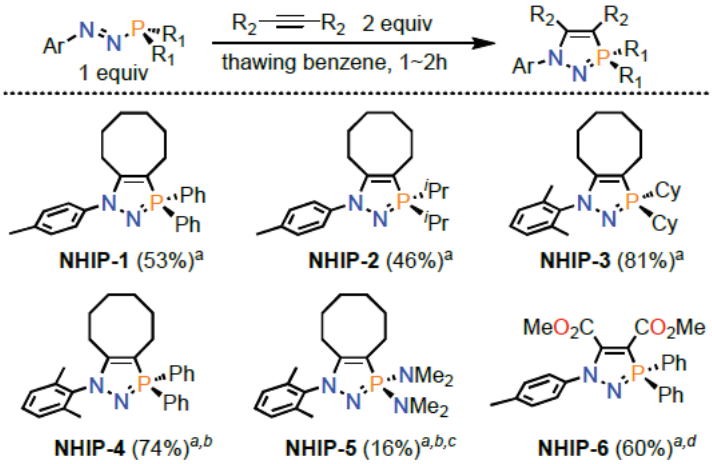
Although detailed synthetic protocols for azophosphines are unavailable, the reaction of Ph_2PCl with Ph–N=N–$SiMe_3$ in DCM at −30 °C (5 h) is reported to give Ph–N=N–PPh_2 as a red solid in 30% yield. Thus, we decided to try similar reaction conditions for preparing azophosphines. The reaction between Tol-N=N–$SiMe_3$ with Ph_2PCl in pentane at 21 °C under atmospheric pressure gave a mixture of products; 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 $^{31}P\{^1H\}$ 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% yield (2.7 g, Scheme 2A). Using the same protocol, (2,6-$Me_2C_6H_3$)–N=N–$P(NMe_2)_2$ (**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. Although the Me_3SiCl elimination route was found to be effective for the preparation of **5**, this method was not applicable to sterically hindered chlorophosphines, including $^iPr_2PCl$. Indeed, the P-atom substituents in reported azophosphines are limited to methyl and phenyl groups.



Scheme 2. Preparation of azophosphines. Reaction conditions for Me_3SiCl elimination route (**A**): azophosphine (1 equiv), R_2PCl (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. [a]isolated yield. [b]2,5-di-*tert*-butylBQ was used. [c]2,5-dimethylBQ was used. [d]the product could not be purified.

To access a wider range of azophosphines, we targeted selective oxidation of phosphinohydrazines (Ar–NH–NH–PR_2, Scheme 2B). Given that Me–NH–NH–P^{i}Pr$_2$ has been prepared using $^iPr_2PCl$, N–P bond formation appears to be less sensitive to steric hindrance. Inspired by a recent study on oxidation of Ar–NH–NH–SiR_3 to Ar–N=N–SiR_3, we screened several oxidants, including di-*tert*butylazodicarboxylate (DBAD) and 1,4-benzoquinone (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 PPh_3 towards select oxidants has been well studied. For example, DBAD is known to react with PPh_3 to form betaine, a key intermediate for the Mitsunobu reaction. Also, in benzene, *p*-chloranil forms P–O bonds with PPh_3 via cationic phosphorus radicals, which are formed by single electron transfer between *p*-chloranil and PPh_3. By contrast, non-substituted BQ, a weaker oxidant than *p*-chloranil in benzene, resulted in the formation of a P–C bond with PPh_3 by conjugate addition. Bearing in mind these facts, oxidation conditions were screened using *p*-Tol–NH–NH–P^{i}Pr2 (**7**) as the model substrate. DBAD, BQ, 2,6-dimethylBQ, 2,5-dimethylBQ and 2,5-di-*tert*-butylBQ were chosen as oxidants. While non-substituted BQ immediately resulted in deep green solution, the other oxidants led to deep red solutions, a characteristic color for azophosphines. In all cases, a resonance at δ 104.7 ppm was observed upon $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixtures. 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 crudereaction mixtures with good conversions (~70%) based on $^{31}P\{^1H\}$ NMR spectra. The efficiency of this reaction may be attributed to the increased BQ's steric hindrance, which suppresses conjugate addition of phosphinohyrazine or azophosphine to BQ. Additionally, alkyl substituent make benzoquinone less oxidizing, preventing the single electron transfer

between the phosphorus center and BQ. 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 (2,6-$Me_2C_6H_3$)–N=N–PCy_2 (**11**) in 53% (0.44 g) yield as a dark-orange solid. The reaction also worked for the preparation of (2,6-$Me_2C_6H_3$)–N=N–PPh_2 (**12**); however, a small amount of unreacted starting material **9** and a side product (2,6-$Me_2C_6H_3$)PPh_2 could not be removed. 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.



Scheme 3. Scope of 1,3-dipolar cycloaddition. Reaction conditions: Azophosphine (1 equiv), cyclooctyne (2 equiv), thawing benzene, 1 or 2 h. [a]isolated yield. [b]crude azophosphine was used. [c]overall yield from Ar–N=N–$SiMe_3$. [d]DMAD (1 equiv) was used.

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. $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture showed a single resonance at δ 40 ppm, which is close to the $^{31}P\{^1H\}$ NMR chemical shift of previously reported cyclic iminophosphorane **1** (δ 49 ppm, Scheme 1C). The crude product was purified by crystallization from DCM/diethyl ether at −20 ◦C to afford orange crystals (**NHIP-1**) in 53% yield (0.435 g). 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 in 46% (0.14 g) and 81% (2.91 g) yield respectively as**NHIP-6** in 60% yield (0.28 g) as a yellow

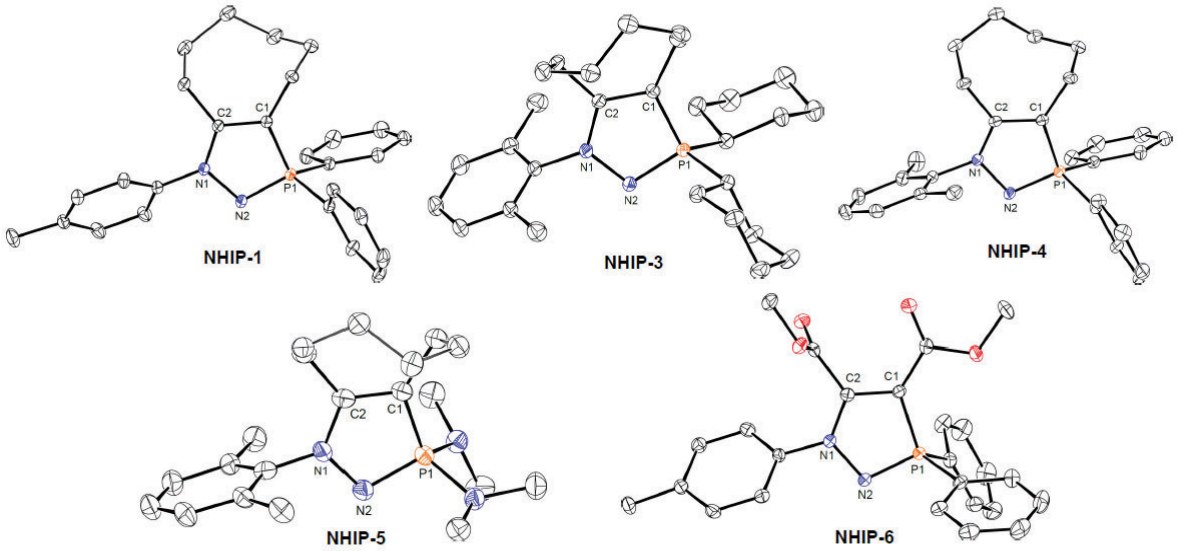


Figure 1. Solid-state structures of **NHIP-1**, **NHIP-3**, **NHIP-4**, **NHIP-5**, and **NHIP-6** drawn using 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) and angles (deg) for **NHIP-1**: P1–N2, 1.6275(10); P1–C1, 1.7433(11); C1–C2, 1.3857(14); C2–N1, 1.3625(16); N1–N2, 1.4258(13); N2–P1–C1, 98.52(5); P1–C1–C2, 105.11(8); C1–C2–N1, 114.26(10); C2–N1–N2, 115.83(9); N1–N2–P1, 106.08(7). For **NHIP-3**: P1–N2, 1.6329(5); P1–C1, 1.7579(5); C1–C2, 1.3831(7); C2–N1, 1.3529(7); N1–N2, 1.4314(7). For **NHIP-4**: P1–N2, 1.6264(8); P1–C1, 1.7429(9); C1–C2, 1.3819(12); C2–N1, 1.3546(11); N1–N2, 1.4321(10). For **NHIP-5**: P1–N2, 1.6273(12); P1–C1, 1.7329(3); C1–C2, 1.3827(19); C2–N1, 1.3562(16); N1–N2, 1.4125(15). For **NHIP-6**: P1–N2, 1.6326(15); P1–C1, 1.7559(17); C1–C2, 1.400(2); C2–N1, 1.328(2); N1–N2, 1.4081(19); N2–P1–C1, 96.96(8); P1–C1–C2, 104.77(12); C1–C2–N1, 116.69(14); C2–N1–N2, 114.3(15); N1–N2–P1, 106.72(11).

solid. 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 4π system of **1** and the smaller atomic radius of nitrogen as compared with carbon.

As many iminophosphoranes are known to be superbasic (pK_{BH+} > 18.6 in MeCN), the basicity of NHIPs was investigated. Protonated NHIPs were treated with 1 equivalent of base with a known pK_{BH+} value, and the concentration of NHIP and conjugate acid at equilibrium was determined by the change of $^{13}C\{^1H\}$ NMR chemical shift of select carbon atoms of NHIPs. Protonation of **NHIP-2**, **NHIP-4**, and **NHIP-5** was achieved using pyridinium triflate; however the complete protonation of **NHIP-6** was not achieved using the same reaction conditions, indicating much weaker basicity of **NHIP-6**. In fact, the pK_{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. The ability to tune the basicity without changing the steric shielding of the basic nitrogen atom is an attractive feature for this new heterocycle class.

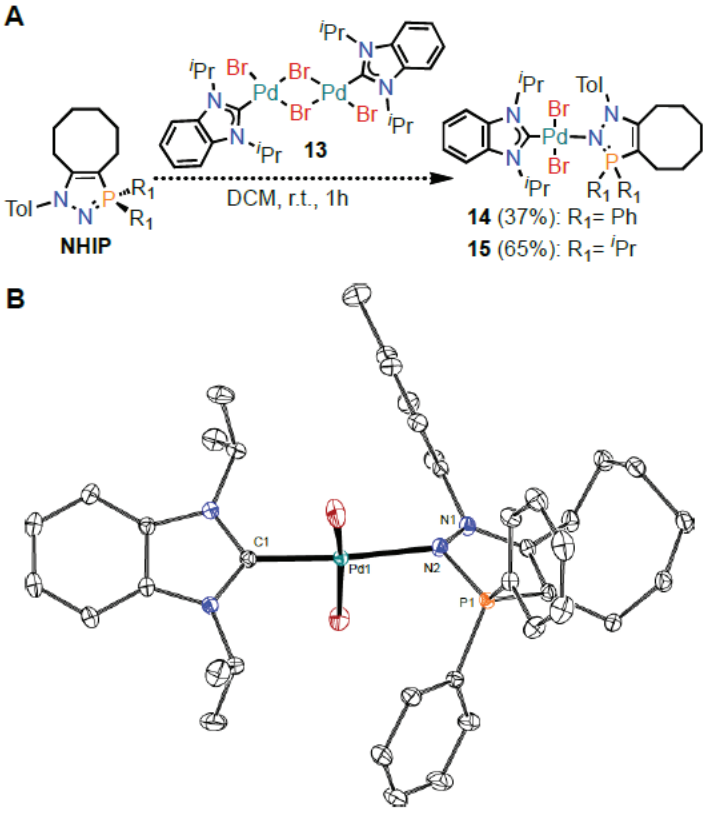
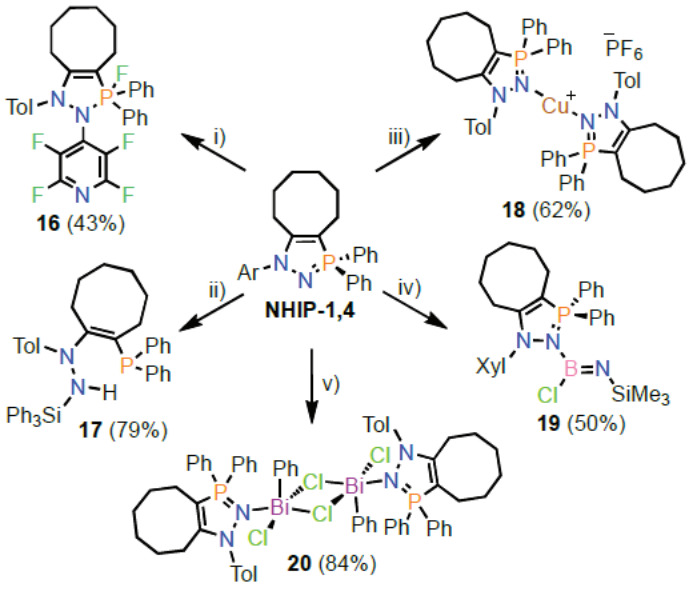


Figure 2. Preparation of Pd-complexes for HEP analysis. **A** (Reaction conditions): NHIP (2 equiv), **13** (1 equiv), DCM, 21 °C, 1 h; **B**: Solid-state structure of **14** drawn using 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Select bond lengths (Å) for **14**: Pd1–N2, 2.0894(11); Pd1–C1, 1.9508(12); P1–N2, 1.6345(11).

Next, we investigated the σ donor strength of the NHIPs. Iminophosphoranes on transition metals are labile ligands due to their poor π accepting character, and they are easily displaced by carbon monoxide, $AsPh_3$, and PPh_3, which might make the preparation of transition metal complexes for the Tolman electronic parameter (TEP) analysis problematic. Thus, we decided to use Huynh electronic parameter (HEP) analysis, which covers a wide variety of σ donors including labile ligands such as pyridines and acetonitrile. For the HEP analysis, the target palladium white solids. The crystalline nature of NHIPs allowed us to use crude azophosphines for the synthesis of **NHIP-4** and **NHIP-5**, which were purified by crystallization to give orange crystals (74%, 0.54 g), pale-yellow crystals (16%, 0.34 g over 2 steps). DMAD was also a good dipolarophile, giving complex **14** was prepared by combining **NHIP-1** with **13** in DCM (Figure 2A), and crystal structure analysis revealed that **NHIP-1** binds *trans* to the carbene ligand (Figure 2B). Interestingly, the nitrogen atom of **NHIP-1** coordinates to the palladium center in an out-of-plane fashion. The $^{13}C\{^1H\}$ 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 $^{13}C\{^1H\}$ NMR chemical shift is 166.32 ppm. Therefore, **NHIP-1** is a stronger σ donor than pyridines (δ 161.97 ppm to 157.33 ppm) and thiols (δ 166.46 ppm to 163.63 ppm), but a weaker σ donor than phosphine ligands (δ > 171.48 ppm). The σ donor strength of **NHIP-**

2 was also evaluated using the same method. The $^{13}C\{^1H\}$ NMR chemical shift of carbene carbon was 166.26 ppm, indicating slightly weaker σ donation than **NHIP-1**.

Finally, reactivity of NHIPs with common organic synthesis reagents was investigated. The treatment of **NHIP-1** with water (10 equiv) in THF resulted in rapid hydrolysis, as is typical behavior for iminophosphoranes. In contrast, under the same reaction conditions, **NHIP-5** showed negligible hydrolysis even after 2 h at 21 °C, consistent with the known water stability of tris(amino)iminophosphoranes. Notably, **NHIP-5** did not decompose in the solid state after it was exposed to air at 21 °C for 2 d. Interestingly, **NHIP-6** underwent hydrolysis at one of the ester groups, while keeping the ring system intact. The lack of P–H coupling for the acidic proton in ^1H NMR spectrum indicates that the nitrogen atom of NHIP was not protonated, which is in agreement with the low basicity of **NHIP-6**. Thus, in this case, the stability of the ring can be attributed to the highly electron withdrawing NHIP backbone, resulting in an electron poor phosphorus center.



Scheme 4. 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), $[Cu(MeCN)_4][PF_6]$ (1 equiv), THF, 21 °C, 30 min; (iv): NHIP-4 (1 equiv), $(Me_3Si)_2NBCl_2$ (1.05 equiv), benzene, 21 °C, 4 h; (v): NHIP-1 (1 equiv), $PhBiCl_2(thf)$ (1 equiv), THF, 21 °C, 30 min.

When a THF solution of **NHIP-1** was combined with pentafluoropyridine, the orange color of NHIP dissipated. $^{31}P\{^1H\}$ 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 ($1J_{PF}$ = 618.7 Hz) ppm. Note that the P–F bond of **16** is stable in solution, unlike that of bis(triphenyl-λ^5-phosphanylidene)ammonium fluoride. The crude product was purified by crystallization from DCM/pentane at −20 °C to afford colorless crystals **16** in 43% yield (0.125 g). The crystal structure revealed pyramidal nitrogen N2 and trigonal bipyramidal geometry at phosphorus (Figure 3). Consistent with a P–N single bond, a P–N bond length of 1.9095(10) Å was found. Additionally, a P–F bond length of 1.6785(7) Å was found, which is similar to those of recently reported fluorophosphoranes. Notably, the C1– C2 and C2–N1 bonds were shortened (0.0282 Å) and elongated (0.0202 Å), respectively, relative to those found in **NHIP-1**, further supporting π delocalization in the NHIP ring system.

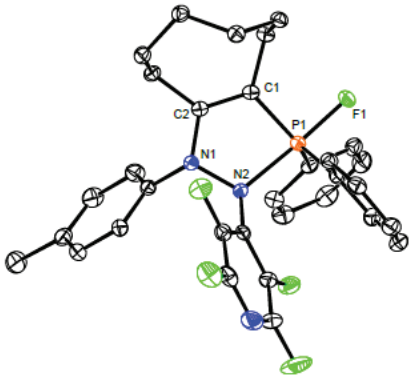


Figure 3. Solid-state structure of **16** drawn using 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Select bond lengths (Å): P1–F1, 1.6785(7); P1–N2, 1.9095(10); P1–C1, 1.7858(11); C1–C2, 1.3574(16); C2–N1, 1.3827(14); N1–N2, 1.4370(13).

Next we investigated the reactivity of **NHIP-1** with silicon-based reducing agents. Upon combining NHIP and $PhSiH_3$ in benzene at 21 °C, the solution turned to pale yellow from orange immediately, and NMR analysis of the reaction mixture revealed two new $^{31}P\{^1H\}$ NMR resonances at δ −10.49, −10.62 ppm. As multiple products were due to the participation of the Si–H bonds of the product, we repeated the same reaction using Ph_3SiH,

which has a single Si–H bond. Although the reaction was extremely slow under the same reaction conditions, heating **NHIP-1** and Ph_3SiH in benzene at 80 °C for 14 h resulted in a single new $^{31}P\{^1H\}$ NMR resonance at δ −10.58 ppm. The crude product was purified by crystallization from diethyl ether/pentane at −20 °C to afford off-white crystals **17** in 79% yield (0.265 g). X-ray analysis (Figure 4) revealed the selective P–N bond cleavage and reduction of P(V) to P(III). The putative reaction mechanism is initial 1,2-addition across the P=N double bond, forming N–Si and P–H bonds, and subsequent reductive elimination to form P(III) and a N–H bond.

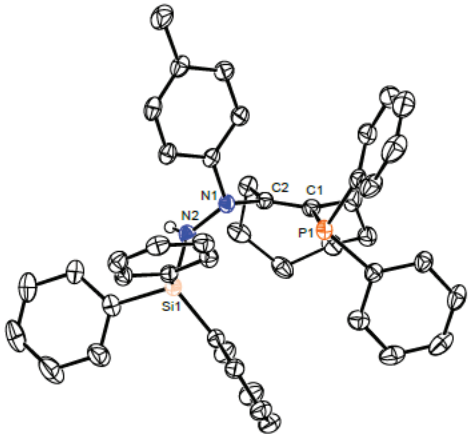


Figure 4. Solid-state structure of **17** drawn using 50% probability ellipsoids. Hydrogen atoms except for the one at N2 are omitted for clarity. Select bond lengths (Å): P1–C1, 1.8388(15); C1–C2, 1.3426(19); C2–N1, 1.504(17).

Inspired by recently developed cationic iminophosphoraneligated copper complexes for catalytic azide-alkyne cycloaddition, corresponding NHIP-ligated copper complexes were targeted. The treatment of **NHIP-1** with $[Cu(MeCN)_4][PF_6]$ in THF resulted in rapid color change from orange to yellow. The $^{31}P\{^1H\}$ NMR spectrum showed clean conversion and a new resonance at δ 43.37 ppm. The crude product was purified by crystallization from DCM/benzene at 21 °C to afford yellow crystals **18** in 62% yield (0.32 g). Crystallographic analysis revealed a cationic, homoleptic copper complex, in which the Cu–N bond length (1.8544(13) ˚A) is comparable to those in the reported copper iminophosphorane complexes (1.865(4) to 1.8902(18) Å), indicating the potential catalytic activity of **18** for azide-alkyne cycloaddition.

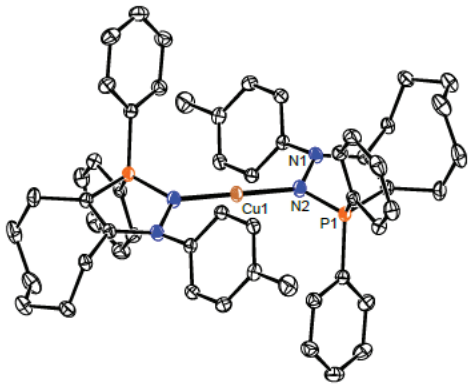


Figure 5. Solid-state structure of **18** drawn using 50% probability ellipsoids. Hydrogen atoms and counter ion PF_6^- are omitted for clarity. Select bond lengths (Å) : Cu1–N2, 1.8544(13); P1–N2, 1.6339(14).

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 corresponding 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, Cl–B≡N–SiMe3, whose CAAC adduct have been prepared, was targeted. When **NHIP-4** was treated with $(Me_3Si)_2NBCl_2$ in benzene, a new resonance at δ 21.7 ppm was observed in the $^{31}P\{^1H\}$ 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. The crude product was purified by washing with pentane to afford **19**, as a pale yellow solid, in 50% yield (0.141 g). **19** was crystalized from pentane at −20 °C and single crystal X-ray diffraction revealed the structure depicted in Figure 6. This structure showed 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

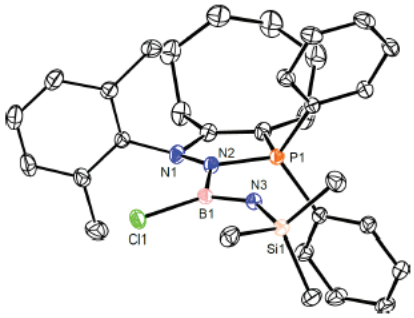


Figure 6. Solid-state structure of **19** drawn using 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Select bond lengths (Å): B1–N2, 1.477(2); B1–N3, 1.346(2); B1–Cl1, 1.8134(16); N2–P1, 1.6591(12); N3–Si1, 1.6989(13).

that B=N and CAAC's ring are perpendicular to each other (torsion angle = 106.4°), which is in agreement with the empty p orbitals of CAACs.

Encouraged by the successful stabilization of an iminoborane via π-donating NHIP, we wondered how NHIPs compare with other σ and π donating ligands, in particular carbodicarbenes(CDC). As NHC-$PhBiCl_2$ and CDC-$PhBiCl_2$, have been prepared, we synthesized the corresponding NHIP adduct. By combining **NHIP-1** and $PhBiCl_2$(THF) in THF, clean conversion and a new resonance at δ 54.69 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum. The crude product was purified by triturating with diethyl ether to afford **20**, as a pale yellow solid, in 84% yield (0.162 g). The crystal structure of **20** (Figure 7) revealed seesaw geometory at bismuth, similar to the recently reported CAAC and CDC adducts.63,64 However, the Bi-NHIP adduct was obtained as a dimer, while the CDC adduct was monomeric.64 Although the CAAC adduct was also obtained as a dimer, the Bi1–Cl2' (2.9835(6) Å) bond of **20** is much shorter than those (3.2729(6) and 3.1276(7) Å) in the CAAC adducts. These data indicate that electron donor strength decreases in the order of CDC > CAAC > NHIP.

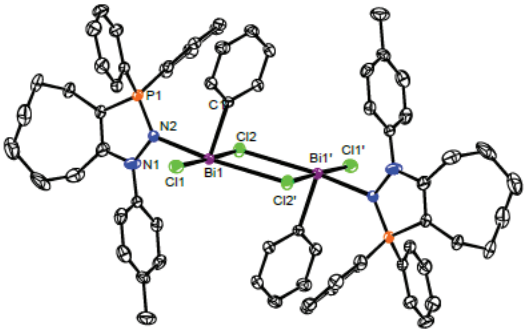


Figure 7. Solid-state structure of **20** drawn using 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Select bond lengths (Å): Bi1–N2, 2.3329(19); Bi1–C1, 2.256(2); Bi1–Cl1, 2.6472(6); Bi1–Cl2, 2.8079(6); Bi1–Cl2', 2.9835(6); P1–N2, 1.647(2).

In conclusion, we have shown that selective oxidation of phosphinohydrazines to azophosphines can be achieved by using sterically demanding, and less-oxidizing BQs. This protocol allowed us to access new azophosphines with sterically hindered and electron donating substituents on phosphorus atoms. Azophosphines smoothly underwent 1,3-dipolar cycloaddition with activated alkynes to afford NHIPs. NHIPs have comparable σ donor strength with DBU, and pK_{BH+} values of the NHIPs in acetonitrile range from 13.13 to 23.14. Although structurally similar CAACs are much stronger σ donors than NHIPs, the extra π donation allowed them to stabilize a highly reactive iminoborane. The further investigation of NHIPs as organocatalysts, superbases, and ligands are currently ongoing.