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Chemoselective Staudinger Reactivity of Bis(azido)phosphines Supported with a π-Donating Imidazolin-2-iminato Ligand

John L. Lortie, Matthew Davies, Paul D. Boyle, Mikko Karttunen,* and Paul J. Ragogna*

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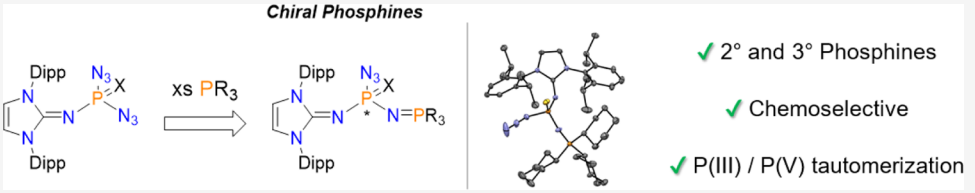

ABSTRACT: Synthesis and characterization of new P(III) and P(V) bis(azido)phosphines/phosphoranes supported by an *N,N′*-bis(2,6-diisopropylphenyl) imidazolin-2-iminato (IPrN) ligand and their reactivity with various secondary and tertiary phosphines result in the formation of chiral and/or asymmetric mono(phosphinimino)azidophosphines via the Staudinger reaction. The reaction of IPrNP$(N_3)_2$ (**2**) or IPrNP(S)$(N_3)_2$ (**4S**) with an excess of tertiary phosphine resulted in the chemoselective formation of IPrNP$(N_3)$$(NPMe_3)$ (**7**) or IPrNP(S)$N_3$$(NPR_3)$ ($\mathbf{5_R}$), respectively. The chemoselective Staudinger reactivity was also observed in reactions using a secondary phosphine ($HPCy_2$) to produce IPrNP(S)$N_3$$[NP(H)Cy_2]$ (**6a**), which exists in equilibrium with a tautomeric IPrNP(S)$N_3$$[N(H)PCy_2]$ form (**6b**), as confirmed by $^{31}P-^{31}P$ nuclear Overhauser effect spectroscopy (NOESY). Density functional theory (DFT) calculations point to a combination of energetically unfavorable lowest unoccupied molecular orbitals (LUMOs) and the accumulation of increasing negative charge at the terminal azido-nitrogen upon a single azide-to-phosphinimine conversion that gave rise to the observed chemoselectivity.

INTRODUCTION

Phosphinimines ($R_3P{=}N{-}R'$) have been exploited both as ligands for stabilizing main group compounds and for their utility as intermediates in organic syntheses.[1,2] Hydrolysis of the P=N bond offers a mild method of reducing azides to primary amines, while a reaction of a phosphinimine with a carbonyl compound can provide access to C=N bond formation via an aza-Wittig reaction (Scheme 1).[3] The electronic structure and multiple bond character resulting from negative hyperconjugation of a phosphinimine P−N bond is comparable to a P−C bond in a phosphonium ylide, while the nitrogen atom of phosphinimines also bears a similar basicity with the class of strongly π-donating N-heterocyclic imines (NHI).[1,4−6]

Arguably, the most versatile reaction for the synthesis of phosphinimines is the Staudinger reaction of organic azides with tertiary phosphines.[7,8] Computational and experimental evidence suggests the Staudinger reaction often proceeds via ring-closure of a *cis*-phosphazide ($R_3P^+{-}N{=}N{-}N^-{-}R'$) intermediate to a 4-membered transition state, followed by liberation of N_2 as the key enthalpic and entropic driving force for the reaction.[7,9−15] An alternative one-step pathway has also been suggested in some instances involving electron-deficient phosphines.[9] The use of an electron-deficient azide, more nucleophilic phosphine, or more polar solvents have all been demonstrated to increase the reaction rate, while electron-donating groups on the azide hinder the reaction.[10] Staudinger reactions of P(III) (azido)phosphines ($R_2P{-}N_3$) have also been reported, but their ambiphilic nature can result in spontaneous decomposition to oligomeric phosphazenes $(RP{=}N)_n$, and the reactivity can be attenuated by steric protection or by electron delocalization.[16] The ambiphilic nature of azidophosphines is also demonstrated by their ability to form a $R_2P{-}N{=}PR_3$ motif or their reaction with an electrophilic azide to produce $R_2P(NPh)(N_3)$.[8,16,17] Bis(azido)phosphines are scarcely reported due to poor thermal stability but have been isolated either using N-aryl[18] or cationic imidazolium ligands.[19] Phosphorus(V) bis(azido)phosphines are intriguing because the conversion of the first azide to a strongly π-donating phosphinimine has been reported to influence the ability of the remaining azide to perform a subsequent Staudinger reaction. For example (Scheme 2), $Et_2N(N_3)_2P{=}NPh$ may perform two subsequent unimpeded Staudinger reactions with PPh_3 to produce $Et_2N(N{=}PPh_3)_2P{=}NPh$,[20] whereas $SP(N_3)_2(NPPh_3)$ will only react with one more equivalent of PPh_3 to produce SP(N=

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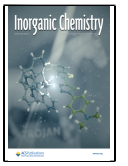

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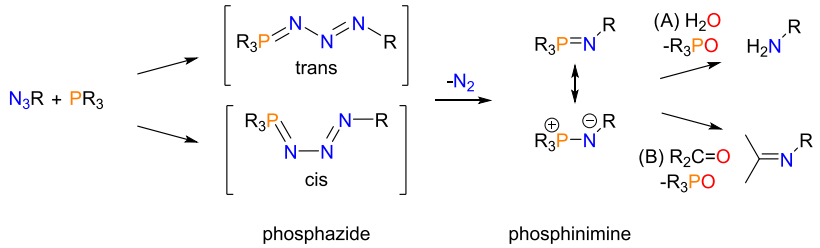
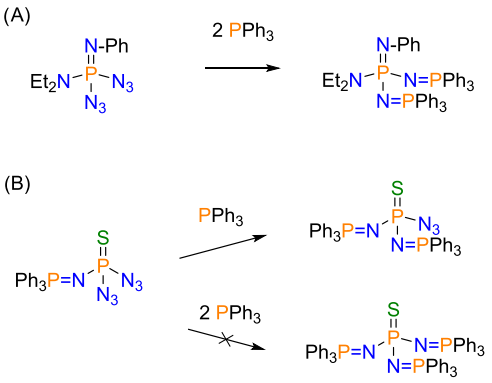
Scheme 1. General Scheme for a Staudinger Reaction to Produce a Phosphinimine with Hydrolysis to an Amine (A) and the Aza-Wittig Reaction (B)



Scheme 2. Comparative Staudinger Reactivities of P(V) Bis(azido)phosphines[20,21a]



[a]Bis(azido)phosphine in part (A) can react with two equivalents of PPh_3. Bis(azido)phosphine in part (B) can react with only one equivalent PPh_3.

$Ph_3)_2(N_3)$,[21] which bears an azide resilient to subsequent Staudinger reactivity.

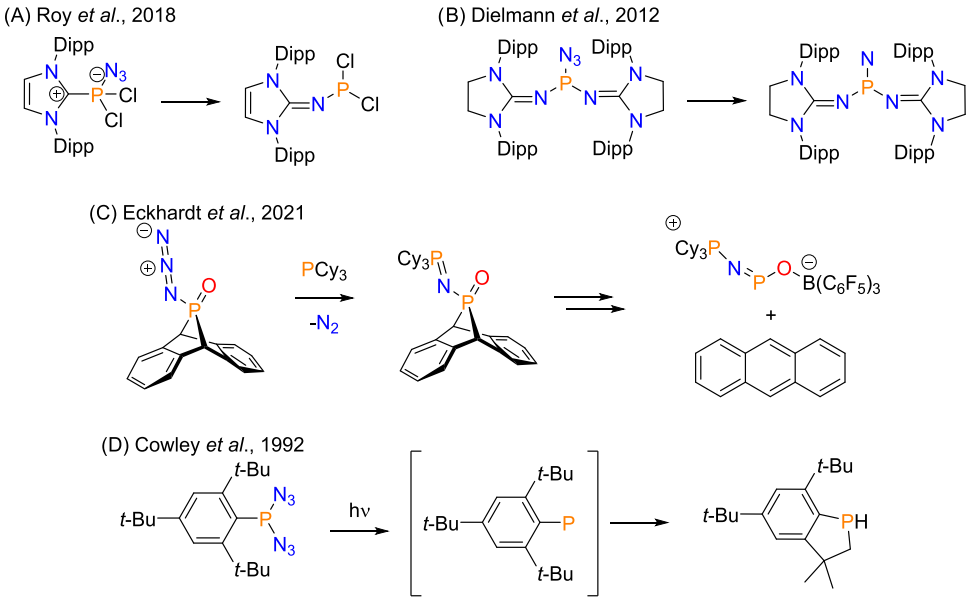
Azidophosphines have functioned as precursors to interesting phosphorus species (Scheme 3), including an NHI-supported phosphine,[22] a bis(NHI)-supported phosphinonitrene ($R_2P{\equiv}N$),[23−25] phosphinidene (R−P),[26] phosphinidene chalcogenide (RP═Ch),[27] phosphorus mononitride (P≡N),[28−30] and a phosphorus-substituted triazole via a click reaction.[29]

We sought to explore the synthesis of phosphorus species containing both a π-donating phosphinimine ligand and a bulky, π-donating NHI ligand to prepare electron-rich phosphines. Electron-rich phosphine ligands have already demonstrated their application as ligands in catalytic transformations,[31,32] and P-stereogenic phosphines further hold promise as ligands in asymmetric catalysis.[33] This work demonstrates the potential of NHI-supported bis(azido)-phosphines to undergo chemoselective Staudinger reactions with both tertiary or secondary phosphines to generate modular mono(azido)phosphines. A combination of DFT-optimized structures, Kohn−Sham orbitals, and charge analyses reveal subtle changes that explain the observed chemoselectivity in the P(V) family. This work highlights the stabilizing nature of the bulky NHI ligand for bottleable bis(azido)phosphines and provides an approach for preparing P-chiral phosphines bearing an azide handle.

RESULTS AND DISCUSSION

Synthesis and Characterization of Bis(azido)-phosphine Compounds. A series of P(III) and P(V) bis(azido)phosphines were prepared (Scheme 4). Salt metathesis reactions of $IPrNPCl_2$ (**1**) with an excess of NaN_3 in acetonitrile, followed by an extraction using benzene, allowed for the facile production and the isolation of $IPrNP(N_3)_2$ (**2**).

Scheme 3. Select examples of transformations of Azidophosphines



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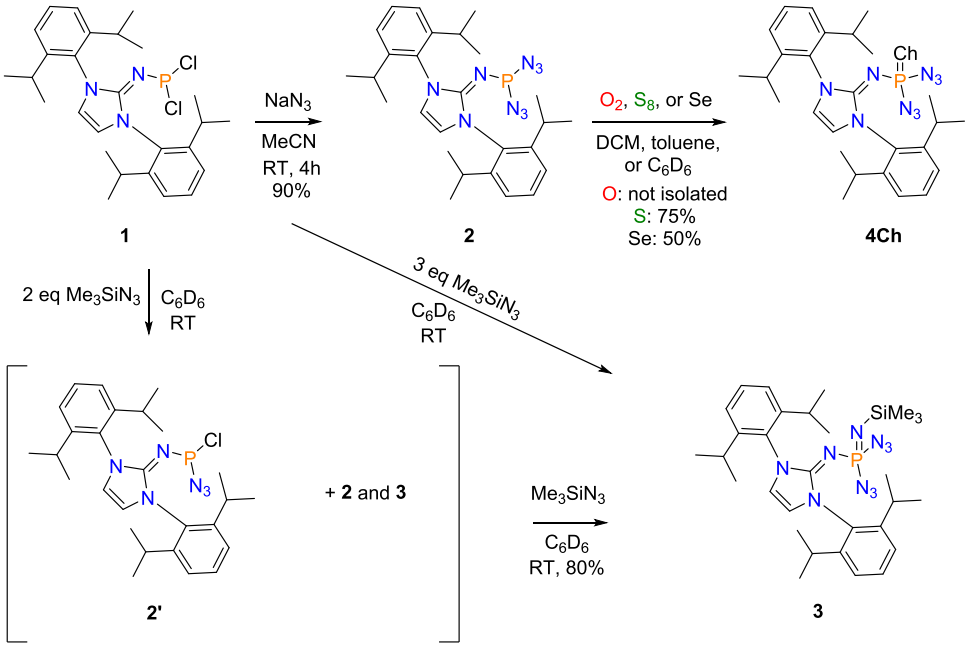
Scheme 4. Synthetic Routes to Bis(azido)phosphines 2, 3, and 4Ch (Ch = O, S, Se)



Trimethylsilylazide (Me_3SiN_3) was also explored as a method of synthesizing compound **2** but was found to concurrently generate mixtures of **2** (δ_P = 123), a transient species IPrP(N_3)Cl (**2′**; δ_P = 148), and a bis(azido)(trimethylsilyliminyl)-phosphine **3** (IPrNP($NSiMe_3$)(N_3)$_2$; δ_P = −28).[16,34] The ambiphilic nature of **2** was noted by the spontaneous decomposition to a complex mixture of species in THF, likely containing oligomers of P−(N−P)$_n$ motifs via Staudinger reactions, while decomposition of **2** was much slower in less polar aromatic solvents (i.e., benzene or toluene). Using aromatic solvents allowed for longer time scale reactions to be performed at or below room temperature (i.e., in the syntheses of **4Ch**, **7**).

Bis(azido)phosphine chalcogenides (**4Ch**, Scheme 4) were subsequently prepared. Compound **4S** was prepared by sulfurization of a standing solution of **2** in toluene using one-eighth molar equivalents of S_8 at −30 °C for 5 days. In an analogous manner, selenation of **2** was performed in toluene but over 7 days of stirring at room temperature due to the low solubility of elemental selenium in toluene. Sulfurization of **2** to **4S** was later optimized to small batches (<500 mg) in CH_2Cl_2 at room temperature, requiring only 30 min of reaction time for complete conversion.[35] Removal of trace unreacted sulfur from **4S** required successive triturations with pentane, cyclohexane, and Et_2O, followed by recrystallization of the bulk material from Et_2O. The poor solubility of elemental selenium allowed for the isolation of **4Se** simply by filtration and recrystallization from Et_2O. Fourier transform infrared spectroscopy (FT-IR) spectra of **2**, **3**, and **4Ch** confirmed the presence of azides with asymmetric stretching bands between 2083 and 2140 cm^{-1} (Section S2).[26] To detect any unreacted sulfur in the crude reaction mixture of **4S** in CH_2Cl_2, a qualitative assay was employed wherein PPh_3 was introduced to a disposable sample. The emergence of $SPPh_3$ (δ_P = 43) within 15 min served as an indication of the presence of residual sulfur. Isolated yields of **4S** were subsequently improved by the incorporation of this qualitative test, by which small quantities of either S_8 or **2** were added to the principal reaction mixture until a tested assay showed no detectable trace of either $SPPh_3$ or **2** by ^{31}P {^1H} NMR spectroscopy.

Following an initial attempt at oxidation of **2** using pyridine N-oxide, which was extremely sluggish and resulted in the formation of multiple new phosphorus species in solution, dry gaseous O_2 or *m*CPBA was explored as the oxidant. Further resistance to oxidation by O_2 was noted of compound **2** following a brief exposure via bubbling of dry O_2 into a solution of **2** in C_6D_6 for 10 min, which did not result in any detectable change by ^{31}P {^1H} NMR spectroscopy. Nevertheless, pressurizing a J-Young NMR tube containing a degassed C_6D_6 solution of **2** with O_2 (1.5 atm) slowly resulted in approximately 50% conversion to **4O** after 6 days (δ_P = −11) with concomitant formation of multiple minor unidentifiable species (Figure S27). Compound **4O** was also identified as the major product by oxidation of **2** using *m*CPBA, though it could not be isolated as a pure compound. Oxidation of NHI-supported phosphines has been demonstrated to proceed cleanly with N_2O.[36] The slow oxidation of **2**, however, can be rationalized from the large P−Se coupling constant of **4Se** ($^1J_{P-Se}$ = 990 Hz), which suggests that the parent compound **2** may be even less basic than $P(OMe)_3$.[37]

Oxidation of **2** to **4Ch** was accompanied by a phosphorus resonance shifted to lower frequency (**2**: δ_P = 123; **4S**: δ_P = 41; **4Se**: δ_P = 30, $^1J_{P-Se}$= 990 Hz; **4O**= δ_P = −11, c.f. $OP(NMe_2)_3$ δ_P = −23.4[38]) and an NHI-backbone proton resonance shifted to higher frequency (**2**: δ = 5.91; **4S**: δ = 6.06; **4Se** δ = 6.07; **4O**: δ = 6.04). This resulted from an increased π-donation from the NHI and exocyclic nitrogen in **4Ch**, as the NHC ring accumulated aromatic and zwitterionic character. Oxidation with $SiMe_3N_3$ to **3** resulted in an even more deshielded phosphorus center (δ_P = −28), without appreciable change to **2** in the NHI-backbone resonance (δ = 5.93) and was indicative of a lower degree of zwitterionic character.

Staudinger Reactivity of Bis(azido)phosphines. Racemic mixtures of chiral phosphines $\mathbf{5_R}$ were prepared from benzene solutions of compound **4S** by the addition of stoichiometric equivalents of PR_3 (where R = Me, Cy, or

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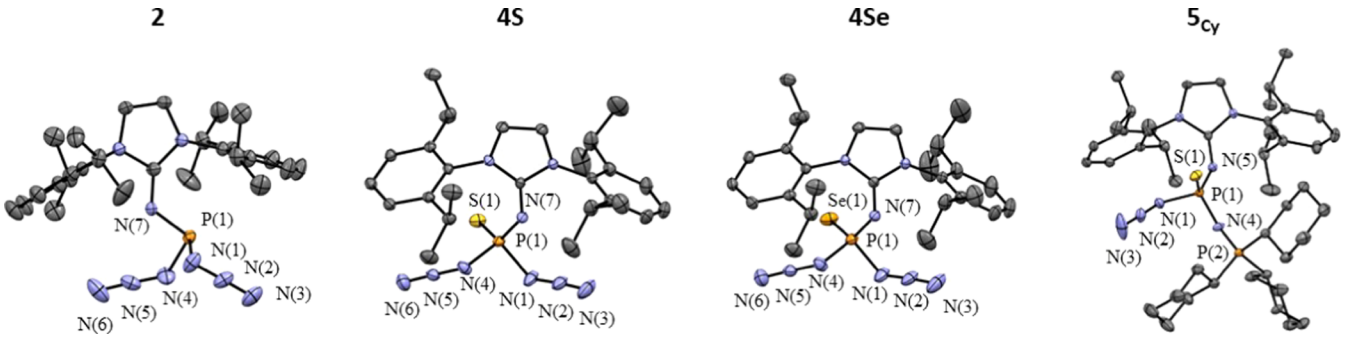
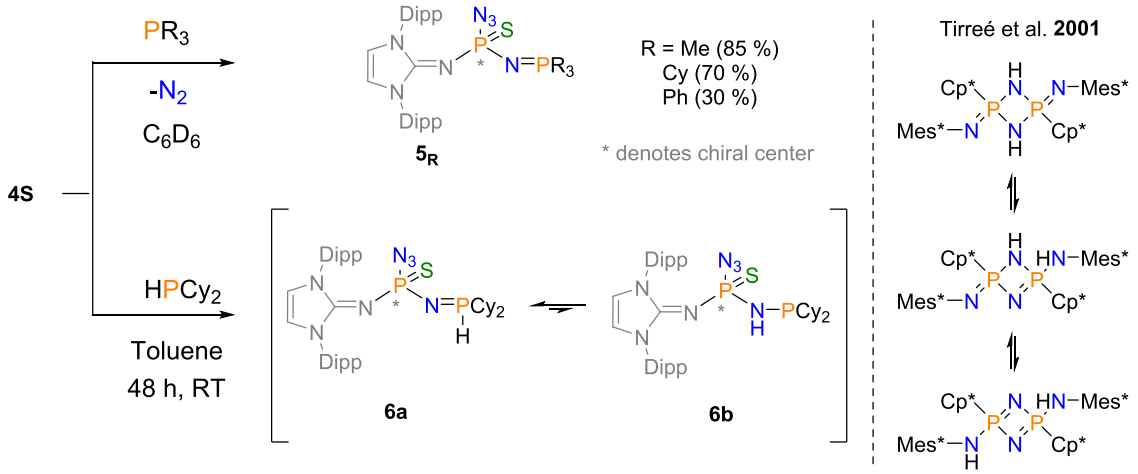


Figure 1. ORTEP drawing of **2**, **4S**, **4Se**, and $\mathbf{5_{Cy}}$. Hydrogen atoms have been omitted for clarity, and selected ellipsoids are shown at the 50% probability level. Azido, imino, and phosphinimino nitrogen atoms, phosphorus atoms, and chalcogen labels have been displayed.

Scheme 5. Chemoselective Staudinger Reactivity of Compound 4S with Tertiary and Secondary Phosphines (Left) and Example of Tautomerization via Hydride Shift (Right)



Ph) at room temperature. The rate of reaction for each derivative was correlated with the nucleophilicity of the respective phosphine.[39] Higher than stoichiometric tertiary phosphine loadings at ambient temperature resulted in an increased reaction rate and, surprisingly, did not induce a second Staudinger reaction in any of the experiments conducted. The selective formation of products $\mathbf{5_R}$ resulting from a single Staudinger reaction was confirmed via multiple spectroscopic methods (see Section S2): (a) a comparison of NHI-backbone protons' resonance with the phosphinimine substituents' ($N{=}PR_3$) integrations in the ^{1}H NMR spectra; (b) integration of the ^{31}P $\{^1H\}$ spectra that characteristically contained two doublets in a 1:1 ratio, with coupling constants consistent with a $^2J_{P-P}$ coupling;[40] (c) stretching modes of unreacted azide functional groups using FT-IR spectroscopy; (d) via electrospray ionization−mass spectroscopy (ESI-MS) detection of the expected molecular ion peak and Na^+/K^+ adducts; and, (e) structural confirmation of $\mathbf{5_{Cy}}$ by SC-XRD (vide infra, Figure 1) along with the ^{1}H and ^{31}P $\{^1H\}$ NMR spectroscopic fingerprinting of the crystals compared with the bulk powder. For the synthesis of $\mathbf{5_{Me}}$, excess PMe_3 was removed *in vacuo*; however, the removal of nonvolatile phosphines from $\mathbf{5_{Cy}}$ and $\mathbf{5_{Ph}}$ necessitated multiple triturations, which contributed to low isolated yields, despite their near-quantitative conversion, as noted by ^{31}P $\{^1H\}$ NMR spectroscopy of reaction mixture samples (Figures S42 and S50). PCy_3 was found to be sufficiently nucleophilic to achieve complete conversion of **4S** to $\mathbf{5_{Cy}}$ within 2 days when a stoichiometric loading was used. We discovered an alternative purification method for species $\mathbf{5_{Cy}}$, $\mathbf{5_{Ph}}$, and **6a**/**6b** (vide infra) that consisted of recrystallization from their respective concentrated hot pentane or hexane solutions. Reactions of **4S** with phosphines containing a P−Cl bond were not selective, likely because of N_3^-/Cl^- exchange that resulted in the formation of complex mixtures.[41]

$HPCy_2$ was also evaluated for Staudinger-type reactivity with **4S**, and the reaction was found to give rise to two species in solution (**6a** and **6b**). 1D- and 2D NMR spectroscopic experiments supported the identities of compounds **6a** and **6b**, which were formed in approximately 2:1 ratio in solution. The P(V)-N=P(V)(H) functionality of **6a** is hallmarked by a doublet-of-doublet-of triplets in the ^{1}H NMR spectrum at δ = 6.27 ($^1J_{P-H}$ = 432 Hz; $^3J_{P-H}$ = 12.2 Hz; $^3J_{H-H}$ = 3.2 Hz), while the N−H signal of the tautomerized species **6b** with P(V)-N(H)-P(III) connectivity appeared as a broad doublet of doublets at δ = 2.77 (Figure S51). Signals for **6b** in the ^{31}P $\{^1H\}$ and ^{31}P NMR spectra (Figures S55 and S56) are at higher frequency than **6a** and exhibited greater P−P coupling (δ_P = 45 and 43, $^2J_{P-P}$ = 56 Hz) than **6a** (δ_P = 39 and 24, $^2J_{P-P}$ = 12 Hz), also exhibited larger coupling than the P(V)−N-P(V) coupled compounds **5**−**7**,[42,43] and are slightly lower than P(V)−N-P(III) coupled compound **7** ($^2J_{P-P}$ = 69 Hz).[44−46] P−H connectivity of **6a** was evident in ^{31}P NMR spectrum from a pair of broad resonances about 24.4 ppm separated by 432 Hz (Figure S57). Chemical exchange of **6a** and **6b** was observed by cross peaks in ^{31}P−^{31}P EXSY at room temperature

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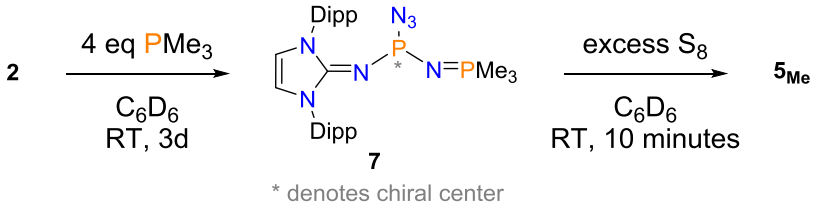
Scheme 6. Chemoselective Staudinger Reactivity of 7 with PMe_3 and Alternate Synthetic Route to 5_{Me}



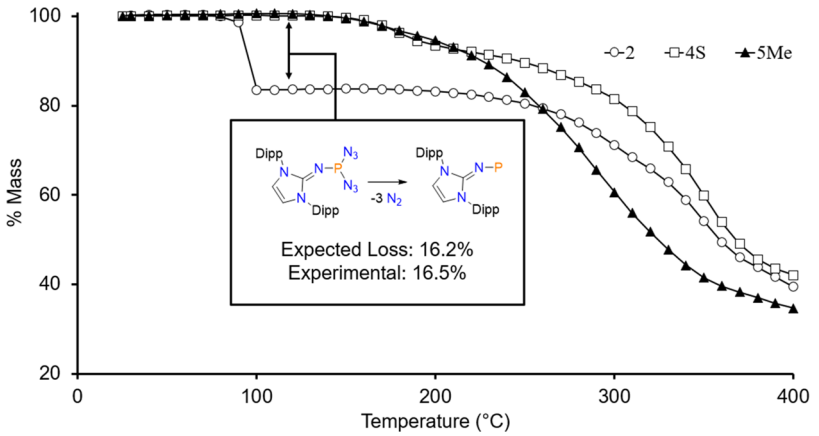


Figure 2. TGA plot of compounds **2**, **4S**, and $\mathbf{5_{Me}}$ [10 °C/min, performed in air under flow of N_2 (10 mL/min)].

(Figure S67), supporting the proposed tautomerization. Examples of imine/amine isomerization have been reported for P-alkoxyphosphaazo compounds that readily rearrange and are dependent on the length of the chain,[8] tautomerization of bis(amino)cyclodiphosph(V)azene and bis(imino)-cyclophosph(V)azane via 1,3-hydride shift (Scheme 5, right),[47] and P,O-chelating sulfonamidophosphorus ligands,[48] which have been used in heterocyclic activation of H_2.[49]

Compound **2** was observed to undergo Staudinger reactions with exogenous PMe_3 to generate compound **7** in solution via a chemoselective selective single Staudinger reaction. Acknowledging the ambiphilic nature and instability of **2** in solution, the decomposition via oligomerization was attenuated with the addition of a large excess (approximately 20 molar equivalents) of PMe_3, which allowed for complete consumption of **2** within 3 h at room temperature to produce **7** as the major species (approximately 80% of normalized ^{31}P $\{^1H\}$ NMR integrations). Attempts to purify compound **7** using hexane washes were complicated by the thermal decomposition of **7** to an unknown major species containing a P−H bond ($^1J_{P-H}$ = 560 Hz) (Section S3). Lyophilization from a frozen benzene matrix could be used to remove excess PMe_3 from the sample while minimizing thermal decomposition of **7**, although a few minor uncharacterized species remain detectable in the baseline of the ^{31}P $\{^1H\}$ NMR spectra (Figure S72). Compound **7** readily dissolved in chlorinated solvents but was unstable and rapidly decomposed to a mixture of phosphorus-containing species. A sample of **7** in C_6D_6 was stored in a foil-wrapped J-Young NMR tube at ambient temperature and monitored periodically over 3 days. In the absence of PMe_3, the species gradually decomposed to yield the same ^{31}P $\{^1H\}$ signals encountered after the washing of crude **7** with hexanes. FT-IR spectroscopic analysis of the lyophilized material confirmed that compound **7** is an azidophosphine by the presence of an intense N_3-asymmetric stretching band at 2127 cm^{-1} with two accompanying combination bands at 2064 and 1999 cm^{-1} (Figure S73).

Unlike the species **2**−**6**, which were stable in acetonitrile for ESI-HRMS analysis, the apparent instability of **7** in polar solvents resulted in the evasion of [M + 1], [M + Na], and [M + K] *m*/*z* ions from detection. The ambiphilic nature of **7**, however, resulted in the detection of a molecular ion fragment that matched for the product of a Staudinger reaction of two stoichiometric equivalents of **7** ($[2\cdot\mathbf{7}\text{-}N_2]^+$), in addition to $[\mathbf{7}\text{-}N_3]^+$. To provide more evidence toward the identity of **7**, a 50-fold excess of S_8 was added to **7** in C_6D_6 to produce two doublets in ^{31}P $\{^1H\}$ NMR spectrum matching for $\mathbf{5_{Me}}$ within 10 min (Scheme 6 and Figure S82). Gratifyingly, the dilution of this reaction mixture using acetonitrile and subsequent filtration of the cloudy mixture allowed for the detection of the characteristic molecular ion signals for $\mathbf{5_{Me}}$ via ESI-HRMS (Figures S83 and S84 and Table S1). This experiment also confirmed that the central phosphorus atom of **7** adopted some nucleophilic character.

X-ray Crystallography. The family of P(III) (**2**) and P(V) (**4S** or **4Se**) bis(azido)phosphines, as well as the Staudinger product $\mathbf{5_{Cy}}$, were analyzed via single-crystal X-ray diffraction and are visualized in Figure 1. Compound **2** exhibited tetrahedral geometry, while **4S** and **4Se** exhibited trigonal pyramidal geometries at the central phosphorus. The average $P-N_{azide}$ bond length for **2** was 1.77 Å, while the more electron-deficient P(V) species **4S** and **4Se** possessed average $P-N_{azide}$ lengths of 1.72 Å. This suggested the bis(azido)-phosphine species developed a slightly higher $P-N_{azide}$ bond order upon oxidation. More significant contractions of the $P-N_{NHI}$ bond lengths were apparent when comparing **2** (1.6290(15) Å) to the oxidized species **4S** and **4Se** (1.5750(13) and 1.5758(16) Å), respectively, as compared to the P−N bonds in triphenylphosphonium-substituted phosphinimines that range from 1.54 to 1.64 Å (∑ (covalent

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radii) P═N = 1.62 Å).[40] Compounds **2**, **4S**, and **4Se** clearly exhibited P−N_{NHI} multiple bond character.

The structure and chirality of $\mathbf{5}_{Cy}$ were confirmed as the species crystallized as a racemic mixture within the $P2_1/n$ space group. Comparing the structures of **5Cy** to **4S** revealed an elongated P−S (0.028 Å), P−N_{NHI} (0.025 Å), and P−N_{N3} (ca. 0.042 Å, averaged), while the remaining P−N bond (which underwent an azide to phosphinimine conversion) experienced a significant contraction by 0.15 Å (averaged). The electronic similarity of the phosphinimine and NHI ligands is evident in both the P−N_{NHI} and P−N_{PCy3} bond lengths (1.6001(11) and 1.5933(11) Å) and in the P−N−C and P−N−P bond angles (132.41(8) and 137.94(7)°).

Thermogravimetric analysis (TGA, Figure 2) of compound **2** revealed that a rapid mass loss of 16.5% occurred at 93 °C and is consistent with the loss of three stoichiometric equivalents of N_2 (theoretical = 16.2%). Following this event, the mass remained constant (<±0.5%) until approximately 194 °C. This suggested that compound **2** may be used as a precursor for phosphinidene chemistry in subsequent studies.[26,50] Compounds **4S** and $\mathbf{5}_{Me}$ were observed to undergo a mass loss equivalent to one N_2 moiety at higher temperatures than **2** (186 and 196 °C, respectively), and the traces for **4S** and $\mathbf{5}_{Me}$ did not suggest the formation of a stable intermediate via N_2 evolution. A melting point analysis of **4S** in a sealed capillary resulted in darkening between 135−145 °C that was indicative of decomposition. In comparison to bulky azidophosphines (R_2P-N_3) supported by tetramethylpiperidyl and/or dimethylpiperidyl ligands, which were reported to decompose between 50 and 60 °C,[51] species **2** and **4Ch** are considerably more thermally stable.

Computational Investigation. To assess the experimentally observed selectivity, a computational study was undertaken on the progression of species **4S** from its initial bisazide state (labeled **I**) to the monoazide state $\mathbf{5}_{Me}$ (labeled **II**) and, finally, into the hypothetical, doubly reacted, species **III** (Figure 3). As might be expected, both azide groups of **I** were

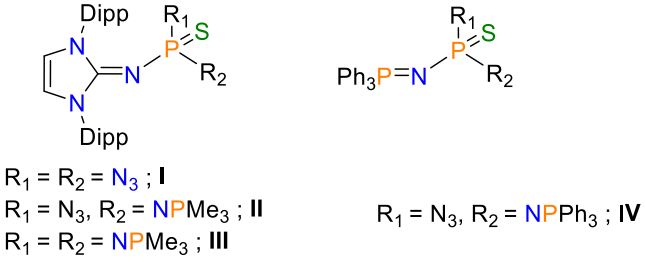

Figure 3. Molecular structures studied by DFT.

equally favorable to initiate the reaction, with no notable differences between the two species, such that the selectivity cannot be explained through a single predetermined preferential azide available attack by the PMe_3. This is in agreement with the crystalographic results, which shows both enantiomers of monoazide species $\mathbf{5}_{Me}$ are produced.

Optimized structures **I**−**III** possessed a P−S bond that was twisted nearly 90° out of the plane of the NHI moiety. The highest occupied molecular orbital (HOMO) for species **I** (−5.992 eV) and **II** (−5.246 eV) were all found to be composed of NHI π-symmetric and sulfur lone pair character (Figure 4A,B), which suggests a nucleophilic sulfur may be amenable to further functionalization. The distinct difference between species **I** and **II** is in the N_3 π^* and P−S σ^* character found in the LUMO level (−0.98 eV) of **I**, but not until LUMO + 4 (−0.023 eV) in **II** (Figure 4C,D). We propose the electronic inaccessibility of this N_3 π^* system as the main driver of the observed chemoselectivity. To test this hypothesis further, we looked at the resilient azide species **IV**[21] shown in Scheme 2 and Figure 3. This analysis revealed no significant N_3 π^* system was observed until the LUMO + 12 (0.081 eV; Section S4).

CONCLUSIONS

We report the formation of P(III) and P(V) bis(azido)-phosphine and bis(azido)phosphine chalcogenides, which undergo chemoselective Staudinger reactions to produce chiral (NHI)(azido)(phosphinimine)phosphine or (NHI)(azido)-(phosphinimine)phosphine chalcogenide at room temperature. The reactions of both **2** and **4S** with stoichiometric excessive loadings of PMe_3 were found to selectively react only once to produce **7** and $\mathbf{5}_{Me}$. Cy_2PH was nucleophilic enough to react with **4S**, and the equilibrium nature of the product was confirmed by $^{31}P-^{31}P$ EXSY. Species $\mathbf{5}_{R}$ and **6** were more thermally resilient than species **7**, which allowed recrystallization and purification from hot pentane/hexanes. Compound **7** decomposed at room temperature and generated an unknown species containing a P−H bond, as indicated by a coupling constant of 560 Hz. DFT calculations were used to offer reasoning for the chemoselectivity of **4S** with PMe_3. Kohn−Sham orbitals of the mono- and bis(azido) species reveal a sharp contrast in energetic accessibility of N_3 antibonding character. The inaccessibility of the resilient azide of **II** was also found for the known literature example of species **V** and explains the observed chemoselectivity of **4S** with various aryl and alkyl phosphines.

EXPERIMENTAL SECTION

General Considerations. All manipulations were conducted under an inert atmosphere using a nitrogen-filled glovebox or using standard Schlenk techniques. All glassware was oven-dried prior to use. All solvents were purchased from Caledon, Sigma-Aldrich, or Alfa Aesar and dried using an MBraun controlled atmosphere solvent purification system and then stored in an N_2-filled glovebox atmosphere over 3 or 4 Å molecular sieves. C_6D_6 and $CDCl_3$ were purchased from Sigma-Aldrich and predried by refluxing over CaH_2, followed by distillation and degassing by multiple freeze−pump−thaw cycles, and finally stored over 4 Å molecular sieves under an N_2 atmosphere. Synthesis of IPr*HCl,[59,60] IPr,[59] and IPrNSiMe_3[61] were prepared following literature procedures and recrystallized from concentrated solutions of ethanol, toluene, and pentane, respectively. Synthesis of IPrNPCl_2 was prepared and isolated using a slightly modified procedure.[22]

Safety Statement! Covalent azides pose an explosion risk and should be handled with extreme caution! Rigorous exclusion of water from samples should be prioritized, and use of halogenated solvents should be avoided when possible due to the possibility of forming hydrazoic acid or di(azido)methane.[62] All syntheses were performed on a submillimole scale for safety. While we never experienced any ignition or detonation while handling these species, caution should be taken to minimize exposure to shock, spark, or light. We recommend the use of a plastic spatula, electrical grounding, and a general avoidance of ground glass joints while handling these materials. The following reactions should not be scaled up without appropriate information regarding the shock or abrasion sensitivity of the azidophosphines.

All computational simulations were undertaken with the ORCA (v5.0.4) software.[63] Geometry optimizations were performed using the Becke three-parameter Lee−Yang−Parr (B3LYP) density func-

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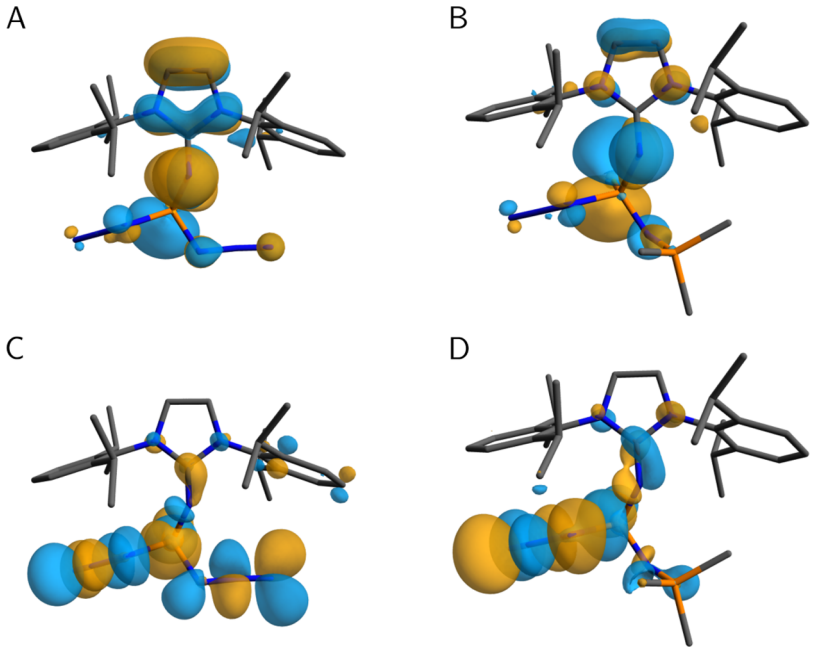

Figure 4. Kohn−Sham orbitals of **I** and **II** at the B3LYP/Def2-TZVP level of theory[52−56] with D4 dispersion correction.[57,58] Yellow color illustrates the negative phase, and blue illustrates the positive phase of orbitals. The HOMO of **I** (A) and **II** (B). The N_3 π^* character seen in **I** at the LUMO (−0.98 eV) level (C) is not observed until the LUMO+4 (−0.023 eV) level in **II** (D). Hydrogen atoms have been omitted for clarity.

tional[52−55] and the def2-TZVP basis set.[56] Atom-pairwise dispersion correction (D4) was used.[57,58] Optimized structures were confirmed to be local minima by ensuring no imaginary frequencies were obtained.

Modified Synthesis of IPrNPCl$_2$. $IPrNSiMe_3$ (1.466 g, 3.08 mmol) was dissolved in 20 mL of toluene, followed by PCl_3 (0.30 mL, 3.4 mmol). NEt_3 (0.04 mL 0.3 mmol) was then added dropwise. A bright yellow solid forms initially, but prolonged stirring results in a gradual color change to an off-white slurry. The mixture was stirred for 16 h at room temperature, and then volatiles were removed. The residue was reconstituted in 15 mL of THF, centrifuged, decanted, and washed again with THF (5 mL). Decanted THF solutions were combined, and volatiles were removed again, resulting in the isolation of an off-white, slightly yellow powder (1.426 g, 2.826 mmol, 92% yield). The purity of the resulting off-white powder was assessed by ^{1}H and ^{31}P $\{^1H\}$ NMR spectroscopy to be suitable for further reactions. Recrystallization from concentrated THF solutions at −30 °C could also be performed to increase purity if deemed necessary.

*Synthesis of IPrNP(N$_3$)$_2$ (**2**). Method 1.* $IPrNPCl_2$ (1.00 g, 1.98 mmol) was dissolved in 20 mL of acetonitrile, and then sodium azide (0.50 g, 7.7 mmol) was added in portions to a stirring solution. After 4 h, volatiles were removed, and then the residue was resuspended in 10 mL benzene, centrifuged, and decanted. Removal of volatiles results in the isolation of a white powder (0.776 g, 76% yield).

Method 2. $IPrNPCl_2$ (0.400 g, 0.9 mmol) was dissolved in 15 mL of toluene at room temperature, and neat $SiMe_3N_3$ (240 μL 1.8 mmol) was added dropwise over 5 min. The mixture was allowed to stir at room temperature for 3 days while periodically monitoring the reaction progress via ^{31}P $\{^1H\}$ NMR spectroscopy. Note (A) IPrNP(N_3)Cl (**2′**) formed *in situ* can be detected at δ = 149 ppm. Note (B) the crude product obtained via this method consistently formed with concurrent generation of **3** at −28 ppm [IPrNP-($NSiMe_3$)(N_3)$_2$].

^{1}H NMR (400 MHz, C_6D_6) δ = 7.23 (t, 2H, *p*-H, 7.8 Hz), 7.08 (d, 4H, *m*-H, 7.8 Hz), 5.91 (s, 2H, N(*CH*)$_2$N). 2.88 (sept, 4H, *CH*(CH_3)$_2$,, 6.8 Hz), 1.37 (d, 12H, CH_3, 6.8 Hz), 1.09 (d, 12H, CH_3, 6.8 Hz). **^{13}C $\{^1H\}$ NMR (100.6 MHz, C_6D_6)** δ = 147.7 (d, NC(NP)N, 27 Hz), 146.9 (*o*-C), 131.9 (ipso-C), 130.6 (*p*-C), 124.0 (*m*-C), 115.7 (N(*CH*)$_2$N), 29.0 (*CH*(CH_3)$_2$), 24.4 (*CH*$_3$), 22.6 (*CH*$_3$). **^{31}P $\{^1H\}$ NMR (162 MHz, C_6D_6)** δ = 123.1. **FT-IR (KBr pellet, cm^{-1})** 2110 and 2083. **ESI-MS** (*m*/*z*) 518.2885 [**2 + H:** 518.2904 expected], 540.2705 [**2·Na:** 540.2723 expected].

*Synthesis of IPrNP(NSiMe$_3$)(N$_3$)$_2$ (**3**).* To a stirred solution of $IPrNPCl_2$ (71.1 mg, 0.139 mmol) in 5 mL of toluene, an excess of $SiMe_3N_3$ (74 μL, 0.556 mmol) was added dropwise. The resulting mixture was then stirred at room temperature over 4 days with periodic monitoring via ^{31}P NMR spectroscopy. Removal of volatiles under reduced pressure resulted in the isolation of white powder of suitable purity by ^{1}H and ^{31}P $\{^1H\}$ NMR spectroscopy (0.0954 g, 0.12 mmol, 84% yield).

^{1}H NMR (400 MHz, C_6D_6) δ = 7.22 (t, 2H, *p*-H, 7.7 Hz), 7.10 (d, 4H, *m*-H, 7.6 Hz), 5.93 (s, 2H, N(*CH*)2N), 2.88 (sept, 4H, *CH*(CH_3)$_2$, 6.8 Hz), 1.43 (d, 12H, CH_3, 6.8 Hz), 1.07 (d, 12H, CH_3, 6.8 Hz). **^{13}C $\{^1H\}$ NMR (100.6 MHz, C_6D_6)** δ = 146.6 (*o*-C), 131.9 (ipso-C), 130.5 (*p*-C), 124.0 (*m*-C), 116.3 (N(*CH*)$_2$N), 28.9 (*CH*(CH_3)2), 24.4 (CH_3), 23.0 (CH_3), 3.48 (d, Si(CH_3)$_3$, $^3J_{P-C}$ = 5.3 Hz). [NCN not observed]. **^{31}P $\{^1H\}$ NMR (162 MHz, C_6D_6)** δ = −28.9. **FT-IR (ATR, cm^{-1})** 2140 and 2116 **ESI-MS** (*m*/*z*) 605.3387 [**3 + H:** 605.3408 expected], 627.3221 [**3·Na:** 627.3228 expected], 643.2963 [**3·K:** 643.2967 expected].

*Synthesis of IPrNPS(N$_3$)$_2$ (**4S**).* A solution of S_8 (21.0 mg, 0.0820 mmol) in 2 mL of CH_2Cl_2 was added to a solution of **2** (0.342g, 0.661 mmol) in 12 mL of CH_2Cl_2, and the vial was rinsed with one additional mL of CH_2Cl_2. The mixture was stirred at room temperature for 30 min, and then volatiles were removed. The residue was rinsed with 5 mL cyclohexane and decanted, and volatiles were removed. (0.353 g, 0.642 mmol, 95% yield).

Method 2: S_8 (31.2 mg, 0.122 mmol) was added to a solution of **2** (0.4793g, 0.926 mmol) in 15 mL of toluene, and the mixture was allowed to sit at −30 °C for 7 days, monitoring conversion by ^{31}P NMR aliquots. Volatiles were then removed, and the solids were triturated with 0.5 mL portions of cold Et_2O and pentane and recrystallized from Et_2O. (0.28 g, 0.51 mmol, 55% yield).

As an aside, a qualitative test for the presence of residual sulfur was carried out by the addition of PPh_3 to a $CDCl_3$ or CH_2Cl_2 solution of a sacrificial sample of **4S**, which lead to the rapid development of $SPPh_3$ (δ^{31}P = 42.7) if any unreacted sulfur remained.[35]

^{1}H NMR (400 MHz, C_6D_6) δ = 7.21 (dd, 2H, *p*-H, 7.7 Hz), 7.09 (d, 4H, *m*-H, 7.7 Hz), 6.06 (s, 2H, N(*CH*)$_2$N), 2.95 (sept, 4H, *CH*(CH_3)$_2$, 6.9 Hz), 1.45 (d, 12H, CH_3, 6.8 Hz), 1.04 (d, 12H, CH_3,

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6.8 Hz). **^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6)** δ = 146.7 (*o*-C), 145.8 (d, NCN, 12 Hz), 131.5 (ipso), 130.7 (*p*-H), 124.2 (*m*-C), 117.0 ($N(CH)_2N$), 28.9 ($CH(CH_3)_2$), 24.9 (CH_3), 23.1 (CH_3). **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)** δ = 40.7. **FT-IR (KBr pellet, cm^{-1})** 2134. **ESI-MS** (*m*/*z*) 572.2455 [**4S·Na:** 572.2444 expected], 588.2216 [**4S·K:** 588.2148 expected]. **Elemental Analysis** Calculated C 59.00; H 6.60; N 22.93; S 5.83. Found C 59.52; H 6.45; N 22.1; S 5.44.

*Synthesis of IPrNPSe(N$_3$)$_2$ (**4Se**).* Selenium powder (85 mg, 1.1 mmol) was added in portions to a stirred solution of **2** (517.6 mg, 0.17 mol) in 5 mL of toluene. The mixture was allowed to stir at room temperature for 7 days. The solution was filtered, and volatiles were removed *in vacuo*. Recrystallization from Et_2O/pentane resulted in the isolation of clear-colorless crystals suitable for X-ray diffraction studies. (45 mg, 0.075 mmol, 45% yield).
^{1}H NMR (400 MHz, C_6D_6) δ = 7.25−7.08 (multiplet, 2H, *p*-H), 7.09 (multiplet, 4H, *m*-H), 6.07 (s, 2H, $N(CH)_2N$), 2.97 (septet, 4H, $CH(CH_3)_2$, 6.8 Hz), 1.47 (d, 12H, $CH(CH_3)_2$, 6.8 Hz), 1.03 (d, 12H, $CH(CH_3)_2$, 6.8 Hz). **^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6)** δ = 146.6 (*o*-C), 131.5 (ipso), 130.7(*p*-C), 124.3 (*m*-C), 117.2 ($N(CH)_2N$), 28.9 ($CH(CH_3)_2$), 25.0 (CH_3), 23.2 (CH_3). **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)** δ = 30.0 ($^{1}J_{P-Se}$ = 891 Hz). **FT-IR (KBr pellet, cm^{-1})** 2132. **ESI-MS** (*m*/*z*) 598.2050 [**4Se + H:** 598.2069 expected], 620.1909 [**4Se·Na:** 620.1889 expected], 636.1659 [**4Se·K:** 636.1628 expected].

*Synthesis of IPrNPO(N$_3$)$_2$ (**4O**). Method 1.* A 0.5 mL C_6D_6 solution of **2** (10 mg, 0.19 mmol) was charged in a J-Young NMR tube. The sample was frozen and degassed three times, and the tube was evacuated a final time. O_2 gas was purged for 10 min and passed over the CaH_2 drying tube before connecting the J-young NMR tube and pressurizing J-Young with 1.5 atm O_2. The reaction was left at room temperature and wrapped in foil for 1 week.

Method 2. A solution of **2** in C_6D_6 was prepared in a nitrogen-filled glovebox and was exposed to air momentarily outside the glovebox during an addition of a couple of crystals of *m*CPBA via a spatula to the open NMR tube. NMR spectrum was collected within 15 min at room temperature, and it showed the formation of two major species. The sample decomposed to crystalline $[IPrNH_2]^+$ salts upon attempts to recrystallize species.
^{1}H NMR (400 MHz, C_6D_6) δ = 7.23 (t, 2H, *p*-H, 7.5 Hz), 7.11 (d, 4H, *m*-H, 7.5 Hz), 6.04 (s, 2H, $N(CH)_2N$), 2.85 (septet, 4H, $CH(CH_3)_2$, 6.4 Hz,), 1.44 (d, 12H, $CH(CH_3)_2$, 6.4 Hz), 1.07(d, 12H, $CH(CH_3)_2$, 6.4 Hz,). **^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6)** δ = 146.8 (*o*-C), 145.8 (NCN, $^{2}J_{P-C}$ = 10.9 Hz), 131.4 (ipso), 130.7(*p*-H), 124.1 (*m*-C), 116.5 ($N(CH)_2N$), 29.0 ($CH(CH_3)_2$), 24.5 (CH_3), 22.8 (CH_3). **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)** δ = −11.3

*Synthesis of IPrNP(S)(N$_3$)(NPMe$_3$) (**5$_{Me}$**).* To a solution of **4S** (0.055 g, 0.1 mmol) in 2 mL of toluene, PMe_3 (32 μL, 0.32 mmol) was added neat and allowed to stir at room temperature until complete consumption of **4S** was determined by ^{31}P NMR analysis. The removal of volatiles *in vacuo*, followed by trituration with a minimal amount of pentane, resulted in the isolation of an off-white, sticky residue (0.0413 g, 69% yield).
^{1}H NMR (400 MHz, C_6D_6) δ = 7.22 (multiplet, 2H, *p*-H), 7.15 (multiplet, 4H, *m*-H), 6.11 (s, 2H, $N(CH)_2N$), 3.28 (septet, 4H, $CH(CH_3)_2$, 6.6 Hz), 1.62 (d, 6H, CH_3, 6.6 Hz), 1.58 (d, 6H, CH_3, 6.6 Hz), 1.74 (d, 6H*, CH_3, 6.8 Hz), 1.15 (d, 6H*, CH_3, 6.8 Hz) {*= overlapped doublets; integration total equals 12 protons}, 0.78 (9H, d, $P(CH_3)_3$, 13.3 Hz). **^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6)** δ = 147.6 (*o*-C), 147.4 (*o*-C), 145.0 (d, NCN, 10.6 Hz), 133.5 (ipso), 129.6 (*p*-C), 123.8 (*m*-C), 123.8 (*m*-C), 116.1 ($N(CH)_2N$), 28.81 (CH_3), 28.79 (CH_3), 25.01 (CH_3), 24.99 (CH_3), 23.5 (d, $P(CH_3)_3$, 10.4 Hz). **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)** δ = 36.3 ([N]*P*(N_3)($NPMe_3$), 17 Hz), 15.3 ([N]P(N_3)(*N*PMe_3), 17 Hz). **FT-IR (KBr pellet, cm^{-1})**: 2113 **ESI-MS** (*m*/*z*) 598.3006 [**5$_{Me}$ + H:** 598.3005 expected], 620.2837 [**5$_{Me}$·Na:** 620.2825 expected], 636.2580 [**5$_{Me}$·K:** 636.2564 expected]. **Elemental Analysis** Calculated C 60.28; H 7.59; N 16.40; S 5.36. Found C 60.71; H 7.47; N 15.20; S 5.06.

*Synthesis of IPrNP(S)(N$_3$)(NPCy$_3$) (**5$_{Cy}$**).* To a solution of **4S** (55 mg, 0.1 mmol) in 2 mL of benzene, PCy_3 (30 mg, 0.11 mmol) was added as a solution in 2 mL of benzene and stirred at room temperature over 2 days. Removal of volatiles resulted in the isolation of crude colorless sticky-oily residue. Recrystallization was performed by suspension of the sticky residue in 8 mL of pentane, followed by gentle heating, hot filtration through a Celite filter pipette, concentrating the solution to approximately 4 mL *in vacuo*, and then finally allowing the solution to sit undisturbed at −30 °C for 1 week. A few crystals were isolated and used for X-ray analysis. The remaining crystals were decanted and dried under reduced pressure (31 mg, 0.039 mmol. 39% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (t, 2H, *p*-H, 7.8 Hz), 7.28−7.24 (m, 4H, overlapped partially with $CHCl_3$ signal, *m*-H), 6.52 (s, 2H, $N(CH)_2N$), 3.15−3.01 (m, 4H, $CH(CH_3)_2$), 1.98−1.83 (m, 3H, $P-CH(C_5H_{10})$), 1.77−1.50 (m, 15H, Cy), 1.47−1.36 (overlapped doublets, 12H, 6.6 Hz, CH_3), 1.23−1.16 (overlapped doublets, 12H, 4.18 Hz, CH_3). **^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6)** δ = 147.4 (*o*-C), 147.2 (*o*-C), 143.3 (NCN,[detected by heteronuclear multiple bond correlation (HMBC) spectroscopy]), 133.3 (ipso), 129.4 (*p*-C), 123.71 (*m*-C), 123.67 (*m*-C), 116.3 ($N(CH)_2N$), 34.6 (dd, P-Cy(H), $^{1}J_{P-C}$ = 58.3; $^{3}J_{P-C}$ = 5.2 Hz), 26.9 (d, Cy, $^{3}J_{P-C}$ = 11.4 Hz), 26.4 (dd, Cy, $^{2}J_{P-C}$ = 6.4 Hz, $^{4}J_{P-C}$ = 1.8 Hz), 26.0 ($P-CH(CH_2)_2CH_2$), 25.12 and 25.09 (CH_3), 23.5 and 23.2 (CH_3). **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)** δ = 25.5 (d, PCy_3, 30 Hz,) 25.1 (d, *P*(S)-N = P, 30 Hz,). **FT-IR (KBr pellet, cm^{-1})** 2117 **ESI-MS** (*m*/*z*) 802.4895 [**5$_{Cy}$ + H:** 802.4883 expected], 803.4925 [**5$_{Cy}$ + 2H:** 803.4961 expected], 824.4699 [**5$_{Cy}$·Na:** 824.4703 expected], 840.4438 [**5$_{Cy}$·K:** 840.4442 expected].

*Synthesis of IPrNP(S)(N$_3$)(NPPh$_3$) (**5$_{Ph}$**).* Method 1: A 1 mL solution of PPh_3 in C_6D_6 was added to **4S** and sealed in a J-Young NMR tube. The reaction was monitored periodically by ^{31}P {^{1}H} NMR spectroscopy, and the sample was heated at 70 °C in an oil bath until complete consumption of starting PPh_3 and **4S** evident via ^{31}P {^{1}H} NMR spectroscopy. Volatiles were removed under vacuum to result in the isolation of a sticky-oily residue. Trituration of this residue with 5 × 1 mL of pentane resulted in collection of a fine white powder. Method 2: Solid PPh_3 (42.1 mg, 0.16 mmol) was added to a stirring solution of **4S** (55.0 mg, 0.1 mmol) in 2 mL of toluene at room temperature for 3 weeks. Two sequential recrystallizations from concentrated pentane solutions at −30 °C for 16 h and 2h, respectively, allowed for the isolation of a fine white powder free of PPh_3 (25.1 mg, 34% yield).
^{1}H NMR (400 MHz, C_6D_6) δ = 7.62 (dd, 4H, *o*-Ph, 6.9 and 17.2 Hz), 7.26 (t, 2H, *p*-H 7.6 Hz), 7.22 (d, 2H, *o*-H, 7.6 Hz), 7.15 (partially overlapped with solvent signal, 2H, *o*-H), 7.02 (partially overlapped with PPh_3, 3H), 6.98 (td, 6H, *m*-Ph, 2.8 Hz & 7.6 Hz), 6.14 (s, 2H, $N(CH_2)_2N$), 3.36 (septet, 2H, $CH(CH_3)_2$, 6.8 Hz,), 3.29 (septet, 2H, $CH(CH_3)_2$, 6.8 Hz), 1.60 (d, 6H, CH_3, 6.8 Hz), 1.55 (d, 6H, CH_3, 6.8 Hz), 1.18 (d, 6H, CH_3, 7.6 Hz), 1.16 (d, 6H, CH_3, 7.6 Hz). **^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6)** δ = 147.5 (*o*-Dipp), 147.3(*o*-Dipp), 144.7 (confirmed by HMBC, NCN), 133.3 (ipso-Dipp), 133.0 (d, *o*-Ph, $^{2}J_{P-C}$ = 10.6 Hz), 131.1 (d, $^{3}J_{P-C}$ = 3.0 Hz, *m*-Ph), 129.6 (*p*-Dipp), 128.2 (d, ipso-Ph, $^{1}J_{P-C}$ = 17.0 Hz), 128.0 (br s, *p*-Ph), 124.0 (*m*-Dipp), 123.9 (*m*-Dipp), 116.2 ($N(CH)_2N$), 128.91 ($CH(CH_3)_2$), 128.89 ($CH(CH_3)_2$), 25.02 ($CH(CH_3)_2$), 24.97($CH-(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$). **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)** δ = 31.1 (d, 36 Hz), 5.0 (d, 36 Hz). **FT-IR (KBr pellet, cm^{-1})** 2116 **ESI-MS** (*m*/*z*) 784.3520 [**5$_{Ph}$ + H:** 784.3475 expected], 785.3549 [**5$_{Ph}$ + 2H:** 785.3553 expected], 806.3330 [**5$_{Ph}$ + Na:** 806.3294 expected], 807.3371 [**5$_{Ph}$ + H + Na:** 807.3372 expected].

*Synthesis of IPrNP(S)(N$_3$)[NP(H)Cy$_2$] (6a) and IPrNP(S)(N$_3$)[N(H)-PCy$_2$] (**6b**).* $HPCy_2$ was added to a solution of **4S** in benzene and allowed to stir at room temperature over 2 days. Complete consumption of **4S** was determined via ^{31}P {^{1}H} NMR analysis. The volatiles were removed *in vacuo*, followed by a resuspension of the sticky residue in 8 mL of hot pentane. Hot filtration was performed through a Celite filter pipette, and the filtrate was subsequently concentrated approximately to 4 mL *in vacuo*. Storage of the turbid solution at −30 °C for 1 week resulted in the formation of spherical crystals, which were unsuitable for X-ray diffraction studies. Note: due to the equilibrium of **6a** and **6b** in solution, we could not unambiguously assign each signal, and resonances for the aryl, methyl,

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and cyclohexyl groups for both species are overlapping. Fortunately, the backbone protons and P−H coupled signals are well separated and easily observed. A combination of 2D NMR experimental spectra allowed for the partial assignment of individual isopropyl groups. **6a** and **6b** appear in a 2:1 ratio in C_6D_6. Due to the flexible nature and the complexity of signals assigning cyclohexyl carbons, not all carbon signals could be unambiguously assigned. Unambiguous signals assignable via 2D correlational spectra are reported below for their respective compounds. Ambiguously assigned "CH_2" cyclohexyl carbons were validated by phasing in heteronuclear single quantum coherence (HSQC) experiment: **^{13}C {^{1}H} NMR (151 MHz, C_6D_6)** δ 27.50, 27.48, 27.42, 27.40, 27.37, 27.33, 27.29, 27.25, 27.21, 27.16, 26.91, 26.86, 26.76, 26.64, 26.53, 26.52, 26.45, 26.42, 26.34, 26.26, 26.25, 26.18, 25.97, 25.85. **FT-IR (KBr pellet, cm^{-1})** 2124. **ESI-MS** (m/z) 720.4078 [**6** + **H**: expected 720.4101], 742.3898 [**6+Na**: expected 742.3920], 758.3637 [**6+K**: expected 758.3659]. **Elemental Analysis** Calculated C 65.05; H 8.26; N 13.62; S 4.45. Found C 66.07; H 8.34; N 13.44; S 4.07.

6a: **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.29−7.23 (m (overlapped with 6b), 2H, *p*-Dipp), 7.22−7.12 (m (overlapped with 6b), 4H, *m*-Dipp), 6.27 (ddt, 1H, P−N = P(*H*), $^1J_{P-H}$ = 435.2 Hz, $^3J_{P-H}$ = 12.0 Hz, $^3J_{H-H}$ = 3.4 Hz), 6.13 (s, 2H, (NC*H*)$_2$), 3.38 (sept, 2H, C*H*(CH$_3$)$_2$, 6.7 Hz), 3.25 (sept, 2H, C*H*(CH$_3$)$_2$, 6.8 Hz), 1.66 (d (overlapped with Cy resonances), 6H, CH$_3$, 6.8 Hz), 1.58 (d (overlapped with Cy resonances), 6H, CH$_3$, 6.8 Hz), 1.17 (d (overlapped with Cy and 6b methyl resonances), 6H, CH$_3$, 6.8 Hz), 1.15 (d (overlapped with Cy resonances), 6H, CH$_3$, 6.8 Hz), 1.92−0.38 (m (overlapped with methyl and pentane signals, 22H + 24H [43H] found when excluding known regions of *n*-hexane and pentane). **^{13}C {^{1}H} NMR (151 MHz, C_6D_6)** δ = 147.9 (*o*-Dipp), 147.7 (*o*-Dipp), 145.8 (dd, NCN, $^2J_{P-C}$ = 11.2 Hz and $^4J_{P-C}$ = 2.8 Hz), 133.8 (ipso-Dipp), 130.05 (*p*-Dipp), 124.3 (overlapped with **6b**, *m*-Dipp), 124.1 (*m*-Dipp), 116.7 (N(*C*H)$_2$N), 33.8−33.4, multiplet, P−C$_{cy}$, $^1J_{P-C}$ approximately 28 Hz, $^3J_{P-C}$ approximately 4 Hz), 33.1 (dd, P−C$_{cy}$, $^1J_{P-C}$ = 31.6 Hz and $^3J_{P-C}$ = 4.3 Hz), 29.7 (d, P−CH(*C*H$_2$)$_2$, $^2J_{P-C}$ = 20.1 Hz), 29.3 ([overlapped with **6b**], CH(*C*H$_3$)$_2$), 29.1 ([overlapped with 6b], *C*H(CH$_3$)$_2$), 28.9 (d, P−CH(*C*H$_2$)$_2$, $^2J_{P-C}$ = 20.1 Hz), 25.6 (CH$_3$), 25.5 (CH$_3$), 25.5(CH$_3$), 25.3(CH$_3$), 24.1 (CH$_3$), 23.8 (CH$_3$). **^{31}P {^{1}H} (243 MHz, C_6D_6)** δ = 39.1 (d, 1P, *P*(S), $^2J_{P-P}$ = 12.8 Hz), 24.4 (d, 1P, *P*(H)Cy$_2$, $^2J_{P-P}$ = 12.8 Hz). **^{31}P (243 MHz, C_6D_6)** δ = 39.1 (dd, 1P, *P*(S), $^2J_{P-P}$ = 12.8 Hz, $^3J_{P-H}$ = 12.1 Hz), 24.4 (broad d, 1P, *P*(H)Cy$_2$, $^1J_{P-H}$ = 434 Hz).

6b: **^{1}H NMR (600 MHz, C_6D_6)** δ = 7.29−7.23 (m (overlapped with **6a**), 2H, *p*-Dipp), 7.22−7.12 (m (overlapped with **6a**), 4H, *m*-Dipp), 6.08 (s, 2H, (NC*H*)$_2$), 3.20 (sept, 2H, C*H*(CH$_3$)$_2$, 6.8 Hz), 3.12 (sept, 2H, C*H*(CH$_3$)$_2$, 6.8 Hz), 2.77 (dd, 1H, PN(*H*)P, $^2J_{P-H}$ = 9.8 Hz & $^2J_{P-H}$ = 6.8 Hz), 1.60 (d (overlapped with Cy resonances), 6H, CH$_3$, 6.8 Hz), 1.57 (d (overlapped with Cy resonances), 6H, CH$_3$, 6.8 Hz), 1.12 (d (overlapped with Cy and **6b** methyl resonances), 6H, CH$_3$, 6.8 Hz), 1.09 (d (overlapped with Cy resonances), 6H, CH$_3$, 6.8 Hz), 1.69−1.06 (m overlapped with methyl and pentane signals, 22H). **^{13}C {^{1}H} NMR (151 MHz, C_6D_6)** δ = 147.6 (*o*-Dipp), 147.4 (*o*-Dipp), 147.1 (d, NCN, $^2J_{P-C}$ = 11.0 Hz), 133.1 (ipso-Dipp), 130.6 (*p*-Dipp), 124.5 (*m*-Dipp), 124.3 (overlapped with 6a, *m*-Dipp), 117.3 (N(*C*H)$_2$N), 36.5 (dt, P−C$_{cy}$, $^1J_{P-C}$ = 16.3 Hz and $^3J_{P-C}$ = 4.7 Hz), 32.6 (d, P−CH(*C*H$_2$)$_2$, $^2J_{P-C}$ = 19.0 Hz), 30.2 (d, P−CH(*C*H$_2$)$_2$, $^2J_{P-C}$ = 10.1 Hz), 29.3 ([overlapped with **6a**], *C*H(CH$_3$)$_2$), 29.1 ([overlapped with **6a**], *C*H(CH$_3$)$_2$), 25.6 (CH$_3$), 25.6 (CH$_3$), 25.2 (CH$_3$), 24.1 (CH$_3$), 24.0 (CH$_3$), 23.4 (CH$_3$). **^{31}P {^{1}H} (243 MHz, C_6D_6)** δ = 45.7 (d, 1P, *P*(S), $^2J_{P-P}$ = 56.5 Hz), 43.8(d, 1P, *P*Cy$_2$, $^2J_{P-P}$ = 56.5 Hz). **^{31}P (243 MHz, C_6D_6)** δ = 45.7 (dd, 1P, *P*(S), $^2J_{P-P}$ = 56.5 Hz, $^2J_{P-H}$ = 9.6 Hz), 43.8 (broad d, 1P, *P*Cy$_2$, $^2J_{P-P}$ = 56.5 Hz).

*Synthesis of IPrNPN$_3$NPMe$_3$ (**7**).* Method (1) To a solution of **2** (0.040g, 0.077 mmol) in 2 mL of benzene, a large excess of PMe_3 (ca. 150 μL, 1.5 mmol) was added neat to the stirred solution. The reaction progress was monitored by taking small aliquots for ^{31}P {^{1}H} NMR spectroscopic analysis. Complete consumption of **2** was reached within 3 h at room temperature, and then the solution was subsequently placed into a freezer at −30 °C for 5 min. The frozen mixture was quickly placed under vacuum within a precooled cold well, and the excess PMe_3 and solvent were removed while maintaining a low temperature, resulting in the isolation of a very pale yellow solid (0.030 g, 69% yield). Note: attempts to isolate **7** following analogous procedures to 5_R using hexane washes resulted in decomposition. Both the undissolved residue and the hexanes rising contained the same decomposition product as the major species, determined by ^{31}P {^{1}H} NMR spectroscopy.

^{1}H NMR (400 MHz, C_6D_6) δ = 7.23 (t, 2H, *p*-Dipp, 7.0 Hz), 7.14−7.05 (m, 4H, *m*-Dipp), 5.96 (s, 2H, N(CH$_2$)$_2$N), 3.33−3.17 (br m, 2H, C*H*(CH$_3$)$_2$), 3.17−3.04 (br m, 2H, C*H*(CH$_3$)$_2$), 1.52−1.43 (br m, 12H, CH$_3$, 9.2 Hz), 1.17 (d, 12H, CH$_3$, 7.1 Hz), 0.80 (d, 9H, NP(C*H*$_3$)$_3$, 13.7 Hz). **^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6)** δ = 147.9 (br s, *o*-Dipp), 147.2 (br s, *o*-Dipp), 146.7 (d, NCN, 18.1 Hz), 134.2 (s, ipso-Dipp), 129.5 (s, *p*-Dipp), 123.6 (br s, *m*-Dipp), 123.5 (br s, *m*-Dipp), 115.1 (N(CH$_2$)$_2$N), 28.9 (br s, CH(CH$_3$)$_2$), 24.6 (s, CH$_3$), 22.9 (br s, CH$_3$), 22.6 (br s, CH$_3$), 17.7 (dd, NP(*C*H$_3$)$_3$, $^1J_{P-C}$ = 65.7 Hz, $^3J_{P-C}$ = 5.7 Hz). **^{31}P {^{1}H} NMR (162 MHz, C_6D_6)** 133.1 (d, IPrN-*P*, $^2J_{PP}$ = 67 Hz), 11.4 (d, N*P*(CH$_3$)$_3$, $^2J_{PP}$ = 67 Hz). **FT-IR (KBr pellet, cm^{-1})** 2127 (antisymmetric N_3 stretch), 2064 (combination band of antisymmetric N_3 stretch: 1260 and 803 cm^{-1}), 1999 (combination band of antisymmetric N_3 stretch: 1260 and 739 cm^{-1}). **ESI-MS** (m/z) 523.3126 [M-N_3: 523.3114 expected], 524.3158 [M + H − N_3: 524.3192 expected], 1103.6465 [2*M + H − N_2: 1103.6435].

Reaction of 7 with Excess S_8 to Generate 5_{Me}. S_8 (12.0 mg, 0.0468 mmol) was weighed into a vial and was dissolved in 1 mL of C_6D_6 and then added to a vial containing minimally decomposed **7** (4.0 mg, 0.0071 mmol). The solution was transferred into an NMR tube and analyzed by ^{1}H and ^{31}P {^{1}H} NMR spectroscopy within 10 min of mixing. 200 μL of this solution was added to 800 μL of acetonitrile and was then filtered through a filter pipette. 50 μL of this solution was then diluted to 1 mL in acetonitrile for ESI-MS analysis (Section S3).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c00120.

Experimental methods and spectra of **1**−**7**, sulfurization of **7** and decomposition analysis of **7**; computational methods and details; crystallographic refinement strategies, asymmetric units, and crystallographic collection and refinement details table for **2**, **4S**, **4Se**, and **5$_{Cy}$**; and unit cell parameters of the indexed minor phase of **4S**. (PDF)

Accession Codes

CCDC 2324390−2324393 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Mikko Karttunen − *Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada; Department of Physics and Astronomy, The University of Western Ontario, London, Ontario N6A 3K7, Canada;* orcid.org/0000-0002-8626-3033; Email: mkarttu@uwo.ca

Paul J. Ragogna − *Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada; Surface Science Western, London, Ontario N6G 0J3,*

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Canada; orcid.org/0000-0003-2727-7635;
Email: pragogna@uwo.ca

Authors

John L. Lortie − *Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada*
Matthew Davies − *Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada*
Paul D. Boyle − *Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.inorgchem.4c00120

Author Contributions

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Dehnicke, K.; Weller, F. Phosphorane Iminato Complexes of Main Group Elements. *Coord. Chem. Rev.* **1997**, *158*, 103−169.
(2) Palacios, F.; Aparicio, D.; Rubiales, G.; Alonso, C.; de los Santos, M. J. Synthetic Applications of Intramolecular Aza-Wittig Reaction for the Preparation of Heterocyclic Compounds. *Curr. Org. Chem.* **2009**, *13*, 810−828.
(3) Lao, Z.; Toy, P. H. Catalytic Wittig and Aza-Wittig Reactions. *Beilstein J. Org. Chem.* **2016**, *12*, 2577−2587.
(4) Ochiai, T.; Franz, D.; Inoue, S. Applications of N-Heterocyclic Imines in Main Group Chemistry. *Chem. Soc. Rev.* **2016**, *45* (22), 6327−6344.
(5) Kuhn, N.; Fawzi, R.; Steimann, M.; Wiethoff, J.; Bläser, D.; Boese, R. Synthese Und Struktur von 2-Imino-1,3-Dimethylimidazolin/Synthesis and Structure of 2-Imino-1,3-Dimethylimidazoline. *Z. Naturforsch. B* **1995**, *50* (12), 1779−1784.
(6) Kuhn, N.; Fawzi, R.; Steimann, M.; Wiethoff, J. Derivate Des Imidazols, XVII. Synthese Und Eigenschaften von Dichlor(1,3-Dimethyl-2-Imidazol-2-Ylidenimino)-Phosphan − Ein Methylenamino-Substituent Mit Ungewöhnlichen Donoreigenschaften. *Chem. Ber.* **1996**, *129* (4), 479−482.
(7) Staudinger, H.; Meyer, J. Über Neue Organische Phosphorverbindungen III. Phosphinmethylenderivate Und Phosphinimine. *Helv. Chim. Acta* **1919**, *2* (1), 635−646.
(8) Gololobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. Sixty Years of Staudinger Reaction. *Tetrahedron* **1981**, *37* (3), 437−472.
(9) Tian, W. Q.; Wang, Y. A. Mechanisms of Staudinger Reactions within Density Functional Theory. *J. Org. Chem.* **2004**, *69* (13), 4299−4308.
(10) Leffler, J. E.; Temple, R. D. Staudinger Reaction between Triarylphosphines and Azides. Mechanism. *J. Am. Chem. Soc.* **1967**, *89* (20), 5235−5246.
(11) Bebbington, M. W. P.; Bourissou, D. Stabilised Phosphazides. *Coord. Chem. Rev.* **2009**, *253* (9), 1248−1261.
(12) Hinz, A.; Schulz, A.; Villinger, A.; Wolter, J.-M. Cyclo-Pnicta-Triazanes: Biradicaloids or Zwitterions? *J. Am. Chem. Soc.* **2015**, *137* (11), 3975−3980.
(13) Seidl, M.; Kuntz, C.; Bodensteiner, M.; Timoshkin, A. Y.; Scheer, M. Reaction of Tungsten−Phosphinidene and − Arsinidene Complexes with Carbodiimides and Alkyl Azides: A Straightforward Way to Four-Membered Heterocycles. *Angew. Chem., Int. Ed.* **2015**, *54* (9), 2771−2775.
(14) Alexandrova, A. V.; Mašek, T.; Polyakova, S. M.; Císařová, I.; Saame, J.; Leito, I.; Lyapkalo, I. M. Synthesis of Electron-Rich Sterically Hindered P1 Phosphazene Bases by the Staudinger Reaction. *Eur. J. Org. Chem.* **2013**, *2013* (9), 1811−1823.
(15) Bock, H.; Schnöller, M. Proof of Nγ Nβ-Elimination from Staudinger Adducts R3P = Nγ-Nβ-Nα-X by 15N-Isotopic Labeling. *Angew. Chem., Int. Ed.* **1968**, *7* (8), 636.
(16) Riesel, L.; Friebe, R.; Sturm, D. Synthesis and Reactivity of N-Phosphanyl Phosphazenes. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1993**, *76* (1−4), 207−210.
(17) Widauer, C.; Grützmacher, H.; Shevchenko, I.; Gramlich, V. Insights into the Staudinger Reaction: Experimental and Theoretical Studies on the Stabilization of Cis-Phosphazides. *Eur. J. Inorg. Chem.* **1999**, *1999* (10), 1659−1664.
(18) Wilson, W. W.; Clough, A. J.; Haiges, R.; Rahm, M.; Christe, K. O. Syntheses of Diphenylaminodiazidophosphane and Diphenylaminofluoroazidophosphane. *Inorg. Chem.* **2015**, *54* (24), 11859−11867.
(19) Weigand, J. J.; Feldmann, K.-O.; Henne, F. D. Carbene-Stabilized Phosphorus(III)-Centered Cations [LPX2]+ and [L2PX]2+ (L = NHC; X = Cl, CN, N3). *J. Am. Chem. Soc.* **2010**, *132* (46), 16321−16323.
(20) Riesel, L.; Friebe, R.; Bergemann, A. Detlef/Sturm. Azidophosphanes: Attractive Starting Materials for the Preparation of Phosphazenes. *Heteroat. Chem.* **1991**, *2* (4), 469−472.
(21) Götz, N.; Herler, S.; Mayer, P.; Schulz, A.; Villinger, A.; Weigand, J. J. On the Staudinger Reaction of SP(N3)3 with PPh3 and(Me3Si)2N−(Me3Si)N−PPh2. *Eur. J. Inorg. Chem.* **2006**, *2006* (10), 2051−2057.
(22) Roy, M. M. D.; Miao, L.; Ferguson, M. J.; McDonald, R.; Rivard, E. An Unexpected Staudinger Reaction at an N-Heterocyclic Carbene-Carbon Center. *Can. J. Chem.* **2018**, *96* (6), 543−548.
(23) Dielmann, F.; Back, O.; Henry-Ellinger, M.; Jerabek, P.; Frenking, G.; Bertrand, G.; Fabian, D.; Olivier, B.; Martin, H.-E.; Paul, J.; Gernot, F.; Guy, B. A Crystalline Singlet Phosphinonitrene: A Nitrogen Atom−Transfer Agent. *Science* **2012**, *337* (6101), 1526−1528.
(24) Schoeller, W.; Rozhenko, A. B. On the Stabilisation of a Singlet Nitrene by the Phosphaniminato and Related Imine-Type Substituents, a Quantum Chemical Investigation. *Eur. J. Inorg. Chem.* **2001**, *2001* (3), 845−850.
(25) Dielmann, F.; Bertrand, G. Reactivity of a Stable Phosphinonitrene towards Small Molecules. *Chem. − Eur. J.* **2015**, *21* (1), 191−198.
(26) Cowley, A. H.; Gabbai, F.; Schluter, R.; Atwood, D. New Approaches to the Generation of Phosphinidenes. *J. Am. Chem. Soc.* **1992**, *114* (8), 3142−3144.
(27) Mardyukov, A.; Keul, F.; Schreiner, P. R. Isolation and Characterization of the Free Phenylphosphinidene Chalcogenides C6H5P = O and C6H5P = S, the Phosphorous Analogues of Nitrosobenzene and Thionitrosobenzene. *Angew. Chem., Int. Ed.* **2020**, *59* (30), 12445−12449.
(28) Eckhardt, A. K.; Riu, M.-L. Y.; Müller, P.; Cummins, C. C. Frustrated Lewis Pair Stabilized Phosphoryl Nitride (NPO), a Monophosphorus Analogue of Nitrous Oxide (N2O). *J. Am. Chem. Soc.* **2021**, *143* (50), 21252−21257.

(29) Eckhardt, A. K.; Riu, M.-L. Y.; Müller, P.; Cummins, C. C. Staudinger Reactivity and Click Chemistry of Anthracene (A)-Based Azidophosphine N3PA. *Inorg. Chem.* **2022**, *61* (3), 1270−1274.
(30) Eckhardt, A. K.; Riu, M.-L. Y.; Ye, M.; Müller, P.; Bistoni, G.; Cummins, C. C. Taming Phosphorus Mononitride. *Nat. Chem.* **2022**, *14* (8), 928−934.
(31) Wünsche, M. A.; Mehlmann, P.; Witteler, T.; Buß, F.; Rathmann, P.; Dielmann, F. Imidazolin-2-Ylidenaminophosphines as Highly Electron-Rich Ligands for Transition-Metal Catalysts. *Angew. Chem., Int. Ed.* **2015**, *54* (40), 11857−11860.
(32) Witteler, T.; Darmandeh, H.; Mehlmann, P.; Dielmann, F. Dialkyl(1,3-Diarylimidazolin-2-Ylidenamino)Phosphines: Strongly Electron-Donating, Buchwald-Type Phosphines. *Organometallics* **2018**, *37* (18), 3064−3072.
(33) Cabré, A.; Riera, A.; Verdaguer, X. P-Stereogenic Amino-Phosphines as Chiral Ligands: From Privileged Intermediates to Asymmetric Catalysis. *Acc. Chem. Res.* **2020**, *53* (3), 676−689.
(34) Eckart, A.; Lux, K.; Karaghiosoff, K. Iminophosphoranyl Dichlorophosphines R3PNPCl2. *Z. Anorg. Allg. Chem.* **2014**, *640* (5), 962−967.
(35) Nguyen, T. B. Convenient Synthesis of Triphenylphosphine Sulfide from Sulfur and Triphenylphosphine. *Clean Technol.* **2022**, *4*, 234−238.
(36) Buß, F.; Rotering, P.; Mück-Lichtenfeld, C.; Dielmann, F. Crystalline, Room-Temperature Stable Phosphine−SO2 Adducts: Generation of Sulfur Monoxide from Sulfur Dioxide. *Dalton Trans.* **2018**, *47* (31), 10420−10424.
(37) McFarlane, W.; Rycroft, D. S. Studies of Organophosphorus Selenides by Heteronuclear Magnetic Triple Resonance. *J. Chem. Soc., Dalton Trans.* **1973**, No. 20, 2162−2166.
(38) Muller, N.; Lauterbur, P. C.; Goldenson, J. Nuclear Magnetic Resonance Spectra of Phosphorus Compounds. *J. Am. Chem. Soc.* **1956**, *78* (15), 3557−3561.
(39) Maraval, A.; Magro, G.; Maraval, V.; Vendier, L.; Caminade, A.-M.; Majoral, J.-P. Functionalized Phosphorus Derivatives of Salpen-like Compounds: Synthesis and Preliminary Complexation Studies. *J. Organomet. Chem.* **2006**, *691* (7), 1333−1340.
(40) Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley, 1993.
(41) Paciorek, K. L. Preparation of Linear Phosphonitrilic Derivatives. *Inorg. Chem.* **1964**, *3* (1), 96−100.
(42) Cupertino, D. C.; Keyte, R. W.; Slawin, A. M. Z.; Woollins, J. D. Synthesis and Coordination Chemistry of Tetrabutyldithioimido-diphosphinates. *Polyhedron* **1999**, *18* (5), 707−716.
(43) Currie, I.; Sleebs, B. E. Synthesis of Acyl Phosphoramidates Employing a Modified Staudinger Reaction. *Org. Lett.* **2021**, *23* (2), 464−468.
(44) Colquhoun, I. J.; McFarlane, W. Studies of Phosphorus−Phosphorus Nuclear-Spin Coupling in Species with Phosphorus−Nitrogen Bonds. *J. Chem. Soc., Dalton Trans.* **1977**, No. 17, 1674−1679.
(45) Bhattacharyya, P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. Monoxidised Sulfur and Selenium Derivatives of Bis(Diphenyl-Phosphino)Amine: Synthesis and Co-Ordination Chemistry. *J. Chem. Soc., Dalton Trans.* **1995**, No. 19, 3189−3194.
(46) Ghisolfi, A.; Fliedel, C.; Rosa, V.; Pattacini, R.; Thibon, A.; Yu Monakhov, K.; Braunstein, P. Solvent-Dependent Reversible Ligand Exchange in Nickel Complexes of a Monosulfide Bis-(Diphenylphosphino)(N-Thioether)Amine. *Chem. − Asian J.* **2013**, *8* (8), 1795−1805.
(47) Tirreé, J.; Gudat, D.; Nieger, M.; Niecke, E. Reversible Tautomeric Transformation between a Bis(Amino)Cyclodiphosph-(V)Azene and a Bis(Imino)Cyclodiphosph(V)Azane. *Angew. Chem., Int. Ed.* **2001**, *40* (16), 3025−3028.
(48) Patureau, F. W.; Kuil, M.; Sandee, A. J.; Reek, J. N. H. METAMORPhos: Adaptive Supramolecular Ligands and Their Mechanistic Consequences for Asymmetric Hydrogenation. *Angew. Chem., Int. Ed.* **2008**, *47* (17), 3180−3183.
(49) Terrade, F. G.; Lutz, M.; van der Vlugt, J. I.; Reek, J. N. H. Synthesis, Coordination Chemistry, and Cooperative Activation of H2 with Ruthenium Complexes of Proton-Responsive METAMORPhos Ligands. *Eur. J. Inorg. Chem.* **2014**, *2014* (10), 1826−1835.
(50) Chu, X.; Yang, Y.; Lu, B.; Wu, Z.; Qian, W.; Song, C.; Xu, X.; Abe, M.; Zeng, X. Methoxyphosphinidene and Isomeric Methyl-phosphinidene Oxide. *J. Am. Chem. Soc.* **2018**, *140* (42), 13604−13608.
(51) Tirrée, J.; Ruban, A. V.; Nieger, M.; Li, C.; Nyulászi, L.; Niecke, E. Overcrowded Aminophospanitrenes: A Case Study. *Z. Naturforsch. B* **2017**, *72* (11), 865−871.
(52) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, *38* (6), 3098−3100.
(53) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37* (2), 785−789.
(54) Becke, A. D. A New Mixing of Hartree−Fock and Local Density-functional Theories. *J. Chem. Phys.* **1993**, *98* (2), 1372−1377.
(55) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648−5652.
(56) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297−3305.
(57) Caldeweyher, E.; Bannwarth, C.; Grimme, S. Extension of the D3 Dispersion Coefficient Model. *J. Chem. Phys.* **2017**, *147* (3), 34112.
(58) Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S. A Generally Applicable Atomic-Charge Dependent London Dispersion Correction. *J. Chem. Phys.* **2019**, *150* (15), No. 154122.
(59) Jafarpour, L.; Stevens, E. D.; Nolan, S. P. A Sterically Demanding Nucleophilic Carbene: 1,3-Bis(2,6-Diisopropylphenyl)-Imidazol-2-Ylidene). Thermochemistry and Catalytic Application in Olefin Metathesis. *J. Organomet. Chem.* **2000**, *606* (1), 49−54.
(60) Hintermann, L. Expedient Syntheses of the N-Heterocyclic Carbene Precursor Imidazolium Salts IPr·HCl, IMes·HCl and IXy·HCl. *Beilstein J. Org. Chem.* **2007**, *3*, 22.
(61) Tamm, M.; Randoll, S.; Herdtweck, E.; Kleigrewe, N.; Kehr, G.; Erker, G.; Rieger, B. Imidazolin-2-Iminato Titanium Complexes: Synthesis, Structure and Use in Ethylene Polymerization Catalysis. *Dalton Trans.* **2006**, No. 3, 459−467.
(62) Bräse, S.; Gil, C.; Knepper, K.; Zimmermann, V. Organic Azides: An Exploding Diversity of a Unique Class of Compounds. *Angew. Chem., Int. Ed.* **2005**, *44* (33), 5188−5240.
(63) Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA Quantum Chemistry Program Package. *J. Chem. Phys.* **2020**, *152* (22), No. 224108.

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