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# Electronic Role of 3-Iminophosphine Ligands in Palladium-Catalyzed Intermolecular Hydroamination

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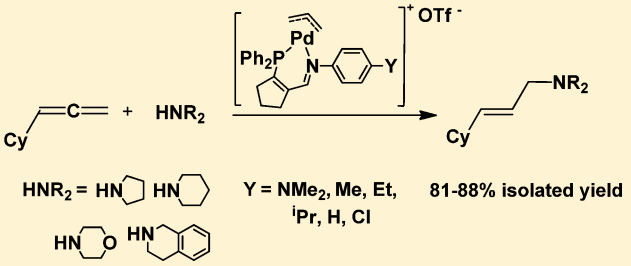
Supporting Information

**ABSTRACT:** This study of the electronic characteristics of (3-iminophosphine)allylpalladium triflate complexes has yielded catalysts with moderate to high activity for the hydroamination of monosubstituted allenes utilizing a wide range of amines. Herein, a new series of these catalysts was synthesized by varying the group on the imine moiety in order to explore the effect of the electronics of the ligand's imine on the catalytic activity for intermolecular hydroamination reactions. Four amine substrates were examined in the catalytic hydroamination of cyclohexylallene, and apparent first-order rate constants were obtained by $^1$H NMR spectroscopy. Kinetic isotope effect studies were also performed in order to support a new proposed catalytic cycle in the hydroamination of cyclohexylallene with secondary amines using [(3IP)Pd(allyl)]OTf catalysts.




## INTRODUCTION

In addition to being 100% atom economical, hydroamination is a particularly versatile method for the production of new C−N bonds in N-containing organic frameworks.[1] By use of a broad diversity of unsaturated substrates, a wide range of target compounds, including amines, enamines, and imines, can be obtained.[2] Over the past two decades, many structurally modified transition-metal catalysts have proven to be capable of regio- and enantioselective intra- and intermolecular hydroamination of C−C unsaturated bonds.[3−13] Intramolecular hydroamination can be utilized in the synthesis of N-heterocycles, facilitating multistep reactions for production of biologically active molecules in fewer steps, whereas intermolecular hydroamination provides acyclic amines that serve as common building blocks for pharmaceuticals and organic syntheses.[1,14−16] Intermolecular hydroamination is much more challenging than intramolecular hydroamination, as the process is calculated to be only slightly exothermic for many substrates, and it also suffers from an unfavorable entropic term.[17,18] As a result, efforts to develop useful intermolecular hydroamination catalysts have recently been a topic of great interest worldwide.[11,19−27] Furthermore, the broad significance of catalytic hydroamination as a tool in both organic and organometallic synthesis has made mechanistic studies for better understanding of the catalytic cycles in these processes a critical pursuit toward enabling organometallic chemists to rationally tune catalyst frameworks and consequently achieve higher catalytic activities and reaction yields.[28−35]

The most significant impact of catalytic hydroamination can be seen through the reduced cost in making valuable products such as allylamines, which serve as convenient organic intermediates in the synthesis of complex molecules.[36,37] Even simple achiral allylamines have attracted a great deal of attention recently, with many efforts undertaken to refine the synthetic methods for this class of compounds.[38,39] Allylamines, in spite of being well-known, still commonly require either multiple steps and tedious workups or stoichiometric amounts of organometallic reagents to produce, except in cases where their production can be effected by catalytic allylic amination.[36,37,40] Beyond their applications in traditional organic synthesis, allylamines can be used as substrates for alkene metathesis reactions, adding to their usefulness and versatility.[41] Conjugated dienes and allenes are two general substrate classes that can serve as precursors to allylamines via catalytic hydroamination.[1,42] Hydroamination of conjugated dienes has been widely investigated, and numerous regioselective and enantioselective transition-metal catalysts have been developed.[28,42−45] In contrast, examples of intermolecular hydroamination of allenes, originally reported in 1992,[46] are less common and few catalysts with high functional group tolerance for unactivated allenes have been reported.[1,19,20,22,47−53] Moreover, due to the limited number of allene hydroamination reports, few comprehensive mechanistic studies have been undertaken to date.[23,34,54]

Over the past few years, our group has focused on the hydroamination of monosubstituted allenes with primary and secondary amines catalyzed by allylpalladium complexes supported by 3-iminophosphine (3IP) ligands.[55−59] Recently, we reported the most active catalyst known for the intermolecular hydroamination of monosubstituted allenes with anilines, which also displayed a high functional group

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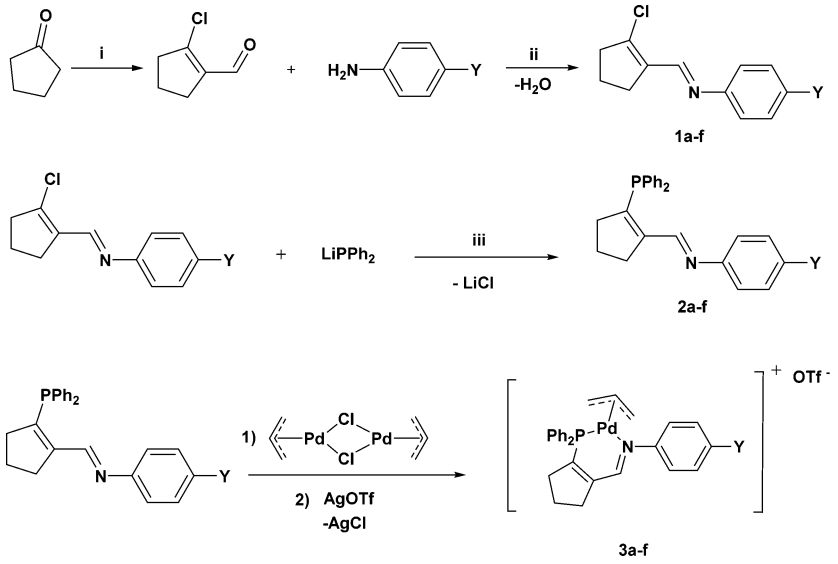
**Scheme 1. General Synthetic Route for [(3IP)Pd(allyl)]OTf Complexes**[a]




[a]Legend: (i) 2 equiv of DMF, 1.2 equiv of $POCl_3$, 0 °C, and then stirring at room temperature for 14 h, 0 °C, $NaHCO_3$; (ii) diethyl ether, 4 Å molecular sieves, 0 °C; (iii) 1.4 equiv of $LiPPh_2$, diethyl ether, 0 °C, and then warming to room temperature.

tolerance.[55] This catalyst operated efficiently at ambient temperature and provided moderate to high yields of hydroamination products.[55] The hydroamination of allenes has also been pursued by the Breit group in Germany quite successfully,[23,60] although their catalyst requires the more expensive rhodium metal center and uses high temperature in the catalytic process, in contrast to our systems, which function at ambient temperature.

In parallel with the current study, we recently reported the correlation of backbone ring size and phosphorus substituent on catalytic activity with these allylpalladium 3-iminophosphine complexes.[56] This parallel study helped elucidate the catalytic effect of $\sigma$ donation from the phosphorus and ring strain due to backbone composition. In a summary of these results, *tert*-butyl groups on the phosphine resulted in higher yields for hydroamination than phenyl groups. We deduced that the stronger electron donation of the *tert*-butyl groups makes the trans-allylic carbon more labile and, additionally, the *tert*-butyl group carries more steric bulk, potentially affecting various steps in the catalytic cycle. Most importantly, the increased steric bulk of the *tert*-butyl group could assist catalysis by increasing the rate of reductive elimination of the product allylamine. In other tests, we found that a smaller backbone ring size was most suitable for the catalysis, which we attributed to increased ring strain and decreased bite angle, both of which promote displacement of the imine from palladium to allow for coordination of reagent amine. In these prior studies, only *tert*-butyl and xylyl groups on the imine unit were tested. Given the limited set of substituents, we were unable to make any significant conclusions regarding the steric and electronic effects of the 3IP imine group, and its correlation to hydroamination catalytic activity remained ambiguous. Thus, we set out to determine the effect of electron-withdrawing and electron-donating imine substituents on the catalytic hydroamination, as reported herein. Additionally, related deuterium kinetic isotope effect experiments are reported. Finally, on the basis of the results herein and our other recent report,[56] we propose a rational catalytic cycle for the hydroamination of monosubstituted allenes with primary and secondary amines, as related to 3-iminophosphine supported palladium catalysts.

## RESULTS AND DISCUSSION

It is important to understand the catalytic mechanism in order to improve the activity of 3IP-Pd catalysts. Thus, we set out to investigate the effect of imine electronics on catalyst activity. For this purpose, a set of new 3IP ligands (**2a–f**) was designed, where the groups on phosphine (phenyl) and alicyclic backbone (cyclopentene) were kept constant (Scheme 1). The only variable for these new ligands involved the electronics of the imine unit, controlled by different substituents (EDG or EWG) at the para position of a phenyl group attached to the nitrogen (Table 1). By varying the para substituents in these new catalysts, we were then poised to correlate our experimental data with Hammett constants,[61] as these empirically derived constants adequately represent the electron-donating and electron-withdrawing character of substituents in reactions involving substituted benzene derivatives. In this fashion, it was feasible to investigate the effect of imine electronics on catalytic hydroamination with sterics held constant.

**Table 1. Hammett Constants and Reaction Yields of [(3IP)Pd(allyl)]OTf Precatalysts**

| Y (para substituent) | Hammett constant ($\sigma_p$) | chloroimine (unisolated) | ligand (% yield; two steps) | precatalyst (% yield) |
|---|---|---|---|---|
| dimethylamino | −0.830 | **1a** | **2a** (74) | **3a** (59) |
| methyl | −0.170 | **1b** | **2b** (69) | **3b** (62) |
| ethyl | −0.150 | **1c** | **2c** (65) | **3c** (54) |
| isopropyl | −0.150 | **1d** | **2d** (63) | **3d** (52) |
| hydrogen | 0.000 | **1e** | **2e** (71) | **3e** (60) |
| chloro | 0.227 | **1f** | **2f** (76) | **3f** (69) |

The ligands **2a–f** and related catalysts **3a–f** were synthesized using protocols related to those developed previously in our group:[56] first, reaction of the Vilsmeier–Haack reagent with



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cyclopentanone, then Schiff base condensation with a para-substituted aniline, and finally treatment with lithium diphenylphosphide to produce each 3IP ligand **2a–f**. During the synthesis of these new 3IP ligands, we observed very poor stability of the newly synthesized $\beta$-chloroimines **1a–f**. Reaction progress in the synthesis of **1a–f** was monitored by $^1$H NMR to result in excellent product formation. Unfortunately, after the reaction workup (involving passage through a short column of silica gel followed by quick drying over $MgSO_4$), as the solvent was removed, compounds **1a–f** started to decompose in less than 1 h, even though they were relatively pure at this point. We also performed the reaction and workup under a nitrogen atmosphere, but it did not resolve these decomposition problems. This instability of **1a–f** forced us to characterize them only by NMR spectroscopy and then use them immediately. Thus, **1a–f** were quickly isolated under a nitrogen atmosphere and treated with lithium diphenylphosphide directly to transform them to ligands **2a–f**. After successful isolation, these ligands were coordinated to commercially available allylpalladium chloride dimer, and a subsequent salt metathesis with silver triflate yielded the precatalysts **3a–f**.

Several years ago, our group investigated the hemilability of 3IP ligands in noncatalytically active (3IP)$PdCl_2$ complexes.[62] These compounds displayed extremely weak coordination by the imine unit of 3IP and a strong affinity toward coordination of amines in place of the chelating imine. We have since come to believe that this hemilability plays a significant role in hydroamination catalysis and that coordination of the amine substrate to 3IP palladium complexes is crucial for catalytic hydroamination. Thus, systematic manipulation of the basicity of this imine unit should have a marked effect on catalytic activity. Bearing this in mind, we set out to investigate a series of catalytic experiments using our new complexes **3a–f**. Given our studies from the past several years,[55−59] we decided to investigate the hydroamination of cyclohexylallene with several amines (pyrrolidine, piperidine, morpholine, and 1,2,3,4-tetrahydroisoquinoline) (Scheme 2). This group of substrates was chosen because we expected slow to moderate catalytic rates, allowing for more accurate comparison of the effects of the different imines in these catalysts. That is, if more rapid substrates were chosen, conversion data would have to be collected immediately, with greater experimental error as a result. Since we have previously developed very effective catalysts for hydroamination of cyclohexylallene with these amines,[57] our goal in the present work was to understand the effect of imine electronics at the expense of the overall reaction rate.

Our early experiments revealed that variation of the imine electronics had a drastic effect on the catalytic activity in these 3IP complexes. Because of our past hemilability experiments, we initially expected catalysts with less electron donating substituents at the para position of the imine to show higher activity in hydroamination, since the resulting imine coordination to palladium would be weaker, facilitating displacement by substrate amine and entry into the catalytic cycle. In contrast, it was observed that upon proceeding from negative values of the Hammett constant (more electron-donating) to positive ones (more electron-withdrawing), there is a significant increase in reaction rate, which reaches a maximum and then subsequently decreases for the most electron-poor imines. To fully understand the observed trend and kinetics of these reactions, detailed $^1$H NMR studies were undertaken.

**Reaction Order of Secondary Amine.** Since our initial experiments revealed **3c** to be the most active hydroamination precatalyst, **3c** was utilized in catalytic reaction **a** to determine the reaction order in amine. In order to accomplish this, pyrrolidine was added to a mixture of benzene (0.50 mmol), $C_6D_6$ (800 $\mu$L) and **3c** (0.025 mmol), followed by addition of cyclohexylallene (0.50 mmol). $^1$H NMR spectra were recorded every 2 min with the temperature preset to 25 °C. Quantities of 0.25, 0.50, and 1.0 mmol of amine were tested in duplicate runs, and ln[initial rate] was plotted versus ln([pyrrolidine]). The near-unity slope of this line indicates that the reaction is first order in amine within experimental error (Figure 1).

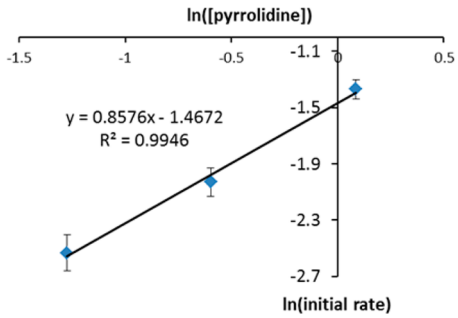
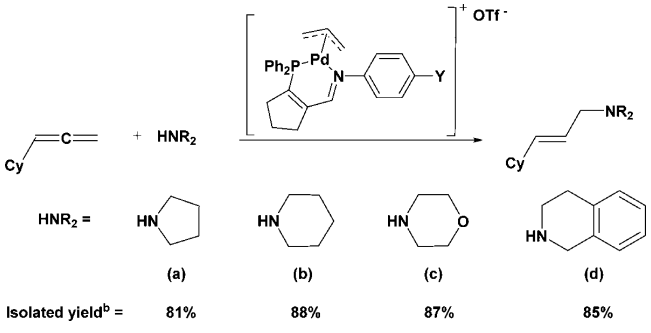



**Figure 1.** Plot of ln(initial rate) versus ln([pyrrolidine]).

**Reaction Order of Allene.** In continued efforts to probe the hydroamination mechanism, we set out to verify that allene insertion was not involved in the rate-determining step by comparing the reaction rates of pyrrolidine with 0.5, 1, and 2 equiv of cyclohexylallene. Similar to the case for the experiments above, catalytic reactions were investigated by $^1$H NMR spectroscopy. Pyrrolidine (0.50 mmol) was added to a mixture of benzene (0.50 mmol), $C_6D_6$ (800 $\mu$L), and **3c** (0.025 mmol), followed by addition of 0.25, 0.50, and 1.0 mmol of cyclohexylallene in separate experiments. $^1$H NMR data were collected every 2 min with the temperature preset to 25 °C. The ln[initial rate] values were plotted versus ln-[cyclohexylallene], giving a slope of 0.0760 (Figure 2), suggesting that the catalytic reaction is zero order in allene.

**Scheme 2. Catalytic Hydroamination of Cyclohexylallene**[a]




[a]Catalytic procedure: reactions were carried out at 25 °C in NMR tubes prepared in a glovebox using benzene-$d_6$ as the solvent (800 $\mu$L), catalyst (0.025 mmol), secondary amine (0.50 mmol), and cyclohexylallene (0.50 mmol), with $C_6H_6$ (0.50 mmol) as an internal standard. Conversion was monitored by $^1$H NMR spectroscopy. [b]Isolated yields were obtained from the average of six hydroamination reactions catalyzed by **3a–f** for each amine.



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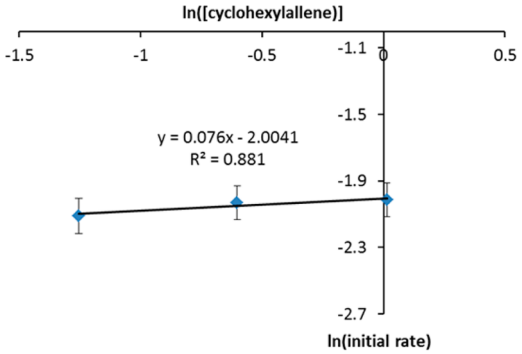



**Figure 2.** Plot of ln(initial rate) versus ln([cyclohexylallene]).

The absence of allene from the rate law is not surprising, as many previous studies have demonstrated rapid insertion of olefins into Pd−C and Pd−H bonds with a variety of ligand sets.[63−65]

**Correlation between Observed Reaction Rates and Hammett Value.** With an understanding of the reaction order of the catalytic substrates, specifically rate = $k_{obs}$[amine], we knew that the secondary amine was involved in the rate-determining step. A possible mechanism involving coordination of the amine requires concomitant dissociation of the ligand's imine unit and thus, the electronics of the imine unit were investigated. In order to achieve this, we determined the observed first-order rate constants ($k_{obs}$) for all six catalysts with three of the secondary amines. These were then plotted versus the Hammett $\sigma_p$ values for the imine fragment of each ligand (Figure 3; see the Supporting Information for the rate constant determinations).

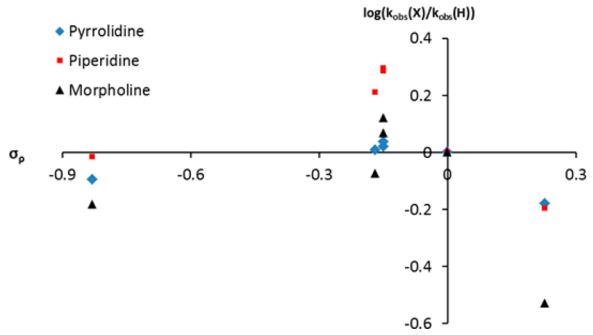
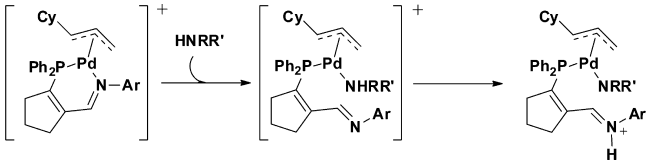



**Figure 3.** Hammett plot of $k_{obs}$ in hydroamination reactions **a**, **b**, and **c**.

As had been the case with our initial test reactions, upon proceeding from electron-donating to electron-withdrawing substituents, reaction rates increase to a maximum in each case and then subsequently decrease (Figure 3). Though initially unexpected, since imines with the largest $\sigma_p$ values would be most amenable to substitution by the substrate amine (EWG would facilitate imine displacement by the amine), this peak in catalytic activity versus Hammett constant implied that there may be two steps in the mechanism with similar rate constants, with one or the other dominant depending on imine electronics. We hypothesized that the two relevant steps in the catalytic cycle involved coordination of reagent amine to the Pd catalyst, followed by intramolecular deprotonation of the coordinated amine by the dissociated imine unit of 3IP (Scheme 3). The reduced reaction rates for the electron-rich

**Scheme 3. Coordination of Amine Followed by Intramolecular Proton Transfer**




imines represent a rate-determining step involving displacement of this coordinated imine by the reactant amine, while the slower reaction rates for the electron-poor imines are consistent with proton transfer becoming kinetically limiting. This latter intramolecular proton transfer step would be expected to be highly dependent on the basicity of the imine fragment of 3IP. Ultimately, this proton transfer step provides a palladium intermediate bearing an amido ligand that can readily undergo reductive elimination in a rapid step, as elegantly demonstrated by Hartwig and co-workers previously.[66−69]

In summary, this mechanism involving two consecutive steps with similarly slow kinetics but opposite correlation with imine electronic character explains why **3e** and **3f**, which are carrying the least electron-donating substituents on the imine unit, do not provide the most active catalysts. Although they almost definitely undergo coordination of the amine, their catalysis is hindered by poor reactivity in the intramolecular deprotonation step, resulting in poor reaction rates. We also investigated two catalysts with different substituents but the same Hammett constant to compare their catalytic activity. Ethyl (**3c**) and isopropyl (**3d**) substituents have identical Hammett constants ($\sigma_p$). Since the steric bulk of the para substituent should have little or no impact on catalysis, the same reaction rate for both was expected (Figure 3). In general, these two catalysts showed very similar catalytic activity for each substrate, although **3d** gave slightly slower rates in each case, which we attribute to a more pronounced albeit slow catalyst decomposition observed with **3d**.

Following the Hammett study, a deuterium-labeled amine was used to explore the kinetic isotope effect on the catalysis, as shown in Figure 4. It was previously shown that $k_H/k_D$ for

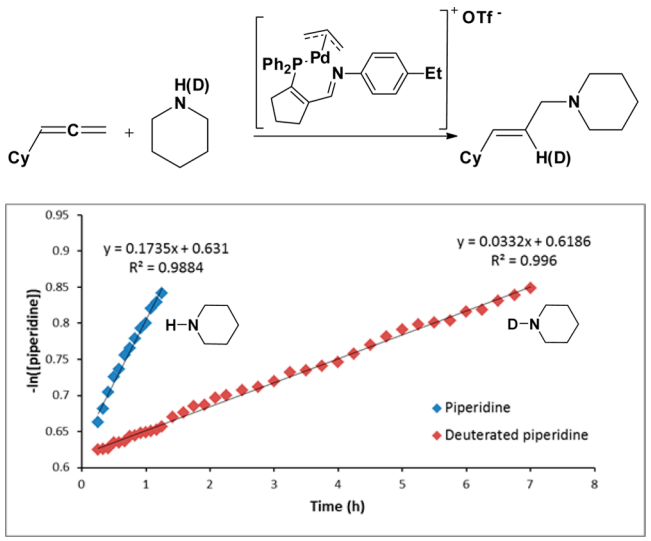



**Figure 4.** Kinetic isotope effects in the hydroamination of cyclohexylallene with piperidine.



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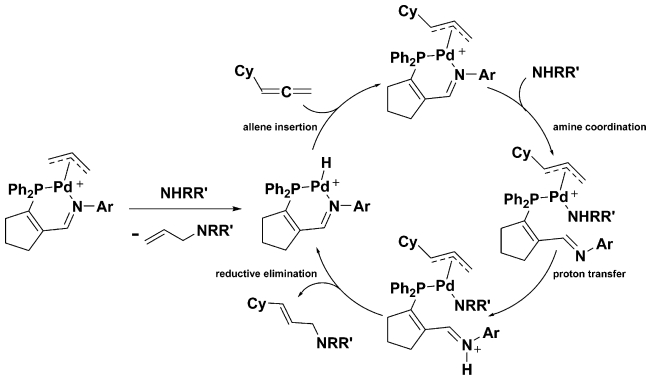
hydroamination of ethylene with aniline catalyzed by an active Ru complex at 80 °C was 2.2 ± 0.1.[70] This number was consistent with earlier studies and was related to N−H(D) bond activation, since this step was considered to be the rate-determining step. For catalyst **3c**, $k_H/k_D$ for the reaction shown in Figure 4 was found to be approximately 5.2. To determine this value, the ratio of the slopes of ln([piperidine]) versus time was utilized (Figure 4). The large primary kinetic isotope effect observed strongly implies that cleavage of the N−H bond is involved in the rate-determining step of the catalysis, consistent with the intramolecular proton transfer step involved in the discussion of Hammett correlation above.

In addition to kinetic rate data, our study on hydroamination using deuterated piperidine revealed that the deuterium becomes attached to the central carbon of allene exclusively. Previous reports involving a Rh(I/III) catalytic system showed that formation of a vinylic species followed by $\beta$-hydride elimination can shift the labeled proton to the terminal carbon of monosubstituted allenes, but we see no evidence of such reactivity using our Pd system.[23]

On the basis of our previous studies regarding hemilability of (3IP)$PdCl_2$ upon treatment with a wide range of amines,[62] the results reported above, and catalytic experiments with high catalyst loading (see the Supporting Information, S6 and S19), we propose a new catalytic cycle for hydroamination of allenes with secondary amines using [(3IP)Pd(allyl)]OTf as the precatalyst (Scheme 4). In this catalytic cycle, the palladium

**Scheme 4. Proposed Catalytic Cycle**




precatalyst, after reaction with the substrate amine, produces a highly reactive and coordinatively unsaturated Pd(II) hydride species. Next, allene rapidly inserts into the Pd−H bond to form a ($\pi$-allyl)palladium complex. Subsequently, the hemilability of 3IP plays a role as substrate amine coordinates to the palladium(II) with displacement of the 3IP imine unit. In the final steps, proton transfer from the coordinated secondary amine to the imine unit of the 3IP provides an amido complex of Pd(II), which then undergoes reductive elimination and protonation of palladium to complete the catalytic cycle. Alternatively, it is also possible that in the last step, after coordination of amine to palladium, an internal attack of the coordinated amine on the allyl group, followed by reductive elimination, forms the product. The results produced herein are incapable of resolving these two mechanisms. Notwithstanding, the $^1$H NMR studies during active catalysis (see the Supporting Information, S19) unequivocally demonstrate monodentate coordination of the 3IP ligand to the metal center in the catalyst resting state, as evidenced by the appearance of a $^1$H resonance at low field (9.62−9.83 ppm) assigned to the HC=N proton of the decoordinated imine moiety. Thus, we assert that the proton transfer step from amine to imine is often rate limiting, especially in cases involving the most active 3IP-palladium complexes, although a rate-limiting internal attack on the allyl group is also consistent with the experimental data for this system.

## CONCLUSIONS

On the basis of our previous reports, as well as the Hammett study and deuterium labeling experiments described in this paper, we have proposed a new catalytic cycle for our 3IP-palladium-catalyzed intermolecular hydroamination. The electronics of the imine unit of the 3IP ligand significantly affect the catalytic activity observed. More specifically, the electron density on the nitrogen of the imine is significant in two ways. First, in the step involving coordination of the substrate amine, less electron density on the iminic nitrogen is favorable to make it less basic and thus easier for the free amine to displace the imine from palladium. On the other hand, in the next step, more electron density on the iminic nitrogen is necessary to help in deprotonation of the coordinated amine. Thus, in every case, these two catalytic steps favor opposite imine electronic trends, making it critically important for us to find the optimum imine electronics in this system. Among the ligands tested so far, this optimum point has correlated to an ethyl group in the para position of a phenyl group attached to the imine with a Hammett constant of −0.150. This idea can be extended to other hydroamination substrates to find the best imine electronics for the 3IP ligand in order to further optimize these catalysts. Further studies will include testing of new substrates and ongoing optimization of the 3IP ligand set, with the continued goal of developing superior hydroamination catalysts.

## EXPERIMENTAL SECTION

**General Methods and Instrumentation.** 2-Chlorocyclopent-1-enecarbaldehyde,[56] lithium diphenylphosphide,[71] 3-iminophosphine ligands **2a−f**, and [(3IP)Pd(allyl)]OTf complexes **3a−f** were prepared via previously published methodology.[58] $\beta$-Chloroimines **1a−f** were synthesized under ambient conditions. All further manipulations were performed under a nitrogen atmosphere using either Schlenk techniques or a nitrogen-filled glovebox, unless otherwise noted. Solvents were dried prior to use; methylene chloride was passed through two columns of 4 Å molecular sieves and degassed with high-purity nitrogen (99.995%). Pentane, diethyl ether, and toluene were passed through columns of activated alumina and 4 Å molecular sieves and degassed with nitrogen. $CDCl_3$ and $C_6D_6$ were purchased from Cambridge Isotope Laboratories and, for air-sensitive usage, dried over calcium hydride and sodium, respectively, freeze−pump−thawed three times, vacuum-transferred, and stored over molecular sieves in a nitrogen-filled glovebox. All other solvents were purchased from either Fisher or Sigma-Aldrich. *n*-Butyllithium (1.6 M in hexane), (allyl)-palladium(II) chloride dimer, diphenylchlorophosphine, lithium aluminum hydride, and silver triflate were purchased from Strem and applied without further purification. Phosphorus oxychloride, pyrrolidine, morpholine, 1,2,3,4-tetrahydroisoquinoline, 4-chloroaniline, and 4-ethylaniline were purchased from Acros; cyclopentanone and dimethyl-4-phenylenediamine were supplied by Alfa Aesar. Piperidine, *p*-toluidine, and cyclohexylallene were purchased from Aldrich. Aniline and 4-isopropylaniline were obtained from Fisher Scientific and Maybridge, respectively. All of the substrates for catalytic reactions, including cyclohexylallene, pyrrolidine, piperidine, morpholine, and 1,2,3,4-tetrahydroisoquinoline, were dried over calcium hydride, freeze−pump−thawed three times, vacuum-transferred, and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stored in the glovebox over molecular sieves. All other chemicals were used as received without further purification. $^{1}H$ and $^{13}C$ NMR data were obtained on a 600 MHz Varian Unity Inova, 600 MHz Avance III Bruker, or 400 MHz Varian VXRS NMR spectrometer at 599.9 MHz for $^{1}H$ NMR and 150.8 for $^{13}C$ NMR with the first two spectrometers and at 399.95 MHz for $^{1}H$ NMR and 100.56 MHz for $^{13}C$ NMR with the VXRS spectrometer. All $^{31}P$ NMR data were obtained on the 400 MHz VXRS NMR spectrometer at 161.90 MHz. $^{1}H$ and $^{13}C$ NMR shifts are reported relative to $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.2 ppm) or $C_6D_5H$ (7.16 ppm) and $C_6D_6$ (128.1 ppm). $^{31}P$ NMR data were externally referenced to 0.00 ppm with a 5% solution of $H_3PO_4$ in $D_2O$. IR samples were prepared between NaCl plates as Nujol mulls, and data were collected on a PerkinElmer Spectrum 2 FT-IR spectrometer. Melting points were determined with a capillary melting point apparatus (Uni-Melt) in sealed capillary tubes under nitrogen. Elemental analysis and high-resolution mass spectrometry data were determined by Atlantic Microlab, Inc., Norcross, GA, USA, and University of Illinois Mass Spectrometry Laboratory, Urbana, IL, USA, respectively.

**Alicyclic $\alpha,\beta$-Unsaturated $\beta$-Chloroimines 1a–f.** To diethyl ether (60 mL) was added activated 4 Å molecular sieves, and this mixture was cooled to 0 °C before addition of chloroaldehyde. The para-substituted aniline (1.1 equiv) was added slowly, and the mixture was stirred overnight. Reaction completion was monitored by $^{1}H$ NMR spectroscopy. For the chloroimines **1a–d** another portion of para-substituted aniline (0.2 equiv) was added after 12 h. After reaction completion, the solution was passed through a plug of silica to remove unreacted aniline, followed by drying over $MgSO_4$ for 30 min before filtering over Celite. The solution containing chloroimine was concentrated under vacuum and degassed with nitrogen before use in the next step. Due to decomposition problems, $\alpha,\beta$-unsaturated $\beta$-chloroimines could not be stored. Thus, they were used upon reaction completion immediately after this quick isolation protocol.

*2-Chlorocyclopentene-1-(4-N,N-dimethylaminophenyl)imine (**1a**):* $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.50 (s, 1H), 7.20 (d, $^{3}J_{H-H}$ = 9.0 Hz, 2H), 6.72 (d, $^{3}J_{H-H}$ = 9.0 Hz, 2H), 2.97 (s, 6H), 2.82–2.79 (m, 4H), 2.17–2.04 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 150.80, 149.65, 141.25, 139.74, 136.38, 122.48, 112.84, 40.78, 39.59, 30.56, 20.93.

*2-Chlorocyclopentene-1-(4-methylphenyl)imine (**1b**):* $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.45 (s, 1H), 7.17 (d, $^{3}J_{H-H}$ = 8.2 Hz, 2H), 7.07 (d, $^{3}J_{H-H}$ = 8.2 Hz, 2H), 2.82–2.75 (m, 4H), 2.35 (s, 3H), 2.12–1.96 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 154.33, 153.66, 149.67, 141.92, 136.13, 129.74, 120.98, 39.66, 30.43, 21.04, 20.85.

*2-Chlorocyclopentene-1-(4-ethylphenyl)imine (**1c**):* $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.46 (s, 1H), 7.20 (d, $^{3}J_{H-H}$ = 8.0 Hz, 2H), 7.10 (d, $^{3}J_{H-H}$ = 8.0 Hz, 2H), 2.81–2.78 (m, 4H), 2.66 (q, $^{3}J_{H-H}$ = 7.6 Hz, 2H), 2.09–2.02 (m, 2H), 1.25 (t, $^{3}J_{H-H}$ = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 154.43, 153.71, 142.47, 137.36, 136.21, 128.61, 121.08, 39.72, 30.50, 28.51, 21.16, 20.91.

*2-Chlorocyclopentene-1-(4-isopropylphenyl)imine (**1d**):* $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.59 (s, 1H), 7.34 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 7.24 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 3.03 (sept, $^{3}J_{H-H}$ = 6.8 Hz, 1H), 2.94–2.89 (m, 4H), 2.20–2.13 (m, 2H), 1.38 (d, $^{3}J_{H-H}$ = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 154.47, 150.21, 147.06, 141.78, 136.29, 127.18, 121.08, 39.75, 33.82, 30.54, 24.19, 20.94.

*2-Chlorocyclopentene-1-(phenyl)imine (**1e**):* $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.44 (s, 1H), 7.35–7.32 (m, 2H), 7.16–7.11 (m, 3H), 2.83–2.75 (m, 4H), 2.08–2.01 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 155.10, 144.04, 139.30, 138.29, 129.13, 126.12, 121.02, 39.71, 30.43, 20.85.

*2-Chlorocyclopentene-1-(4-chlorophenyl)imine (**1f**):* $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.41 (s, 1H), 7.52 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 7.08 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 2.82–2.74 (m, 4H), 2.13–1.98 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 155.34, 150.84, 143.08, 136.08, 131.68, 129.26, 122.41, 39.80, 30.43, 20.88.

**3-Iminophosphine Ligands 2a–f.** All of the manipulations were performed under nitrogen atmosphere using Schlenk techniques. A solution of freshly prepared chloroimine (used in situ as a solution in ether) was degassed and cooled to 0 °C. To this was added $LiPPh_2$ (1 equiv) dissolved in diethyl ether via cannula. The amount of $LiPPh_2$ was calculated on the basis of the mass of the chloroaldehyde used for the production of chloroimine. The mixture was stirred for 2 h, and then the reaction solution was filtered over Celite to remove LiCl formed in the reaction. The resulting solution was concentrated under vacuum and was kept under nitrogen at 21 °C overnight to give the 3IP ligand as a yellow solid. Subsequently, the supernatant was filtered and the solid residue was placed under vacuum to remove the volatiles. For ligands **2a** and **2e**, the solid residue was recrystallized in concentrated pentane to remove phosphine impurities. Percent yields for the 3IP ligands **2a–f** were calculated on the basis of the mass of starting chloroaldehyde.

*2-Diphenylphosphinocyclopentene-1-(4-N,N-dimethylaminophenyl)imine (**2a**):* yellow solid (2.258 g, 74%); mp 180–183 °C; $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.98 (d, $^{4}J_{P-H}$ = 4.0 Hz, 1H), 7.41–7.33 (m, 10H), 7.16 (d, $^{3}J_{H-H}$ = 9.0 Hz, 2H), 6.70 (d, $^{3}J_{H-H}$ = 9.0 Hz, 2H), 2.98–2.95 (m, 2H), 2.96 (s, 6H), 2.44–2.40 (m, 2H), 1.93–1.88 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 154.3 (d, $^{3}J_{P-C}$ = 21.1 Hz), 152.9 (d, $^{2}J_{P-C}$ = 22.6 Hz), 149.7, 147.3 (d, $^{1}J_{P-C}$ = 21.1 Hz), 141.3, 136.6 (d, $^{1}J_{P-C}$ = 7.5 Hz), 133.3 (d, $^{2}J_{P-C}$ = 19.6 Hz), 128.7, 128.6 (d, $^{3}J_{P-C}$ = 6.0 Hz), 122.7, 112.9, 40.9, 37.7 (d, $^{3}J_{P-C}$ = 3.0 Hz), 34.2 (d, $^{2}J_{P-C}$ = 4.5 Hz), 22.8; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ −24.20; IR (Nujol) 3049 (m), 2805 (m), 1612 (s), 1579 (s), 1566 (m), 1514 (s), 1477 (s), 1446 (s), 1432 (m), 1358 (s), 1261 (w), 1227 (m), 1204 (w), 1167 (s), 1125 (m), 1093 (m), 1075 (m), 1067 (m), 1027 (w), 998 (w), 948 (m), 820 (s), 795 (w), 746 (m), 702 (m), 697 (m) $cm^{-1}$; HRMS $m/z$ calcd for $C_{26}H_{28}N_2P$ 399.1990 $[M + H]^+$, found 399.1990.

*2-Diphenylphosphinocyclopentene-1-(4-methylphenyl)imine (**2b**):* yellow solid (1.952 g, 69%); mp 123–126 °C; $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.94 (d, $^{4}J_{P-H}$ = 4.2 Hz, 1H), 7.41–7.35 (m, 10H), 7.14 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 7.04 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 2.99–2.96 (m, 2H), 2.46–2.44 (m, 2H), 2.35 (s, 3H), 1.96–1.91 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 156.4 (d, $^{3}J_{P-C}$ = 22.6 Hz), 153.7 (d, $^{2}J_{P-C}$ = 21.1 Hz), 150.0, 149.8, 136.3 (d, $^{1}J_{P-C}$ = 9.1 Hz), 136.0, 133.3 (d, $^{1}J_{P-C}$ = 19.6 Hz), 129.8, 128.8, 128.7 (d, $^{2}J_{P-C}$ = 7.5 Hz), 121.2, 37.9 (d, $^{3}J_{P-C}$ = 3.0 Hz), 34.1 (d, $^{2}J_{P-C}$ = 6.0 Hz), 22.7 (d, $^{3}J_{P-C}$ = 1.5 Hz), 21.2; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ −24.17; IR (Nujol) 3053 (m), 1663 (w), 1614 (w), 1584 (m), 1570 (m), 1519 (m), 1502 (m), 1433 (s), 1378 (s), 1348 (w), 1325 (w), 1306 (w), 1278 (m), 1260 (m), 1214 (w), 1193 (w), 1179 (w), 1168 (w), 1157 (w), 1090 (m), 1068 (m), 1027 (m), 829 (m), 814 (m), 752 (m), 744 (m), 697 (s) $cm^{-1}$; HRMS $m/z$ calcd for $C_{25}H_{25}NP$ 370.1725 $[M + H]^+$, found 370.1723.

*2-Diphenylphosphinocyclopentene-1-(4-ethylphenyl)imine (**2c**):* pale yellow solid (1.909 g, 65%); mp 123–125 °C; $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.94 (d, $^{4}J_{P-H}$ = 4.0 Hz, 1H), 7.42–7.34 (m, 10H), 7.17 (d, $^{3}J_{H-H}$ = 8.0 Hz, 2H), 7.06 (d, $^{3}J_{H-H}$ = 8.0 Hz, 2H), 2.99–2.95 (m, 2H), 2.64 (q, $^{3}J_{H-H}$ = 7.6 Hz, 2H), 2.46–2.42 (m, 2H), 1.96–1.89 (m, 2H), 1.23 (t, $^{3}J_{H-H}$ = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 156.4 (d, $^{3}J_{P-C}$ = 21.1 Hz), 153.7 (d, $^{2}J_{P-C}$ = 19.6 Hz), 150.0, 149.9 (d, $^{1}J_{P-C}$ = 24.1 Hz), 142.4, 136.4 (d, $^{1}J_{P-C}$ = 9.1 Hz), 133.3 (d, $^{2}J_{P-C}$ = 18.1 Hz), 128.8, 128.7 (d, $^{3}J_{P-C}$ = 7.5 Hz), 128.6, 121.3, 37.9 (d, $^{3}J_{P-C}$ = 4.5 Hz), 34.1 (d, $^{2}J_{P-C}$ = 4.5 Hz), 28.6, 22.7, 15.8; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ −24.21; IR (Nujol) 3064 (m), 1609 (w), 1581 (w), 1571 (w), 1499 (m), 1477 (m), 1462 (m), 1433 (m), 1415 (w), 1377 (m), 1348 (w), 1261 (s), 1091 (s), 1058 (s), 1021 (s), 953 (w), 939 (w), 862 (m), 835 (m), 800 (s), 754 (m), 702 (m), 662 (w) $cm^{-1}$; HRMS $m/z$ calcd for $C_{26}H_{27}NP$ 384.1881 $[M + H]^+$, found 384.1885.

*2-Diphenylphosphinocyclopentene-1-(4-isopropylphenyl)imine (**2d**):* yellow solid (1.918 g, 63%); mp 124–125 °C; $^{1}H$ NMR ($CDCl_3$) $\delta$ 8.94 (d, $^{4}J_{P-H}$ = 4.0 Hz, 1H), 7.41–7.34 (m, 10H), 7.19 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 7.06 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 2.99–2.95 (m, 2H), 2.90 (sept, $^{3}J_{H-H}$ = 6.8 Hz, 1H), 2.46–2.42 (m, 2H), 1.96–1.89 (m, 2H), 1.25 (d, $^{3}J_{H-H}$ = 6.8 Hz, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ 156.5 (d, $^{3}J_{P-C}$ = 22.6 Hz), 153.8 (d, $^{2}J_{P-C}$ = 21.1 Hz), 150.1, 149.9 (d, $^{1}J_{P-C}$ = 22.6 Hz), 147.0, 136.4 (d, $^{1}J_{P-C}$ = 9.1 Hz), 133.3 (d, $^{2}J_{P-C}$ = 18.1 Hz), 128.8, 128.7 (d, $^{3}J_{P-C}$ = 7.5 Hz), 127.1, 121.3, 37.9 (d, $^{3}J_{P-C}$ = 3.0 Hz), 34.1 (d, $^{2}J_{P-C}$ = 4.5 Hz), 33.8, 24.2, 22.7; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) $\delta$ −24.82; IR (Nujol) 3067 (m), 2722 (m), 1896 (w), 1614 (m), 1584 (m), 1577 (m), 1516 (m), 1500 (m), 1476 (s), 1458 (s), 1379 (m), 1362 (m), 1351 (w), 1329 (w), 1296 (w), 1276 (w), 1260 (w), 1211 (m), 1180 (w), 1145 (w), 1110 (w), 1100 (m), 1089 (m), 1081 (m), 1068 (w), 1054 (m), 1026 (m), 1015 (w), 999 (w), 861


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(w), 834 (m), 746 (s), 699 (s) $cm^{-1}$; HRMS *m/z* calcd for $C_{27}H_{29}NP$ 398.2038 $[M + H]^+$, found 398.2036.

*2-Diphenylphosphinocyclopentene-1-(phenyl)imine (**2e**):* yellow solid (1.933 g, 71%); mp 120−122 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 8.93 (d, $^4J_{P-H}$ = 4.0 Hz, 1H), 7.45−7.30 (m, 10H), 7.25−7.08 (m, 5H), 3.02−2.95 (m, 2H), 2.50−2.42 (m, 2H), 1.98−1.89 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 157.1 (d, $^3J_{P-C}$ = 21.1 Hz), 153.6 (d, $^2J_{P-C}$ = 19.6 Hz), 152.4, 150.6 (d, $^1J_{P-C}$ = 22.6 Hz), 136.3 (d, $^1J_{P-C}$ = 7.5 Hz), 133.3 (d, $^2J_{P-C}$ = 19.6 Hz), 129.1, 128.8, 128.7 (d, $^3J_{P-C}$ = 6.0 Hz), 126.1, 121.3, 37.9 (d, $^3J_{P-C}$ = 3.0 Hz), 34.1 (d, $^2J_{P-C}$ = 4.5 Hz), 22.7; $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$ −24.20; IR (Nujol) 3064 (m), 1602 (m), 1570 (s), 1501 (w), 1483 (m), 1475 (s), 1465 (s), 1431 (s), 1377 (m), 1348 (w), 1328 (w), 1308 (w), 1261 (w), 1177 (w), 1091 (m), 1071 (m), 1023 (w), 760 (m), 745 (s), 699 (s), 684 (m) $cm^{-1}$; HRMS *m/z* calcd for $C_{24}H_{23}NP$ 356.1568 $[M + H]^+$, found 356.1566.

*2-Diphenylphosphinocyclopentene-1-(4-chlorophenyl)imine (**2f**):* yellow solid (2.269 g, 76%); mp 132−133 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 8.86 (d, $^4J_{P-H}$ = 4.2 Hz, 1H), 7.40−7.35 (m, 10H), 7.28 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 7.02 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 2.96−2.93 (m, 2H), 2.46−2.44 (m, 2H), 1.95−1.90 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 157.4 (d, $^3J_{P-C}$ = 21.1 Hz), 153.2 (d, $^2J_{P-C}$ = 19.6 Hz), 151.5 (d, $^1J_{P-C}$ = 22.6 Hz), 150.9, 136.1 (d, $^1J_{P-C}$ = 9.1 Hz), 133.3 (d, $^2J_{P-C}$ = 18.1 Hz), 131.6, 129.2, 128.9, 128.7 (d, $^3J_{P-C}$ = 6.0 Hz), 122.6, 38.1 (d, $^3J_{P-C}$ = 4.5 Hz), 34.0 (d, $^2J_{P-C}$ = 6.0 Hz), 22.7; $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$ −23.91; IR (Nujol) 3414 (m), 1888 (w), 1602 (s), 1581 (s), 1480 (s), 1466 (m), 1433 (m), 1402 (w), 1377 (w), 1260 (w), 1204 (w), 1100 (m), 1089 (s), 1070 (w), 1026 (w), 1009 (m), 825 (w), 812 (w), 746 (m), 704 (m), 698 (s) $cm^{-1}$; HRMS *m/z* calcd for $C_{24}H_{22}ClNP$ 390.1178 $[M + H]^+$, found 390.1174.

**[(3IP)Pd(allyl)]OTf Catalysts (3a−f).** Solutions of 3-iminophosphine ligand (1.1 equiv) and allylpalladium chloride dimer (0.5 equiv) in dichloromethane were combined at ambient temperature and stirred overnight. The resulting solution was placed under vacuum to remove all the volatiles and the residue washed with pentane. The solid residue was then dissolved in dichloromethane and concentrated to form a saturated solution, followed by layering with pentane to induce precipitation. The solution was filtered to yield the catalyst, which was washed with pentane and dried under vacuum before transferring into the glovebox. Percent yields for the [(3IP)Pd(allyl)]-OTf precatalysts were calculated on the basis of the allylpalladium chloride dimer used.

*[(2-diphenylphosphinocyclopentene-1-(4-N,N-dimethylaminophenyl)imine)Pd(allyl)]OTf (**3a**):* red solid (561 mg, 59%); mp 91 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 7.96 (d, $^4J_{P-H}$ = 1.8 Hz, 1H), 7.59−7.49 (m, 10H), 7.28 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 6.78 (b, 2H), 5.87−5.80 (m, 1H), 4.15 (d, $^3J_{H-H}$ = 7.2 Hz, 1H), 3.94 (m, 1H), 3.33 (d, $^3J_{H-H}$ = 5.4 Hz, 1H), 3.06−3.01 (m, 2H), 3.03 (s, 6H), 2.63−2.58 (m, 3H), 2.10−2.01 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 159.8 (d, $^3J_{P-C}$ = 7.5 Hz), 153.8 (d, $^2J_{P-C}$ = 18.1 Hz), 135.2, 133.1 (d, $^4J_{P-C}$ = 14.3 Hz), 132.6 (d, $^4J_{P-C}$ = 13.2 Hz), 132.0 (d, $^1J_{P-C}$ = 31.5 Hz), 130.6 (d, $^2J_{P-C}$ = 11.0 Hz), 129.8 (d, $^3J_{P-C}$ = 11.0 Hz), 129.1 (d, $^1J_{P-C}$ = 49.5 Hz), 128.8 (d, $^1J_{P-C}$ = 47.3 Hz), 123.0 (d, $^2J_{P-C}$ = 5.5 Hz), 122.8, 122.1, 120.0, 112.6, 89.1 (d, $^2J_{P-C}$ = 28.6 Hz), 54.7 (d, $^2J_{P-C}$ = 3.3 Hz), 40.5, 39.0 (d, $^2J_{P-C}$ = 12.1 Hz), 36.1, 22.8, 22.5 (d, $^3J_{P-C}$ = 5.5 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$ 13.11; IR (Nujol) 1615 (w), 1576 (w), 1505 (w), 1463 (m), 1296 (s), 1231 (s), 1167 (s), 1100 (m), 1021 (s), 893 (w), 844 (w), 802 (w), 749 (w), 721 (w), 697 (w), 635 (s) $cm^{-1}$.

*[(2-diphenylphosphinocyclopentene-1-(4-methylphenyl)imine)-Pd(allyl)]OTf (**3b**):* dark brown solid (610 mg, 62%); mp 98 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 8.02 (d, $^4J_{P-H}$ = 2.4 Hz, 1H), 7.62−7.48 (m, 10H), 7.23 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 7.19 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 5.80−5.73 (m, 1H), 3.97−3.95 (m, 1H), 3.88−3.84 (m, 1H), 3.40 (d, $^3J_{H-H}$ = 5.4 Hz, 1H), 3.08−2.98 (m, 2H), 2.65−2.58 (m, 2H), 2.46 (d, $^3J_{H-H}$ = 12.0 Hz, 1H), 2.39 (s, 3H), 2.09−2.02 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 163.0 (d, $^3J_{P-C}$ = 7.5 Hz), 155.5, 138.4, 136.5 (d, $^1J_{P-C}$ = 33.2 Hz), 133.1 (d, $^4J_{P-C}$ = 13.6 Hz), 132.6 (d, $^4J_{P-C}$ = 12.1 Hz), 131.1 (d, $^2J_{P-C}$ = 34.7 Hz), 130.9, 130.1 (d, $^2J_{P-C}$ = 15.1 Hz), 129.6 (d, $^3J_{P-C}$ = 12.1 Hz), 129.3 ($^1J_{P-C}$ = 52.8 Hz), 128.6 ($^1J_{P-C}$ = 51.3 Hz) 123.0 (d, $^2J_{P-C}$ = 4.5 Hz), 122.7, 121.3, 120.8, 89.2 (d, $^2J_{P-C}$ = 28.7 Hz), 54.9 (d, $^2J_{P-C}$ = 4.5 Hz), 38.9 (d, $^2J_{P-C}$ = 12.1 Hz), 36.1, 22.4 (d, $^3J_{P-C}$ = 4.5 Hz), 21.1; $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$ 12.83; IR (Nujol) 1641 (w), 1614 (w), 1574 (w), 1503 (m), 1462 (s), 1440 (m), 1377 (m), 1296 (s), 1260 (s), 1156 (m), 1098 (m), 1021 (s), 863 (w), 803 (m), 747 (m), 721 (w), 695 (m) $cm^{-1}$. Anal. Calcd for $C_{29}H_{29}F_3NO_3PPdS{\cdot}3CH_2Cl_2$: C, 41.74; H, 3.83; N, 1.52. Found: C, 42.36; H, 3.98; N, 1.67.

*[(2-diphenylphosphinocyclopentene-1-(4-ethylphenyl)imine)Pd-(allyl)]OTf (**3c**):* yellow solid (522 mg, 54%); mp 88−90 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 8.01 (d, $^4J_{P-H}$ = 2.4 Hz, 1H), 7.62−7.52 (m, 10H), 7.26 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.24 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 5.83−5.76 (m, 1H), 3.96−3.91 (m, 2H), 3.37 (d, $^3J_{H-H}$ = 5.4 Hz, 1H), 3.08−3.03 (m, 2H), 2.68 (q, $^3J_{H-H}$ = 7.8 Hz, 2H), 2.65−2.60 (m, 3H), 2.11−2.03 (m, 2H), 1.24 (t, $^3J_{H-H}$ = 7.8 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 162.7 (d, $^3J_{P-C}$ = 7.5 Hz), 155.7, 153.5 (d, $^2J_{P-C}$ = 18.1 Hz), 144.4, 136.5 (d, $^1J_{P-C}$ = 33.2 Hz), 133.1 (d, $^4J_{P-C}$ = 13.6 Hz), 132.8 (d, $^4J_{P-C}$ = 12.1 Hz), 132.0 (d, $^2J_{P-C}$ = 22.6 Hz), 129.8 (d, $^3J_{P-C}$ = 10.6 Hz), 129.1 (d, $^1J_{P-C}$ = 48.3 Hz), 128.7, 128.5 (d, $^1J_{P-C}$ = 45.3 Hz), 123.0 (d, $^3J_{P-C}$ = 6.0 Hz), 122.2, 121.1, 120.1, 89.2 (d, $^2J_{P-C}$ = 28.7 Hz), 54.7 (d, $^2J_{P-C}$ = 3.0 Hz), 38.9 (d, $^2J_{P-C}$ = 10.6 Hz), 36.1, 28.5, 22.4 (d, $^3J_{P-C}$ = 4.5 Hz), 15.6; $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$ 12.73; IR (Nujol) 2293 (w), 1612 (w), 1574 (w), 1502 (m), 1481 (m), 1461 (s), 1437 (s), 1377 (m), 1260 (s), 1222 (s), 1183 (m), 1146 (s), 1099 (s), 1073 (m), 1029 (s), 998 (m), 963 (w), 841 (w), 802 (w), 751 (m), 696 (m) $cm^{-1}$. Anal. Calcd for $C_{30}H_{31}F_3NO_3PPdS$: C, 52.99; H, 4.60; N, 2.06. Found: C, 52.45; H, 4.75; N, 2.06.

*[(2-diphenylphosphinocyclopentene-1-(4-isopropylphenyl)-imine)Pd(allyl)]OTf (**3d**):* brown solid (495 mg, 52%); mp 93 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 8.01 (d, $^4J_{P-H}$ = 2.4 Hz, 1H), 7.66−7.52 (m, 10H), 7.26 (s, 4H), 5.82−5.76 (m, 1H), 3.97−3.91 (m, 2H), 3.37 (d, $^3J_{H-H}$ = 5.4 Hz, 1H), 3.08−3.02 (m, 2H), 2.94 (sept, $^3J_{H-H}$ = 6.6 Hz, 1H), 2.66 (d, $^3J_{H-H}$ = 12.0 Hz, 1H), 2.64−2.60 (m, 2H), 2.10−2.03 (m, 2H), 1.25 (d, $^3J_{H-H}$ = 6.6 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 162.8 (d, $^3J_{P-C}$ = 6.0 Hz), 155.8, 153.5 (d, $^2J_{P-C}$ = 18.1 Hz), 149.1, 136.5 (d, $^1J_{P-C}$ = 33.2 Hz), 133.1 (d, $^4J_{P-C}$ = 13.6 Hz), 132.7 (d, $^4J_{P-C}$ = 15.1 Hz), 132.0 (d, $^2J_{P-C}$ = 22.6 Hz), 129.8 (d, $^3J_{P-C}$ = 12.1 Hz), 129.5 (d, $^1J_{P-C}$ = 34.0 Hz), 128.8, 128.7 (d, $^1J_{P-C}$ = 36.9 Hz), 127.3, 123.0 (d, $^2J_{P-C}$ = 4.5 Hz), 121.5, 121.1, 89.2 (d, $^2J_{P-C}$ = 28.7 Hz), 54.7 (d, $^2J_{P-C}$ = 4.5 Hz), 38.9 (d, $^2J_{P-C}$ = 12.1 Hz), 36.1, 33.9, 24.1, 22.4 (d, $^3J_{P-C}$ = 6.0 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$ 12.72; IR (Nujol) 1611 (m), 1574 (m), 1501 (m), 1482 (m), 1437 (s), 1378 (m), 1366 (m), 1259 (s), 1222 (s), 1148 (s), 1099 (s), 1028 (s), 999 (s), 922 (w), 863 (m), 838 (m), 801 (s), 749 (m), 696 (m), 635 (s) $cm^{-1}$. Anal. Calcd for $C_{31}H_{33}F_3NO_3PPdS{\cdot}0.5CH_2Cl_2$: C, 51.37; H, 4.65; N, 1.90. Found: C, 50.99; H, 4.98; N, 1.91.

*[(2-diphenylphosphinocyclopentene-1-(phenyl)imine)Pd(allyl)]-OTf (**3e**):* brown solid (600 mg, 60%); mp 102−104 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 8.02 (d, $^4J_{P-H}$ = 2.4 Hz, 1H), 7.60−7.45 (m, 8H), 7.43−7.38 (m, 2H), 7.33−7.24 (m, 5H), 5.80−5.74 (m, 1H), 3.91−3.86 (m, 2H), 3.37 (d, $^3J_{H-H}$ = 5.4 Hz, 1H), 3.08−3.03 (m, 2H), 2.66 (d, $^3J_{H-H}$ = 12.6 Hz, 1H), 2.64−2.59 (m, 2H), 2.10−2.03 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 163.2 (d, $^3J_{P-C}$ = 6.0 Hz), 157.8, 153.4 (d, $^2J_{P-C}$ = 18.1 Hz), 136.9 (d, $^1J_{P-C}$ = 33.2 Hz), 133.1 (d, $^4J_{P-C}$ = 13.6 Hz), 132.7 (d, $^4J_{P-C}$ = 13.6 Hz), 132.0 (d, $^2J_{P-C}$ = 22.6 Hz), 129.8 (d, $^3J_{P-C}$ = 12.1 Hz), 129.5, 128.9 (d, $^1J_{P-C}$ = 49.8 Hz), 128.4 (d, $^1J_{P-C}$ = 48.3 Hz), 128.0, 123.0 (d, $^2J_{P-C}$ = 7.5 Hz), 122.1, 121.1, 119.9, 89.0 (d, $^2J_{P-C}$ = 28.7 Hz), 54.8 (d, $^2J_{P-C}$ = 3.0 Hz), 38.9 (d, $^2J_{P-C}$ = 10.6 Hz), 36.2, 22.4 (d, $^3J_{P-C}$ = 6.0 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$ 12.70; IR (Nujol) 1570 (w), 1482 (w), 1463 (s), 1438 (m), 1377 (m), 1261 (s), 1222 (m), 1148 (m), 1099 (m), 1029 (s), 999 (w), 800 (w), 774 (w), 752 (w), 736 (w), 695 (m) $cm^{-1}$; Anal. Calcd for $C_{28}H_{27}F_3NO_3PPdS$: C, 51.58; H, 4.17; N, 2.15. Found: C, 51.21; H, 4.45; N, 2.32.

*[(2-diphenylphosphinocyclopentene-1-(4-chlorophenyl)imine)-Pd(allyl)]OTf (**3f**):* brown solid (663 mg, 69%); mp 109 °C dec; $^1H$ NMR ($CDCl_3$) $\delta$ 8.02 (d, $^4J_{P-H}$ = 2.4 Hz, 1H), 7.61−7.51 (m, 10H), 7.38 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 7.34 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 5.80−5.73 (m, 1H), 3.95−3.93 (m, 1H), 3.92−3.88 (m, 1H), 3.36 (d, $^3J_{H-H}$ = 4.8 Hz, 1H), 3.09−3.03 (m, 2H), 2.66 (d, $^3J_{H-H}$ = 12.6 Hz, 1H), 2.63−2.59 (m, 2H), 2.08−2.03 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 163.8 (d, $^3J_{P-C}$ = 7.5 Hz), 156.2, 153.5 (d, $^2J_{P-C}$ = 16.6 Hz), 137.2 (d, $^1J_{P-C}$


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= 33.2 Hz), 133.6, 133.1 (d, $^4J_{P-C}$ = 15.1 Hz), 132.8 (d, $^4J_{P-C}$ = 13.6 Hz), 132.0 (d, $^2J_{P-C}$ = 19.6 Hz), 130.4, 129.8 (d, $^3J_{P-C}$ = 10.6 Hz), 129.5, 129.0 (d, $^1J_{P-C}$ = 48.3 Hz), 128.4 (d, $^1J_{P-C}$ = 48.3 Hz), 123.0 (d, $^3J_{P-C}$ = 7.5 Hz), 122.8, 121.5, 88.9 (d, $^2J_{P-C}$ = 28.7 Hz), 54.9 (d, $^2J_{P-C}$ = 3.0 Hz), 38.9 (d, $^2J_{P-C}$ = 12.1 Hz), 36.2, 22.4 (d, $^3J_{P-C}$ = 6.0 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta$ 12.62; IR (Nujol) 1611 (w), 1575 (w), 1483 (s), 1463 (s), 1438 (s), 1377 (m), 1337 (m), 1315 (m), 1261 (s), 1231 (s), 1208 (s), 1155 (s), 1099 (s), 1029 (s), 1012 (s), 999 (m), 983 (m), 860 (w), 832 (w), 747 (m), 720 (w), 695 (m) $cm^{-1}$; Anal. Calcd for $C_{28}H_{26}ClF_3NO_3PPdS{\cdot}CH_2Cl_2$: C, 45.16; H, 3.66; N, 1.82. Found: C, 44.37; H, 3.69; N, 1.94.

**General Procedure for the Catalytic Hydroamination Screening of Catalysts 3a–f.** All manipulations were performed in an NMR tube inside a nitrogen-filled glovebox. Cyclohexylallene (61 mg, 0.50 mmol) was added to a mixture of $C_6H_6$ (0.50 mmol as internal standard), secondary amine (0.50 mmol), [(3IP)Pd(allyl)]-OTf (0.025 mmol), and deuterated benzene (800 $\mu$L). The ratio of each substrate to hydroamination product was monitored by $^1H$ NMR spectroscopy. After reaction completion was observed, the volatiles were removed from the reaction mixture under vacuum. The residue was washed with pentane/ethyl acetate (90/10 by volume) and passed through a plug of silica. Solvents were removed, and the colorless liquid was isolated and characterized as the hydroamination products. Two of the observed hydroamination products, 1-[(2*E*)-3-cyclohexyl-2-propen-1-yl]pyrrolidine,[72] and 4-[(2*E*)-3-cyclohexyl-2-propen-1-yl]-morpholine,[73] were reported previously (isolated yields 81% and 87%, respectively).

*(E)-2-(3-Cyclohexylallyl)-1,2,3,4-tetrahydroisoquinoline:* colorless liquid; yield 85%; $^1H$ NMR ($C_6D_6$) $\delta$ 7.05–7.02 (m, 2H), 6.98 (dd, $^3J_{H-H}$ =5.5 Hz, $^4J_{H-H}$ = 2.2 Hz, 1H), 6.90 (dd, $^3J_{H-H}$ = 6.6 Hz, $^4J_{H-H}$ = 1.9 Hz, 1H), 5.60–5.59 (m, 2H), 3.55 (s, 1H), 3.03–3.02 (m, 2H), 2.78 (t, $^3J_{H-H}$ = 5.8 Hz, 3H), 2.58 (t, $^3J_{H-H}$ = 5.8 Hz, 2H), 1.94–1.89 (m, 1H), 1.73–1.70 (m, 2H), 1.65 (dt, $^2J_{H-H}$ = 13.2 Hz, $^3J_{H-H}$ = 3.7 Hz, 2H), 1.61–1.57 (m, 1H), 1.19 (tt, $^2J_{H-H}$ = 12.4 Hz, $^3J_{H-H}$ = 3.3 Hz, 2H), 1.11–1.05 (m, 3H); $^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ 139.8, 135.8, 135.0, 129.0, 126.9, 126.3, 125.8, 125.3, 61.2, 56.4, 50.9, 40.9, 33.4, 29.9, 26.6, 26.4; HRMS *m*/*z* calcd for $C_{18}H_{26}N$ 256.2065 $[M + H]^+$, found 256.2062.

*(E)-1-(3-Cyclohexylallyl)piperidine:* colorless liquid; yield 88%; $^1H$ NMR ($C_6D_6$) 5.60 (dt, $^3J_{H-H}$ = 15.8 Hz, $^3J_{H-H}$ = 6.2 Hz, 1H), 5.55 (dd, $^3J_{H-H}$ = 15.8 Hz, $^3J_{H-H}$ = 5.9 Hz, 1H), 2.93 (d, $^3J_{H-H}$ = 6.2 Hz, 2H), 1.93–1.87 (m, 1H), 1.73–1.55 (m, 11H), 1.20–1.02 (m, 9H); $^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ 138.3, 126.5, 58.8, 54.2, 40.9, 33.5, 26.6, 26.5, 25.8, 24.0; HRMS *m*/*z* calcd for $C_{14}H_{26}N$ 208.2065 $[M + H]^+$, found 208.2067.

## ■ ASSOCIATED CONTENT

### Supporting Information

Text, tables, and figures giving synthetic procedures for piperidine-$d_1$, reaction rate plots, and NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/om500792k.

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### Notes

The authors declare no competing financial interest.

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