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Investigation of Steric and Electronic Features of 3-Iminophosphine-Based Palladium Catalysts for Intermolecular Hydroamination

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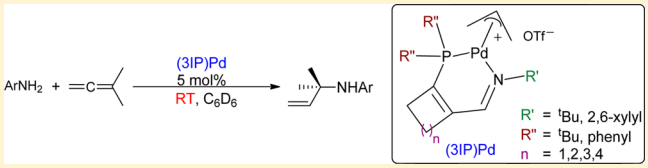
Supporting Information

ABSTRACT: A series of (3-iminophosphine)allylpalladium triflate complexes with systematic variation of both steric and electronic features was isolated and characterized. The ability of the complexes in this series to catalyze the regioselective hydroamination of 3-methyl-1,2-butadiene with aryl amines to form solely the kinetic product was probed by observing conversion to products via NMR spectroscopy. The previously unstudied 3-iminophosphine ligand composed of a di-*tert*-butyl phosphine, cyclobutene backbone, and *tert*-butyl imine provided the most active palladium hydroamination catalyst for this transformation known to date.

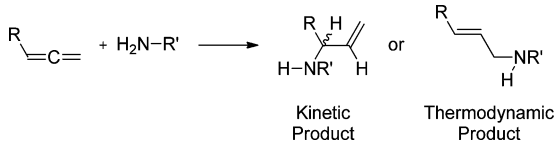


INTRODUCTION

Hydroamination is an advantageous method for the preparation of primary, secondary, and tertiary amines due to its 100% atom economy[1] and the wide range of regio-, stereo-, and enantioselective metal complexes that are available to catalyze this transformation.[2−10] The hydroamination process is characterized by the addition of an N−H bond of ammonia or of a primary or secondary amine across an unsaturated C−C bond of an alkene, alkyne, or allene. The reaction can take place either intermolecularly at a high entropic demand using affordable and readily obtained substrates or intramolecularly with low entropic demand, but requiring less accessible starting materials. Although hydroamination is slightly exothermic, the direct [2+2] cycloaddition of an N−H across a C−C unsaturated bond is orbitally forbidden under thermal conditions, making a catalytic route for this process a virtual necessity.[2]

The hydroamination of allenes allows for the synthesis of allylic amines, which can be further transformed using a wide variety of reactions including hydroboration,[11] hydroformylation,[12] alkene metathesis,[13] and heterocycle synthesis.[2] Allylic amines also play a major role in the synthesis of pharmaceutical and natural products.[14] Early transition metal complexes have been shown to catalyze allene hydroamination with addition of the nitrogen group to the central carbon of the allene and subsequent tautomerization of the resulting enamine to form an imine in the case of primary amine substrates, whereas late transition metal catalysts are known to hydroaminate allenes with addition of the nitrogen moiety to one of the terminal carbons, resulting in retention of the allyl group.[2] Intramolecular hydroamination of allenes leads to nitrogen-containing heterocycles. Although intramolecular hydroamination of allenes has been studied briefly,[15−22] with a focus on enantioselective conversion to products, examples of intermolecular allene hydroamination are more prevalent and include those published by Bertrand,[5,23,24] Widenhoefer,[25−27] Yamamoto,[28,29] Toste,[30] and Schafer,[31,32] as well as our own group.[3,33] Late transition metal catalyzed intermolecular hydroamination of substituted allenes yields two possible regioisomers. Addition of the amino moiety to the substituted carbon terminus of a monosubstituted allene yields a new chiral carbon center and a vinyl-terminated product, which is typically the kinetic product of these reactions (Scheme 1). Addition of the amine at the less-substituted carbon atom yields an internal alkene, commonly the thermodynamic product (Scheme 1). Regioselective hydroamination of substituted allenes to form the thermodynamic product is much more common and has been accomplished previously with aryl amines and a gold catalyst,[25,28] secondary alkylamines and gold[24,29] or platinum[26] catalysts, ammonia and a gold catalyst,[23] and hydrazine with a gold catalyst.[5] Also notable is Toste's mechanistic study involving the hydroamination of a symmetrical allene with methyl carbazate, which demonstrated activation of the allene as the rate-limiting step and implied that there was no coordinated amine in the catalytic mechanism.[30] Regioselective intermolecular hydroamination of substituted allenes to form the kinetic (branched) product, though much rarer, has been accomplished via a gold(I) N-heterocyclic carbene complex,

Scheme 1. Late Transition Metal Catalyzed Hydroamination of Substituted Allenes



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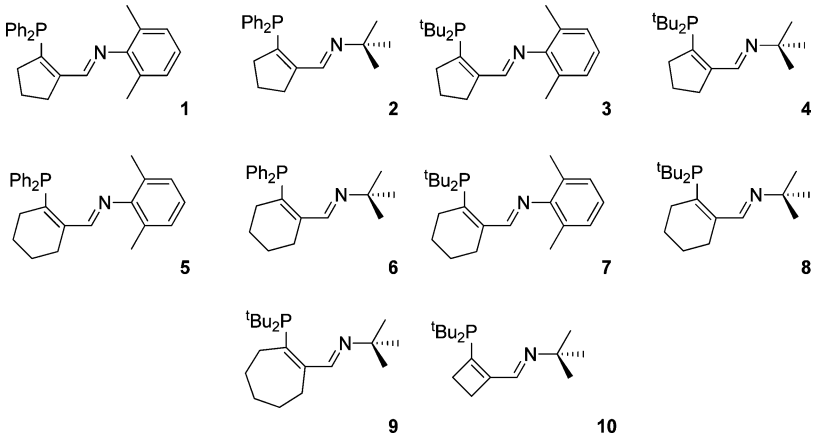


Figure 1. 3-Iminophosphine (3IP) ligands **1**−**10**.

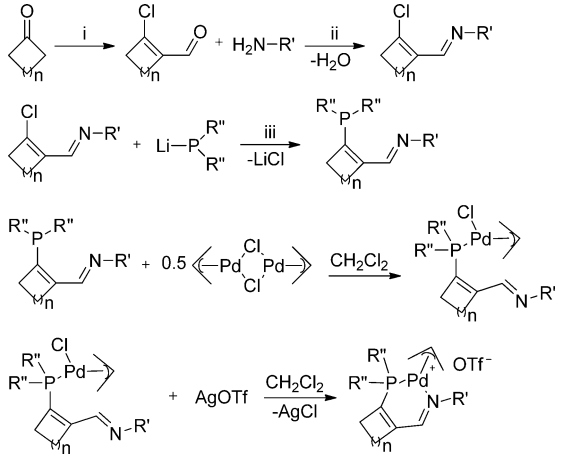
although substrate scope was limited to the addition of an N-unsubstituted carbamate,[4] as well as with a rhodium(I) Josiphos complex that was able to add a series of anilines enantioselectively to the more substituted side of the allene.[34] The development of new catalysts capable of producing the branched product in these reactions would be considerably advantageous in order to expand upon this limited substrate scope and to allow a much larger variety of allylic amines to be synthesized via hydroamination. Also of interest is the development of more cost-effective metal catalysts, as gold, platinum, and rhodium are among the most expensive of the transition metals.

Synthesized previously in our group were 3-iminophosphine (3IP) ligands **2**,[35] **4**,[3] and **5**[33] (Figure 1), as well as their respective [(3IP)Pd(allyl)]OTf complexes **2Pd**,[35] **4Pd**,[3] and **5Pd**.[33] **2Pd** was shown to hydroaminate phenylacetylene and 1,3-cyclohexadiene in moderate yields,[35] whereas **5Pd** was shown to hydroaminate 3-methyl-1,2-butadiene (1,1-dimethylallene) and 2,3-dimethyl-1,3-butadiene with secondary alkylamines regioselectively to form the thermodynamic (linear) products in moderate to excellent yields.[33] The most significant advance in the development of these catalysts came with the discovery of **4Pd**, which was found to regiospecifically hydroaminate 1,1-dimethylallene using a variety of aryl amines (anilines) to form solely the kinetic (branched) products in good to excellent yields.[3] Because the observed catalysis of these three different ligand frameworks varied dramatically, it was hypothesized that the specific steric and electronic features of the ligand were responsible for the greatly varying catalytic activity. Unfortunately, in the development of our hydroamination catalysts (**2Pd**, **4Pd**, and **5Pd**), the ligand framework was not altered in a systematic fashion, but rather involved changes to two ligand components with each new catalyst explored. Thus, the catalytic data generated with our three previously published [(3IP)Pd(allyl)]OTf complexes were insufficient in determining which alterations to ligand design were critical in order to optimize catalytic activity. As a means to address this deficiency, synthesized herein is an array of eight [(3IP)Pd(allyl)]OTf complexes with systematic variance of the steric and electronic features of the 3IP ligands. Each palladium complex was screened for catalytic activity in the hydroamination of 1,1-dimethylallene with a selection of seven aryl amines spanning a wide range of steric and electronic parameters. Also reported herein is the synthesis of two additional ligands and their respective [(3IP)Pd(allyl)]OTf complexes whose designs were based upon the results of the catalytic screening of the original array of eight complexes.

RESULTS AND DISCUSSION

The effectiveness of 3-iminophosphine allylpalladium triflate complexes as catalysts for the hydroamination of 1,3-dienes, allenes, and alkynes with primary and secondary amines has been shown previously.[33] These results implied that the steric and electronic properties of the 3IP supporting ligands have a significant effect on the rates observed in hydroamination catalysis. These ligand properties can be governed via substitution of three tunable domains: the size of the alicyclic backbone and the substituent groups of the imine and phosphine moieties. For example, cyclic ketones that vary in ring size can be reacted with the Vilsmeier−Haack reagent, various amines can be used for the Schiff base condensation, and phosphination can be completed with different disubstituted lithium phosphides in the synthesis of these ligands (Scheme 2). Our previous reports detail the synthesis and isolation of ligands **2**,[35] **4**,[3] and **5**,[33] as well as their respective allyl palladium triflate complexes **2Pd**,[35] **4Pd**,[3] and **5Pd**.[33]

Scheme 2. General Synthesis of [(3IP)Pd(allyl)]OTf Complexes[a]



[a] n = 1−4, R′ = ^{t}Bu or 2,6-dimethylphenyl, R″ = ^{t}Bu or Ph. (i) 2 equiv of DMF, 1.6 equiv of $POCl_3$, 0 °C, 4 h then 55 °C, 14 h; 0 °C, $NaHCO_3$; (ii) 1.3 equiv of H_2NR', pentane, 4 Å molecular sieves, 0 °C; (iii) 1.6 equiv of $LiPR''_2$, Et_2O, 3 h, RT.

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Unfortunately, the ligands described in our previous reports varied two tunable domains with each catalyst improvement. The synthesis of complexes with systematic variation of the three tunable domains would allow for correlation of catalytic activity with each domain involved in ligand construction. Thus, in the current contribution, we set out to produce a complete series of 3IP ligands utilizing both backbone ring sizes (cyclopentenyl and cyclohexenyl), imines (*tert*-butyl and 2,6-xylyl), and phosphines (*tert*-butyl and phenyl) to determine the impact of each unit on catalytic activity (**1**−**8**, Figure 1). Then, by use of the palladium complexes of these eight ligands in catalysis, we hoped that an empirical understanding of the effectiveness of these ligand components would allow for the rational design of improved hydroamination catalysts.

Compounds **1**, **3**, and **6** were synthesized using procedures analogous to those for 3-iminophosphines **2**,[35] **4**,[3] and **5**,[33] respectively, while ligands **7**, **8**, **9**, and **10** required significant modifications to the experimental methodology (Scheme 2). The main change involved the dropwise addition of a dilute solution of lithium di-*tert*-butylphosphide in diethyl ether to a rapidly stirred solution of the selected chloroimine in diethyl ether at ambient temperature. The attempted use of our previous synthetic procedures consistently resulted in multiple unidentifiable phosphorus-containing products that were inseparable from both the target ligand and the final palladium complex. Overall, the syntheses of ligands **7**−**10** were especially sensitive, requiring the purest of starting materials. Chloroaldehyde of high purity was produced via neat reaction of the cyclic ketone with the Vilsmeier−Haack reagent (Scheme 2), under a nitrogen atmosphere using degassed reagents. After reacting for 14 h at 55 °C, the resulting solution was made basic and extracted with pentane, in contrast to diethyl ether as cited previously.[35] This improved methodology, analogous to that of Paquette,[36] is vital for achieving reaction completion and ensuring chloroaldehyde purity, as well as improving product stability at both low and ambient temperatures. Prior to its use, lithium di-*tert*-butylphosphide was recrystallized from diethyl ether and rinsed with pentane to minimize highly reactive impurities that were found to complicate phosphination of the various chloroimines, leading to multiple unidentifiable phosphorus-containing products. Ligand coordination and ion exchange reactions yielding the final [(3IP)Pd(allyl)]OTf complexes proceeded analogously to Beck and Schmidt[3] (Scheme 2) with only slight workup modifications. Specifically, the intermediate 3IP allylpalladium chloride complex was rinsed of excess ligand before treatment with silver triflate because we have found that byproduct silver chloride is readily coordinated by excess 3IP ligand. Furthermore, toluene was excluded from the anion exchange step, as its presence seems to destabilize the palladium complex, resulting in presumed palladium(0) byproducts that were not soluble in the readily available solvents.

All of the ligands and palladium complexes described in this report are diamagnetic, and so an analysis of their NMR spectroscopic features proves quite insightful. As one would anticipate, substantial differences were noted between ^{1}H, ^{13}C, and ^{31}P NMR spectra of the free 3-iminophosphine ligands and those of the [(3IP)Pd(allyl)]OTf complexes. Further differences were evident when comparing ligands and their respective complexes with di-*tert*-butylphosphino moieties to those possessing diphenylphosphino moieties. Downfield shifts in the ^{31}P NMR signals were observed upon coordination of the ligand to the palladium, with a further downfield shift upon chloride abstraction (Table 1). The absolute change in ppm for the ^{31}P NMR signal between free ligands and the target

Table 1. Comparison between Selected ^{31}P and ^{1}H NMR Resonances of [(3IP)Pd(allyl)]OTf Complexes and Their Respective Free 3IP Ligands (all values in ppm)

	3IPPd[a] ^{31}P δ	3IP[b] ^{31}P δ	Δ^{31}P δ	3IPPd[a] R′N=CH ^{1}H δ	3IP[b] R′N=CH ^{1}H δ	Δ^{1}H δ
1	13.11	−23.20	36.31	7.88	8.64	−0.76
2	16.90	−24.70	41.60	7.94	8.72	−0.78
3	59.48	13.24	46.24	7.84	8.82	−0.98
4	61.80	13.20	48.60	8.06	8.88	−0.82
5	25.20	−12.60	37.80	7.70	9.05	−1.35
6	31.78	−12.70	44.48	7.65	9.09	−1.44
7	71.63	20.05	51.58	7.65	9.32	−1.67
8	75.37	19.98	55.39	7.85	9.37	−1.52
9	80.64	24.81	55.83	8.07	9.37	−1.30
10	55.18	11.36	43.82	7.94	8.27	−0.33

[a]**3IPPd** refers to [(3IP)Pd(allyl)]OTf complex. [b]**3IP** refers to uncoordinated ligand.

[(3IP)Pd(allyl)]OTf complexes ($\Delta^{31}P\delta$) varied greatly depending on the ligand used. $\Delta^{31}P\delta$ was always larger for complexes with larger backbone size while holding phosphine and imine substituents constant. Also, in every case complexes with di-*tert*-butylphosphino moieties had larger $\Delta^{31}P\delta$ values than the corresponding complexes with diphenylphosphino moieties. Furthermore, all ^{31}P NMR resonances for complexes and ligands with di-*tert*-butylphosphino moieties were located further downfield than those of the corresponding diphenylphosphino moieties. Keeping imine and phosphine moieties constant, all complexes with larger backbone sizes displayed signals that were also located further downfield than those with smaller backbone sizes. These ^{31}P NMR spectroscopic trends imply that the phosphorus of the ligand is more tightly bound to the metal for the larger backbone rings and for the di-*tert*-butylphosphino complexes. All ^{1}H NMR resonances for the imine C−H of the palladium complexes rested at or slightly below 8 ppm, an upfield shift from that of the free ligands, which were typically found around 9 ppm. Ligand **10** displayed a significantly upfield imine proton resonance compared to the rest of the free ligands. It also showed the smallest change in ^{1}H NMR resonance ($\Delta^{1}H\delta$) upon coordination to form complex **10Pd**, with a mere −0.33 ppm shift (the negative number denoting an upfield shift from ligand to triflated complex). The other species shifted from −0.76 to −1.67 ppm upon formation of the triflate complexes. In general, the upfield shift in the imine proton resonance can be attributed to reduction in the carbon−nitrogen double-bond character upon coordination of the imine lone pair to palladium. A smaller than normal upfield shift correlates to a smaller loss of double-bond character consistent with weaker imine nitrogen coordination to palladium. Thus, it seems that ligand **10** binds less strongly to the metal center through its imine nitrogen atom than the other ligands in this series. The trends in the ^{13}C NMR spectra parallel those of the ^{1}H NMR spectra, as there are significant changes in the chemical shift of the imine carbon between free and coordinated ligands. The terminal carbons of the allyl ligands (*cis* and *trans* to phosphorus) were readily differentiated based upon both the magnitude of the J_{P-C} coupling constant and their relative chemical shift values. The *trans* carbon was

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typically located downfield from the *cis* carbon and displayed a J_{P-C} coupling constant an order of magnitude larger.

Many of the palladium allyl triflate complexes (**1Pd**, **2Pd**,[35] **4Pd**,[3] **5Pd**,[33] **8Pd**, and **9Pd**) were structurally characterized via X-ray crystallography. In all cases, X-ray quality single crystals were grown from pentane-layered THF solutions at −25 °C. Each complex had an outer-sphere triflate anion with palladium's coordination sphere occupied by the chelating 3-iminophosphine ligand and a single $^3\eta$-allyl group, producing a distorted square-planar geometry. Structures of **1Pd** (see Supporting Information; Figure S1) and **5Pd**,[33] differing only in the size of the alicyclic backbone, both exhibited disorder in their allyl ligands to the extent that no discernible comparison could be made between their bite angles. The series of three complexes with *tert*-butyl groups on both nitrogen and phosphorus, but with variation of the backbone size from five to seven carbon atoms, varied less dramatically in bite angle and seemed more dependent on the position of the allyl group relative to that of the alicyclic backbone. Viewing the molecule along the P−Pd−N plane, an allyl group pointing in the direction of the backbone is denoted as *cis*, while one pointing in the opposite direction is denoted as *trans*. Complex **4Pd** exists as the *trans* isomer, **8Pd** exists as the *cis* isomer (see Supporting Information; Figure S2), and **9Pd** has both the *cis* and *trans* isomers in its asymmetric unit (Figures 2 and 3).

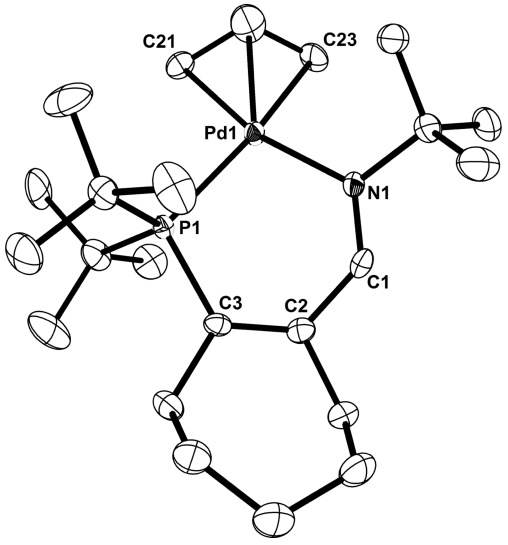

Figure 2. ORTEP diagram (50% thermal ellipsoids) of *trans*-**9Pd** (top view). Triflate anion and hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å): Pd1−P1 = 2.331(1), Pd1−N1 = 2.098(4), Pd1−C21 = 2.162(5), Pd1−C23 = 2.257(5), P1−C3 = 1.845(5), C1−C2 = 1.472(6), C2−C3 = 1.361(6), N1−C1 = 1.288(6). Bond angles (in deg): P1−Pd1−N1 = 92.1(1), C21−Pd1−C23 = 66.4(2), N1−Pd1−C21 = 166.8(2), N1−Pd1−C23 = 101.5(2), P1−Pd1−C21 = 100.9(1), P1−Pd1−C23 = 162.5(1), Pd1−P1−C3 = 109.1(2), P1−C3−C2 = 122.4(4), C1−C2−C3 = 126.2(4), N1−C1−C2 = 131.7(4), Pd1−N1−C1 = 123.2(3).

Those with the *trans* relationship had more strained bite angles, i.e., **4Pd** at 92.52(6)° and *trans*-**9Pd** at 92.1(1)°, while the *cis* complexes **8Pd** and *cis*-**9Pd** had bite angles of 89.8(2)° and 90.1(1)°, respectively. Again, the cyclopentenyl complex (**4Pd**) deviated the most from the ideal 90° bite angle. Complex **2Pd**, which is a hybrid of the two series, has a bite angle of 92.9(5)°, very close to that of **4Pd**, most likely due to its similar *trans* configuration. This may also indicate that the imine's

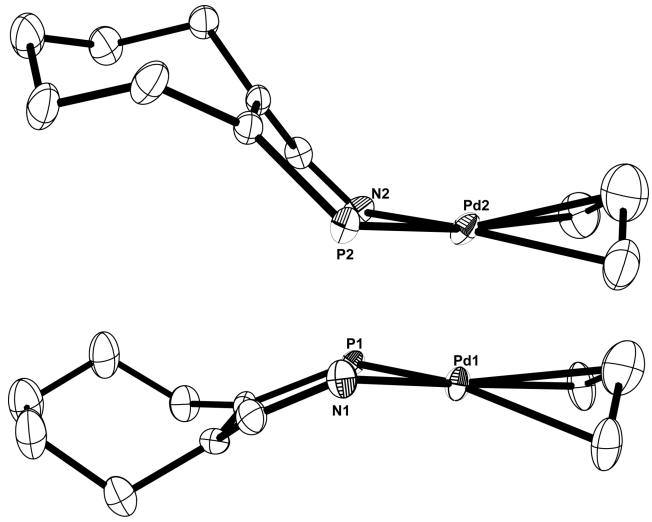

Figure 3. ORTEP diagrams (50% thermal ellipsoids) of *cis* (top) and *trans* (bottom) isomers of **9Pd** (side views). Triflate anion, hydrogen atoms, and *tert*-butyl groups have been omitted for clarity.

substituent group is more significant in determining the angle than those of the phosphine. All Pd−N distances varied little, whereas Pd−P distances were generally shorter for diphenylphosphino moieties (∼2.27 Å) than for di-*tert*-butylphosphino moieties (∼2.33 Å), which likely reflects the larger steric bulk of the *tert*-butyl groups. Similar disubstituted bidentate phosphine palladium complexes show similar Pd−P bond distance patterns.[37,38]

In our most recent report, compound **4Pd** was shown to readily catalyze the hydroamination of 1,1-dimethylallene with primary aryl amines (anilines) to form exclusively the kinetic (terminal alkene) products at room temperature (product A; Table 2).[3] Sterically hindered anilines prevented hydroamination in all cases, while halogenated anilines required heating to a temperature of 70 °C in order to achieve appreciable conversion to product. In an effort to more fully understand this reactivity, to improve upon the catalytic performance of **4Pd**, and to test our previously reported complexes **2Pd**[35] and **5Pd**[33] in allene hydroamination, the complete array of ligands **1**−**8** and their respective complexes **1Pd**−**8Pd** were synthesized. All eight palladium complexes were then tested in the hydroamination of 1,1-dimethylallene with a selection of seven anilines displaying diverse steric and electronic properties (Table 2). The results generated by screening these eight palladium complexes were generally disappointing, as most of these complexes showed no catalytic turnover for the hydroamination of 1,1-dimethylallene with anilines. From this array, only our previously reported **4Pd** was found to catalyze this hydroamination effectively. Complex **2Pd** also catalyzed the reaction, albeit with extremely poor conversions compared to that of **4Pd**. Complexes **2Pd** and **4Pd** are very similar, differing only in the substituent groups of their phosphine moieties. The phosphine *tert*-butyl groups of **4Pd** seem to play a vital role in its catalytic activity, as substituting them with phenyl groups in **2Pd** virtually eliminated catalytic activity. Changing the *tert*-butyl group of the imine moiety into the quite sterically hindered 2,6-dimethylphenyl group resulted in complete loss of catalytic activity in all four complexes containing that substituent (**1Pd**, **3Pd**, **5Pd**, **7Pd**). Furthermore, increasing the backbone ring size to a cyclohexene ring also destroyed catalytic activity across

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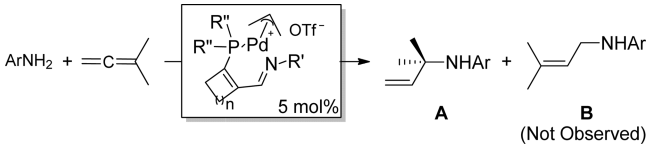
Table 2. Conversion to Product A for the [(3IP)Pd(allyl)]OTf-Catalyzed Hydroamination of 1,1-Dimethylallene with Aryl Amines[a]



	1Pd	2Pd	3Pd	4Pd	5Pd	6Pd	7Pd	8Pd	9Pd	10Pd
aniline	--[b]	--	--	60%	--	--	--	--	--	91%
2-methyl aniline	--	--	--	--	--	--	--	--	--	--
3-methyl aniline	--	13%	--	>95%	--	--	--	6%	--	92%
4-methyl aniline	--	16%	--	>95%	--	--	--	--	--	>95%
4-*tert*butyl aniline	--	17%	--	88%	--	--	--	--	--	>95%
4-fluoro aniline	--	9%	--	65%[c]	--	--	--	--	--	90%
3-methoxy aniline	--	12%	--	62%	--	--	--	6%	--	72%

[a]Conversion was monitored via ^{1}H NMR spectroscopy. [b]"--" indicates <5%. [c]Reaction at 70 °C.

the series of complexes (see **5Pd**–**8Pd**). Overall, as is so often noted in catalyst design, a very specific set of features (found in **4Pd**) was crucial to achieve catalysis, with minor changes having a devastating impact on catalytic activity.

Despite the fact that no improved catalysts were discovered upon screening the array of **1Pd**–**8Pd**, we were convinced that this method would yield an improved catalyst, and so further investigation into ligand design was undertaken. The results observed for complexes **1Pd**–**8Pd** necessitated that further ligand designs incorporate *tert*-butyl groups on both the phosphine and imine moieties of the 3IP ligands. Believing that the conformational stability of the cyclohexene ring was the downfall of **8Pd** when compared to the less stable cyclopentene ring of **4Pd**, ligand **9** and complex **9Pd** (each bearing a cycloheptenyl ring) were synthesized. Unfortunately, the conformational effects of the cycloheptene ring of **9Pd** did not grant any greater catalytic performance than that of the cyclohexene ring. Thus, we explored the opposite approach, utilizing the smaller and highly strained cyclobutenyl ring, leading to the synthesis of **10** and **10Pd**. The smaller alicyclic ring size of **10Pd** significantly enhanced catalytic activity, producing the same regiospecific product as **4Pd**, but at higher conversions for virtually every substrate and at lower temperature for those that had required heating with **4Pd**. Most notably, **10Pd** catalyzed the reaction of 4-fluoroaniline with 1,1-dimethylallene at room temperature to give 90% conversion, as compared to the 65% conversion at 70 °C when using **4Pd**. Also, the reaction of unsubstituted aniline was also significantly improved, converting 91% of substrate to product, a 31% increase over that previously reported.[3] Due to the superior performance of **10Pd** compared to all of the other 3IP complexes investigated thus far, it is clear that the size of the alicyclic ring is a critical component in the design of [(3IP)Pd(allyl)]OTf catalysts, with the cyclobutenyl backbone proving to be preferred over larger ring sizes.

CONCLUSIONS

A collection of 10 [(3IP)Pd(allyl)]OTf complexes was investigated in the catalytic hydroamination of 1,1-dimethylallene with electronically and sterically diverse aryl amines. There is a strong correlation between the three tunable ligand structural domains and the catalytic activity of these complexes. The ligand composed of di-*tert*-butyl phosphine, cyclobutenyl backbone, and *tert*-butyl imine domains led to the most active palladium catalyst when compared to the other ligands in this collection. Better electron-donating substituents on the phosphine and imine moieties grant greater catalytic ability to these complexes, while larger alicyclic backbone ring sizes almost completely eliminate catalytic activity. Excellent regiospecific hydroamination of 1,1-dimethylallene is now attainable for all but the most sterically hindered anilines. Further refinement of the 3IP ligand set, including investigation into the effects of phosphine and imine moieties of even greater electron-donating character, is ongoing. Additionally, use of these palladium complexes in other catalytic transformations, as well as one-pot multistep syntheses, continues to be under investigation in our laboratory.

EXPERIMENTAL SECTION

General Methods and Instrumentation. Alicyclic α,β-unsaturated β-chloroaldehydes and β-chloroimines were synthesized under ambient atmospheric conditions. All other manipulations were performed under an inert N_2 atmosphere using standard Schlenk and drybox techniques. Solvents were predried prior to use; methylene chloride was passed through two columns of 4 Å molecular sieves and degassed with nitrogen. Pentane, diethyl ether, and toluene were passed through columns of activated alumina and 4 Å molecular sieves and degassed with nitrogen. Tetrahydrofuran was distilled from sodium metal and degassed with nitrogen. *n*-Butyllithium (1.6 M in hexanes), (allyl)palladium(II) chloride dimer, diphenylchlorophosphine, di-*tert*-butylchlorophosphine, lithium aluminum hydride, and silver triflate were purchased from Strem and used without further purification. Phosphorus oxychloride, *tert*-butylamine, 2,6-dimethyl aniline, and cyclopentanone were purchased from Acros and used without further purification. Cyclohexanone, 1,1-dimethylallene, and cycloheptanone were purchased from Alfa Aesar and used without further purification. Cyclobutanone was purchased from Sigma Aldrich and used without further purification. Dimethylformamide was purchased from BDH and stored over 4 Å molecular sieves. Anilines were purchased from Sigma-Aldrich or another commercial source and dried over calcium hydride, either neat (liquid anilines) or as solutions in methylene chloride (solid anilines). Liquid anilines were freeze–pump–thawed three times and vacuum distilled. Solutions of solid anilines in methylene chloride were freeze–pump–thawed three times and filtered, and the methylene chloride was removed via reduced pressure. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, vacuum transferred from CaH_2, and stored over 4 Å molecular sieves. Benzene-d_6 was also purchased from Cambridge Isotope Laboratories, vacuum transferred from sodium metal, and stored over 4 Å molecular sieves. Silica gel (Porosity: 60 Å, particle size: 40–63 μm) was purchased from Sorbent Technologies and used as received. ^{1}H and ^{13}C NMR data were obtained on a 600 MHz Inova or 400 MHz VXRS

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NMR spectrometer at ambient temperature at 599.9 MHz for ^{1}H NMR and 150.8 MHz for ^{13}C NMR and 399.95 MHz for ^{1}H NMR and 100.56 MHz for ^{13}C NMR, respectively. All ^{31}P NMR spectra were collected on a 400 MHz VXRS NMR spectrometer at ambient temperature at 161.90 MHz. All spectra were taken using C_6D_6 or $CDCl_3$ as the NMR solvent. ^{1}H NMR shifts are given relative to the residual solvent resonances at 7.16 and 7.26 ppm, respectively, and ^{13}C NMR shifts are given relative to the residual solvent peak of $CDCl_3$ (77.36 ppm). ^{31}P NMR spectra were externally referenced to 0.00 ppm with 5% H_3PO_4 in D_2O. IR samples were prepared as Nujol mulls and taken between KBr plates on a Perkin-Elmer XTL FTIR spectrophotometer. Melting points were observed on a capillary melting point (Uni-Melt) apparatus in sealed capillary tubes and are uncorrected. X-ray structure determinations were performed at the Ohio Crystallographic Consortium, housed at The University of Toledo. Elemental analyses were determined by Atlantic Microlab, Inc., Norcross, GA, or Galbraith Laboratories, Inc., Knoxville, TN, USA. High-resolution mass spectrometry using electrospray ionization was performed at the University of Illinois Mass Spectrometry Laboratory, Urbana, IL, USA. The following compounds were synthesized as previously reported: $LiPPh_2$,[35] LiP^tBu_2,[3] 2-chlorocyclopentenecarboxaldehyde,[35] 2-chlorocyclohexenecarboxaldehyde,[33] 2-chlorocyclohexene-1-(2,6-xylyl)imine,[33] 2-chlorocyclopentene-1-(*tert*-butyl)imine,[35] 2-diphenylphosphinocyclopentene-1-(*tert*-butyl)imine (**2**),[35] 2-di-*tert*-butylphosphinocyclopentene-1-(*tert*-butyl)imine (**4**),[3] 2-diphenylphosphinocyclohexene-1-(2,6-xylyl)imine (**5**),[33] [(2-diphenylphosphinocyclopentene-1-(*tert*-butyl)imine)Pd(allyl)]OTf (**2Pd**),[35] [(2-di-*tert*-butylphosphinocyclopentene-1-(*tert*-butyl)imine)-Pd(allyl)]OTf (**4Pd**),[3] and [(2-diphenylphosphinocyclohexene-1-(2,6-xylyl)imine)Pd(allyl)]OTf (**5Pd**).[33]

General Procedure for the Catalytic Hydroamination Screening of Compounds 1Pd−10Pd. All manipulations were performed under an N_2 atmosphere. 3-Methyl-1,2-butadiene (68 mg, 1 mmol) was added to a mixture of amine (0.5 mmol), [(3IP)Pd-(allyl)]OTf complex (5 mol %), and deuterated benzene (0.8 mL). Conversion to products was monitored via ^{1}H NMR spectroscopy. Hydroamination products formed were reported previously.[3]

Alicyclic α,β-Unsaturated β-Chloroaldehydes. The following was performed with degassed reagents and solvents, and an atmosphere of nitrogen was maintained over the mixture as the reaction proceeded. Dimethylformamide (9.00 g, 123 mmol) was cooled to 0 °C. $POCl_3$ (15.00 g, 97 mmol) was then added dropwise with rapid stirring. Formation of the Vilsmeier−Haack reagent was allowed to proceed for 4 h, slowly warming to room temperature. The reagent was again cooled to 0 °C before dropwise addition of the respective cyclic ketone (61 mmol). After slowly warming to room temperature, the mixture was heated at 55 °C for 14 h. The crude reaction mixture was quenched over water at 0 °C to produce the chloroaldehyde. The mixture was made basic with an excess of sodium bicarbonate before extracting into pentane (4 × 100 mL). The organic layer was rinsed with water and brine and dried over magnesium sulfate for 20 min. The organic layer had ethyl acetate added up to 2% and was passed through a plug of silica. Solvent was evaporated to yield the final product as a lightly colored liquid.

Alicyclic α,β-Unsaturated β-Chloroimines. *tert-Butyl Imines.* To pentane (20 mL) was added activated 4 Å molecular sieves. This was cooled to 0 °C before adding freshly prepared chloroaldehyde and 1.3 equivalents of *tert*-butylamine. The reaction was allowed to proceed for 14 h, slowly warming to ambient temperature. Magnesium sulfate was added to the reaction mixture and allowed to stir for 20 min before filtering over Celite. Diethyl ether and excess *tert*-butylamine were evaporated, yielding the final product.

2,6-Dimethyl Phenyl Imines. To pentane (20 mL) was added activated 4 Å molecular sieves. This was cooled to 0 °C before adding freshly prepared chloroaldehyde and 1.3 equivalents of 2,6-dimethylaniline. The reaction was stirred for 96 h, slowly warming to ambient temperature. Magnesium sulfate was added to the reaction mixture and allowed to stir for 20 min before filtering over Celite. Diethyl ether was evaporated and the product redissolved in pentane. Ethyl acetate was added up to 2%, and the product solution was passed through a plug of silica to remove excess aniline. Solvent was evaporated, yielding the final product.

3-Iminophosphine Ligands. Unless otherwise noted, all 3-iminophosphine ligands were prepared via the following methodology. To a Schlenk tube with attached addition funnel was added degassed chloroimine (1 equiv) and diethyl ether (15 mL). Lithium di-*tert*-butylphosphide (1.6 equiv) was dissolved in diethyl ether (30 mL) in a separate flask. The lithium phosphide was transferred to the addition funnel and then added dropwise to the rapidly stirring chloroimine solution at ambient temperature over a time period of 1 h. The reaction was allowed to stir for an additional 2 h before concentration in vacuo to an approximate volume of 10 mL. At this time, pentane (20 mL) was added to help precipitate excess lithium phosphide. The supernatant was separated via cannula filtration, solvent removed in vacuo, and the resulting oil triturated with pentane (2 × 10 mL). The oil was then extracted into pentane (2 × 20 mL) and passed through a Celite padded frit. Solvent was again removed in vacuo to yield the final product.

(3-Iminophosphine)allylpalladium Triflate Complexes. Solutions of both ligand (1.05 equiv) and allylpalladium chloride dimer (0.5 equiv) in dichloromethane (10 mL each) were combined at ambient temperature and allowed to stir for 14 h. Solvent was removed in vacuo, and the crude solid was triturated and rinsed with pentane (10 mL each). The solid was redissolved in methylene chloride (10 mL), added to a slurry of silver triflate (0.65 equiv) in methylene chloride (10 mL), and stirred in the dark for 14 h. The crude reaction mixture was then passed through a thick pad of Celite, and solvent removed in vacuo. The resulting solid was triturated with pentane (10 mL), dissolved in a minimal amount of tetrahydrofuran, layered with pentane, and cooled to −20 °C to promote crystal growth.

2-Chlorocycloheptenecarboxaldehyde: light yellow liquid (6.128 g, 63.18%); ^{1}H NMR ($CDCl_3$) δ 10.11 (s, 1H), 2.83−2.80 (m, 2H), 2.49−2.47 (m, 2H), 1.80−1.76 (m, 2H), 1.71−1.65 (m, 2H), 1.49−1.43 (m, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 191.1, 156.6, 138.7, 41.9, 31.8, 25.7, 25.1, 24.9; IR: 3331 (w), 2926 (s), 2854 (s), 2740 (w), 2698 (w), 1737 (s), 1675 (s), 1638 (s), 1607 (s), 1446 (s), 1389 (m), 1373 (m), 1337 (m), 1239 (s), 1218 (s), 1140 (s), 1083 (m), 1062 (s), 1047 (m), 1016 (m), 974 (s), 959 (s), 907 (m), 886 (m), 829 (m), 808 (m), 761 (s), 689 (s) cm^{-1}.

2-Chlorocyclobutenecarboxaldehyde: light yellow liquid (1.39 g, 19.3%); ^{1}H NMR ($CDCl_3$) δ 9.69 (s, 1H), 2.85 (t, $^{3}J_{H-H}$ = 3.6 Hz, 2H), 2.65 (t, $^{3}J_{H-H}$ = 3.6 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 183.8, 143.3, 141.5, 35.4, 25.1; IR 3326 (m), 2978 (s), 2945 (s), 2815 (m), 2717 (w), 1782 (m), 1722 (s), 1673 (s), 1607 (s), 1439 (m), 1417 (m), 1373 (s), 1286 (s), 1210 (s), 1112 (s), 965 (s), 878 (m), 791 (w), 769 (m), 731 (s) cm^{-1}.

2-Chlorocyclopentene-1-(2,6-xylyl)imine: orange-red liquid (3.563 g, 95.77%); ^{1}H NMR ($CDCl_3$) δ 8.23 (s, 1H), 7.05 (d, $^{3}J_{H-H}$ = 7.8 Hz, 2H), 6.94 (t, $^{3}J_{H-H}$ = 7.8 Hz, 1H), 2.86 (td, $^{3}J_{H-H}$ = 7.8 Hz, $^{2}J_{H-H}$ = 2.1 Hz, 1H), 2.85 (td, $^{3}J_{H-H}$ = 7.8 Hz, $^{2}J_{H-H}$ = 2.4 Hz, 1H), 2.82 (td, $^{3}J_{H-H}$ = 7.8 Hz, $^{2}J_{H-H}$ = 2.1 Hz, 1H), 2.81 (td, $^{3}J_{H-H}$ = 7.8 Hz, $^{2}J_{H-H}$ = 2.4 Hz, 1H), 2.12 (s, 6H), 1.96 (pent, $^{3}J_{H-H}$ = 7.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 157.6, 151.4, 141.7, 135.8, 128.2, 127.9, 124.0, 39.9, 30.5, 20.9, 18.6; IR: 3062 (w), 3020 (w), 2957 (s), 2915 (s), 2852 (m), 2727 (w), 2360 (w), 2035 (w), 1918 (w), 1839 (w), 1724 (w), 1656 (m), 1625 (s), 1609 (s), 1593 (s), 1467 (s), 1441 (m), 1378 (m), 1347 (m), 1274 (m), 1247 (m), 1190 (s), 1158 (w), 1090 (m), 1033 (w), 985 (w), 938 (m), 912 (w), 844 (m), 760 (s), 723 (m), 671 (w) cm^{-1}.

2-Chlorocyclohexene-1-(*tert*-butyl)imine: yellow-orange liquid (1.626 g, 81.30%); ^{1}H NMR ($CDCl_3$) δ 8.46 (s, 1H), 2.50−2.46 (m, 2H), 2.42−2.38 (m, 2H), 1.77−1.71 (m, 2H), 1.68−1.62 (m, 2H), 1.21 (s, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 154.2, 138.7, 131.7, 57.4, 35.2, 29.8, 26.0, 23.7, 21.8; IR: 2964 (s), 2932 (s), 2859 (s), 2356 (w), 2324 (w), 1717 (w), 1691 (w), 1623 (m), 1560 (w), 1455 (w), 1434 (w), 1366 (m), 1266 (w), 1240 (w), 1209 (m), 1172 (w), 1135 (w), 1115 (w), 1099 (w), 1072 (w), 1025 (w), 989 (m), 957 (w), 905 (w), 868 (w), 826 (w), 779 (w), 695 (w) cm^{-1}.

2-Chlorocycloheptene-1-(*tert*-butyl)imine: light yellow liquid (3.640 g, 50.97%); ^{1}H NMR ($CDCl_3$) δ 8.37 (s, 1H), 2.74−2.71 (m,

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2H), 2.67−2.64 (m, 2H), 1.77−1.75 (m, 2H), 1.65−1.62 (m, 2H), 1.50−1.47 (m, 2H), 1.21 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.0, 142.8, 137.4, 57.7, 40.7, 32.0, 30.3, 26.9, 26.1, 25.5; IR: 3217 (w), 2968 (s), 2926 (s), 2698 (w), 1737 (w), 1680 (m), 1618 (s), 1446 (s), 1368 (s), 1332 (m), 1280 (m), 1259 (s), 1213 (s), 1140 (m), 1099 (m), 1083 (m), 1062 (m), 1016 (w), 974 (s), 959 (s), 922 (m), 901 (s), 876 (w), 829 (m), 808 (w), 761 (s), 684 (m), 626 (m) cm^{-1}.

2-Chlorocyclobutene-1-(*tert*-butyl)imine: yellow liquid (0.833 g, 40.7%); ^1H NMR ($CDCl_3$) δ 7.94 (s, 1H), 2.74−2.73 (m, 2H), 2.66−2.64 (m, 2H), 1.20 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.4, 141.2, 130.3, 57.9, 34.7, 29.9, 26.0; IR 3196 (w), 2967 (s), 2935 (s), 2869 (m), 1787 (w), 1673 (m), 1646 (s), 1607 (m), 1515 (w), 1466 (m), 1422 (w), 1390 (w), 1362 (s), 1335 (m), 1297 (m), 1259 (s), 1205 (s), 1112 (s), 1096 (m), 1020 (m), 976 (s), 954 (m), 894 (m), 878 (m), 802 (m), 785 (m), 731 (m), 573 (s) cm^{-1}.

2-Diphenylphosphinocyclopentene-1-(2,6-xylyl)imine (1): prepared in a manner analogous to that of Shaffer et al.;[35] yellow-orange solid (0.618 g, 61.8%); mp 99−100 °C; ^1H NMR ($CDCl_3$) δ 8.64 (d, $^4J_{P-H}$ = 3.6 Hz, 1H), 7.38−7.34 (m, 10H), 7.00 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 6.90 (t, $^3J_{H-H}$ = 7.8 Hz, 1H), 3.03−3.00 (m, 2H), 2.46−2.44 (m, 2H), 2.04 (s, 6H), 1.96 (pseudo pent, $^3J_{H-H}$ = 7.8 Hz, $^3J_{H-H}$ = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 159.8 (d, $^3J_{P-C}$ = 22.0 Hz), 153.1 (d, $^2J_{P-C}$ = 21.4 Hz), 151.7, 150.2 (d, $^1J_{P-C}$ = 22.6 Hz), 136.5 (d, $^1J_{P-C}$ = 8.7 Hz), 133.4 (d, $^2J_{P-C}$ = 19.4 Hz), 129.0, 128.8 (d, $^3J_{P-C}$ = 6.9 Hz), 128.2, 127.2, 123.8, 38.1 (d, $^3J_{P-C}$ = 4.4 Hz), 34.0 (d, $^2J_{P-C}$ = 5.4 Hz), 22.7 (d, $^3J_{P-C}$ = 2.0 Hz), 18.5; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −23.20; IR 2961 (s), 2919 (s), 2857 (s), 2720 (w), 1612 (m), 1586 (w), 1455 (s), 1376 (m), 1298 (w), 1240 (w), 1193 (m), 1156 (w), 1088 (w), 1025 (w), 999 (w), 968 (w), 915 (w), 842 (w), 764 (m), 738 (m), 722 (m), 696 (m) cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{26}H_{27}NP$ 384.1882, found 384.1874.

2-Di-*tert*-butylphosphinocyclopentene-1-(2,6-xylyl)imine (3): prepared in a manner analogous to that of Beck et al.;[3] deep red oil (0.910 g, 75.8%); ^1H NMR ($CDCl_3$) δ 8.82 (d, $^4J_{P-H}$ = 5.4 Hz, 1H), 7.00 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 6.89 (t, $^3J_{H-H}$ = 7.8 Hz, 1H), 2.98−2.95 (m, 2H), 2.88−2.85 (m, 2H), 2.07 (s, 6H), 1.99−1.96 (m, 2H), 1.19 (d, $^3J_{P-H}$ = 11.4 Hz, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 161.5 (d, $^3J_{P-C}$ = 29.9 Hz), 156.2 (d, $^2J_{P-C}$ = 20.7 Hz), 152.1, 151.9 (d, $^1J_{P-C}$ = 36.5 Hz), 128.1, 127.1, 123.6, 40.1 (d, $^2J_{P-C}$ = 6.5 Hz), 32.9 (d, $^3J_{P-C}$ = 5.7 Hz), 32.6 (d, $^1J_{P-C}$ = 19.9 Hz), 31.1 (d, $^2J_{P-C}$ = 14.3 Hz), 23.9, 18.7; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 13.24; IR: 2945 (s), 2853 (s), 1608 (s), 1466 (s), 1360 (m), 1324 (m), 1254 (m), 1190 (m), 1169 (m), 1084 (m), 1062 (m), 1013 (m), 843 (w), 801 (m), 758 (s), 716 (w) cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{22}H_{35}NP$ 344.2507, found 344.2509.

2-Diphenylphosphinocyclohexene-1-(*tert*-butyl)imine (6): prepared in a manner analogous to that of Kuchenbeiser et al.;[33] off-white liquid (0.824 g, 82.4%); ^1H NMR ($CDCl_3$) δ 9.09 (d, $^4J_{P-H}$ = 3.6 Hz, 1H), 7.38−7.32 (m, 10H), 2.56−2.53 (m, 2H), 1.90−1.88 (m, 2H), 1.66−1.63 (m, 2H), 1.58−1.56 (m, 2H), 1.13 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.4 (d, $^3J_{P-C}$ = 40.2 Hz), 147.6 (d, $^2J_{P-C}$ = 17.7 Hz), 140.7 (d, $^1J_{P-C}$ = 20.4 Hz), 136.7 (d, $^1J_{P-C}$ = 10.8 Hz), 133.6 (d, $^2J_{P-C}$ = 18.9 Hz), 128.6 (d, $^3J_{P-C}$ = 6.3 Hz), 128.6, 57.7, 30.2 (d, $^3J_{P-C}$ = 3.6 Hz), 30.1, 27.0 (d, $^2J_{P-C}$ = 5.8 Hz), 23.7, 22.3; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −12.70; IR: 3126 (w), 3054 (w), 2962 (s), 2921 (s), 2849 (m), 2664 (w), 2274 (w), 1952 (w), 1885 (w), 1814 (w), 1757 (w), 1618 (s), 1582 (w), 1475 (w), 1448 (w), 1428 (s), 1362 (m), 1326 (w), 1305 (w), 1259 (m), 1202 (s), 1090 (m), 1064 (m), 1023 (m), 961 (w), 900 (w), 843 (w), 802 (m), 740 (s), 694 (s) cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{23}H_{29}NP$ 350.2038, found 350.2043.

2-Di-*tert*-butylphosphinocyclohexene-1-(2,6-xylyl)imine (7): bright yellow solid (1.100 g, 91.67%); mp 90−91 °C; ^1H NMR ($CDCl_3$) δ 9.32 (d, $^4J_{P-H}$ = 9.6 Hz, 1H), 7.01 (d, $^3J_{H-H}$ = 7.2 Hz, 2H), 6.89 (t, $^3J_{H-H}$ = 7.2 Hz, 1H), 2.72−2.70 (m, 2H), 2.66 (br s, 2H), 2.08 (s, 6H), 1.79−1.77 (m, 2H), 1.72−1.69 (m, 2H), 1.21 (d, $^3J_{P-H}$ = 11.4 Hz, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.5 (d, $^3J_{P-C}$ = 48.9 Hz), 151.9, 149.0 (d, $^2J_{P-C}$ = 18.6 Hz), 148.4 (d, $^1J_{P-C}$ = 36.8 Hz), 127.7, 126.9, 123.0, 32.6 (d, $^1J_{P-C}$ = 24.1 Hz), 32.1 (d, $^3J_{P-C}$ = 5.0 Hz), 31.1 (d, $^2J_{P-C}$ = 15.1 Hz), 26.6 (d, $^2J_{P-C}$ = 6.5 Hz), 23.1, 22.2, 18.4; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.05; IR: 2926 (s), 2854 (s), 1612 (w), 1592 (w), 1462 (s), 1379 (m), 1259 (w), 1197 (w), 1171 (w), 1088 (w), 1016 (w), 844 (w), 803 (w), 761 (w), 720 (w) cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{23}H_{37}NP$ 358.2664, found 358.2656.

2-Di-*tert*-butylphosphinocyclohexene-1-(*tert*-butyl)imine (8): light brown liquid (0.715 g, 71.5%); ^1H NMR ($CDCl_3$) δ 9.37 (d, $^4J_{P-H}$ = 10.8 Hz, 1H), 2.58−2.56 (m, 2H), 2.50−2.48 (m, 2H), 1.68−1.59 (m, 4H), 1.20 (d, $^3J_{P-H}$ = 7.2 Hz, 18H), 1.19 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 159.2 (d, $^3J_{P-C}$ = 47.1 Hz), 149.5 (d, $^2J_{P-C}$ = 18.1 Hz), 144.1 (d, $^1J_{P-C}$ = 35.4 Hz), 57.4 (d, $^5J_{P-C}$ = 1.4 Hz), 32.2 (d, $^3J_{P-C}$ = 5.0 Hz), 31.4 (d, $^2J_{P-C}$ = 14.9 Hz), 31.0 (d, $^1J_{P-C}$ = 15.2 Hz), 30.4, 27.5 (d, $^2J_{P-C}$ = 5.0 Hz), 23.5, 22.6; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 19.98; IR: 2926 (s), 2854 (s), 1618 (m), 1462 (s), 1363 (s), 1259 (m), 1202 (m), 1171 (m), 1088 (m), 1016 (m), 964 (w), 901 (w), 803 (m), 720 (w) cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{19}H_{37}NP$ 310.2664, found 310.2659.

2-Di-*tert*-butylphosphinocycloheptene-1-(*tert*-butyl)imine (9): yellow oil (0.540 g, 61.6%); ^1H NMR ($CDCl_3$) δ 9.37 (d, $^4J_{P-H}$ = 10.8 Hz, 1H), 2.77−2.71 (m, 4H), 1.78−1.75 (m, 2H), 1.62−1.59 (m, 2H), 1.45−1.43 (m, 2H), 1.20 (s, 9H), 1.18 (d, $^3J_{P-H}$ = 12.0 Hz, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 159.4 (d, $^3J_{P-C}$ = 48.6 Hz), 157.3 (d, $^2J_{P-C}$ = 18.3 Hz), 149.6 (d, $^1J_{P-C}$ = 36.8 Hz), 57.4 (d, $^5J_{P-C}$ = 1.4 Hz), 35.5 (d, $^3J_{P-C}$ = 5.6 Hz), 33.4 (d, $^1J_{P-C}$ = 24.7 Hz), 32.9, 31.4 (d, $^2J_{P-C}$ = 15.2 Hz), 30.5, 29.4 (d, $^2J_{P-C}$ = 6.8 Hz), 28.1, 26.3; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 24.81; IR: 2916 (s), 2854 (s), 1612 (m), 1462 (s), 1363 (s), 1259 (m), 1213 (m), 1171 (m), 1088 (w), 1016 (m), 959 (w), 876 (w), 808 (m) cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{20}H_{39}NP$ 324.2820, found 324.2817.

2-Di-*tert*-butylphosphinocyclobutene-1-(*tert*-butyl)imine (10): brown oil (0.365 g, 68.9%); ^1H NMR ($CDCl_3$) δ 8.27 (d, $^4J_{P-H}$ = 2.0 Hz, 1H), 2.87−2.86 (m, 4H), 1.20 (s, 9H), 1.19 (d, $^3J_{P-H}$ = 11.6 Hz, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 159.1 (d, $^3J_{P-C}$ = 21.6 Hz), 151.4 (d, $^1J_{P-C}$ = 39.8 Hz), 151.0 (d, $^2J_{P-C}$ = 5.3 Hz), 57.7, 33.4 (d, $^1J_{P-C}$ = 4.7 Hz), 33.0 (d, $^2J_{P-C}$ = 16.5 Hz), 30.7 (d, $^2J_{P-C}$ = 13.3 Hz), 30.1, 29.4 (d, $^3J_{P-C}$ = 11.4 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 11.36; IR: 2956 (s), 2869 (m), 1628 (w), 1571 (w), 1529 (w), 1472 (m), 1389 (m), 1363 (m), 1259 (s), 1213 (m), 1192 (m), 1176 (m), 1093 (s), 1021 (s), 865 (m), 803 (s), 663 (m) cm^{-1}; HRMS (m/z) $[M + H]^+$ calcd for $C_{17}H_{33}NP$ 282.2351, found 282.2351.

[(2-Diphenylphosphinocyclopentene-1-(2,6-xylyl)imine)Pd-(allyl)]OTf (1Pd): yellow solid (0.154 g, 92.1%); mp 191 °C dec; ^1H NMR ($CDCl_3$) δ 7.88 (d, $^4J_{P-H}$ = 2.4 Hz, 1H), 7.58−7.55 (m, 8H), 7.51−7.48 (m, 2H), 7.11−7.05 (m, 3H), 5.81−5.77 (m, 1H), 3.66−3.62 (m, 1H), 3.55−3.50 (m, 1H), 3.49 (d, $^3J_{H-H}$ = 2.4 Hz, 1H), 3.11−3.04 (m, 2H), 2.70 (d, $^3J_{H-H}$ = 12.0 Hz, 1H), 2.65−2.57 (m, 2H), 2.21 (s, 3H), 2.14−2.08 (m, 2H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.4 (d, $^3J_{P-C}$ = 7.2 Hz), 155.8, 153.0 (d, $^2J_{P-C}$ = 17.2 Hz), 137.8 (d, $^1J_{P-C}$ = 32.6 Hz), 133.2 (d, $^4J_{P-C}$ = 13.6 Hz), 132.8 (d, $^4J_{P-C}$ = 13.1 Hz), 132.4 (d, $^2J_{P-C}$ = 24.3 Hz), 130.2 (d, $^3J_{P-C}$ = 10.7 Hz), 130.17 (d, $^3J_{P-C}$ = 10.9 Hz), 129.2, 129.0, 128.6 (d, $^1J_{P-C}$ = 50.1 Hz), 128.2 (d, $^1J_{P-C}$ = 49.8 Hz), 127.3, 123.9 (d, $^2J_{P-C}$ = 5.9 Hz), 122.4, 120.2, 87.1 (d, $^2J_{P-C}$ = 28.4 Hz), 55.0 (d, $^2J_{P-C}$ = 3.5 Hz), 39.0 (d, $^2J_{P-C}$ = 11.3 Hz), 36.5, 22.4 (d, $^3J_{P-C}$ = 5.4 Hz), 18.9, 18.8; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 13.11; IR 2926 (s), 2854 (s), 2719 (w), 2677 (w), 1462 (s), 1379 (s), 1301 (w), 1259 (w), 1218 (w), 1145 (w), 1093 (w), 1031 (w), 969 (w), 798 (w), 720 (w), 637 (w) cm^{-1}. Anal. Calcd for $C_{30}H_{31}F_3NO_3PPdS$: C, 52.99; H, 4.60; N, 2.06. Found: C, 52.99; H, 4.57; N, 2.17.

[(2-Di-*tert*-butylphosphinocyclopentene-1-(2,6-xylyl)imine)-Pd(allyl)]OTf (3Pd): dark brown solid (0.736 g, 61.5%); mp 131 °C dec; ^1H NMR ($CDCl_3$) δ 7.84 (d, $^4J_{P-H}$ = 1.2 Hz, 1H), 7.14−7.07 (m, 3H), 5.69−5.64 (m, 1H), 4.16 (d, $^3J_{H-H}$ = 6.6 Hz, 1H), 3.58−3.54 (m, 1H), 3.18−3.15 (m, 2H), 3.10−3.08 (m, 1H), 2.95−2.90 (m, 2H), 2.77 (d, $^3J_{H-H}$ = 12.6 Hz, 1H), 2.20 (s, 3H), 2.12−2.07 (m, 2H), 2.09 (s, 3H), 1.44 (d, $^3J_{P-H}$ = 15.6 Hz, 9H), 1.34 (d, $^3J_{P-H}$ = 15.6 Hz, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.7 (d, $^3J_{P-C}$ = 6.2 Hz), 157.5, 153.3 (d, $^2J_{P-C}$ = 11.9 Hz), 140.2 (d, $^1J_{P-C}$ = 15.8 Hz), 129.2, 128.9, 127.3, 127.1, 126.9, 121.8 (d, $^2J_{P-C}$ = 5.4 Hz), 88.7 (d, $^2J_{P-C}$ = 26.5 Hz), 53.1 (d, $^2J_{P-C}$ = 2.7 Hz), 41.1 (d, $^3J_{P-C}$ = 2.1 Hz), 38.7 (d, $^2J_{P-C}$ = 10.0 Hz), 38.6 (d, $^1J_{P-C}$ = 15.8 Hz), 38.3 (d, $^1J_{P-C}$ = 16.0 Hz), 31.0 (d, $^2J_{P-C}$ = 6.2 Hz), 30.7 (d, $^2J_{P-C}$ = 6.5 Hz), 24.0 (d, $^3J_{P-C}$ = 3.6 Hz), 18.8;

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$^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 59.48; IR 2926 (s), 2854 (s), 2719 (w), 1612 (w), 1566 (w), 1457 (s), 1379 (s), 1270 (w), 1140 (w), 1083 (w), 1026 (w), 720 (w), 637 (m) cm^{-1}. Anal. Calcd for $C_{26}H_{39}F_3NO_3PPdS$: C, 48.79; H, 6.14; N, 2.19. Found: C, 48.88; H, 6.07; N, 2.33.

[(2-Diphenylphosphinocyclohexene-1-(*tert*-butyl)imine)Pd-(allyl)]OTf (6Pd): light brown solid (0.340 g, 85.1%); mp 160 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.65 (d, $^{4}J_{P-H}$ = 3.6 Hz, 1H), 7.51 (br s, 6H), 7.34−7.33 (m, 4H), 5.77−5.70 (m, 1H), 4.90−4.87 (m, 1H), 3.89−3.85 (m, 1H), 3.39 (s, 1H), 2.96 (d, $^{3}J_{P-H}$ = 10.8 Hz, 1H), 2.56 (s, 2H), 1.85−1.81 (m, 4H), 1.73−1.64 (m, 2H), 1.14 (s, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 163.9 (d, $^{3}J_{P-C}$ = 11.5 Hz), 148.8 (d, $^{2}J_{P-C}$ = 12.2 Hz), 133.3, 132.1 (d, $^{4}J_{P-C}$ = 31.5 Hz), 129.8 (d, $^{2}J_{P-C}$ = 19.6 Hz), 129.3 (d, $^{1}J_{P-C}$ = 32.9 Hz), 127.8 (d, $^{1}J_{P-C}$ = 45.7 Hz), 121.0 (d, $^{2}J_{PC}$ = 6.5 Hz), 80.7 (d, $^{2}J_{P-C}$ = 31.1 Hz), 64.3, 56.9 (d, $^{2}J_{P-C}$ = 4.8 Hz), 31.6 (d, $^{2}J_{P-C}$ = 9.8 Hz), 30.4, 29.9, 22.5 (d, $^{3}J_{P-C}$ = 4.5 Hz), 21.5; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 31.78; IR: 2916 (s), 2854 (s), 2719 (m), 2667 (m), 1628 (w), 1586 (w), 1457 (s), 1379 (s), 1259 (s), 1145 (m), 1099 (m), 1026 (m), 974 (m), 912 (m), 798 (m), 720 (m), 637 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{33}F_3NO_3PPdS{\cdot}1/2(C_4H_8O)$: C, 51.07; H, 5.47; N, 2.05. Found: C, 51.14; H, 5.44; N, 2.08.

[(2-Di-*tert*-butylphosphinocyclohexene-1-(2,6-xylyl)imine)-Pd(allyl)]OTf (7Pd): dark brown solid (0.483 g, 36.5%); mp 155−160 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.65 (s, 1H), 7.15−7.08 (m, 3H), 5.69−5.64 (m, 1H), 4.13 (d, $^{3}J_{H-H}$ = 6.6 Hz, 1H), 3.54−3.50 (m, 1H), 3.12−3.09 (m, 1H), 2.89−2.86 (m, 1H), 2.79 (d, $^{3}J_{H-H}$ = 12.6 Hz, 1H), 2.75−2.72 (m, 1H), 2.65−2.56 (m, 2H), 2.22 (s, 3H), 2.12 (s, 3H), 1.87−1.81 (m, 4H), 1.49 (d, $^{3}J_{P-H}$ = 15.6 Hz, 9H), 1.39 (d, $^{3}J_{P-H}$ = 15.0 Hz, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 169.0 (d, $^{3}J_{P-C}$ = 8.6 Hz), 158.1, 146.7 (d, $^{2}J_{P-C}$ = 7.8 Hz), 139.4 (d, $^{1}J_{P-C}$ = 13.1 Hz), 129.4, 129.0, 127.3, 127.1, 126.8, 122.0 (d, $^{2}J_{P-C}$ = 5.4 Hz), 88.0 (d, $^{2}J_{P-C}$ = 26.2 Hz), 55.1 (d, $^{2}J_{P-C}$ = 3.9 Hz), 39.5 (d, $^{1}J_{P-C}$ = 13.1 Hz), 38.8 (d, $^{1}J_{P-C}$ = 13.9 Hz), 35.7 (d, $^{2}J_{P-C}$ = 8.7 Hz), 32.9 (d, $^{3}J_{P-C}$ = 2.9 Hz), 31.8 (d, $^{2}J_{P-C}$ = 6.6 Hz), 31.4 (d, $^{2}J_{P-C}$ = 6.9 Hz), 21.8 (d, $^{3}J_{P-C}$ = 2.3 Hz), 21.4 (d, $^{4}J_{P-C}$ = 1.2 Hz), 18.9; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 71.63; IR: 2916 (s), 2854 (s), 1618 (w), 1560 (w), 1457 (s), 1379 (s), 1270 (s), 1223 (m), 1140 (m), 1031 (m), 912 (w), 798 (w), 720 (w), 637 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{41}F_3NO_3PPdS$: C, 49.58; H, 6.32; N, 2.14. Found: C, 49.58; H, 6.37; N, 2.16.

[(2-Di-*tert*-butylphosphinocyclohexene-1-(*tert*-butyl)imine)-Pd(allyl)]OTf (8Pd): green-brown solid (0.706 g, 53.0%); mp 105 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.85 (d, $^{4}J_{P-H}$ = 3.0 Hz, 1H), 5.64−5.57 (m, 1H), 5.08−5.05 (m, 1H), 3.91 (d, $^{3}J_{H-H}$ = 7.2 Hz, 1H), 3.79−3.76 (m, 1H), 2.82 (d, $^{3}J_{H-H}$ = 12.0 Hz, 1H), 2.57−2.56 (m, 4H), 1.78−1.67 (m, 4H), 1.45 (s, 9H), 1.45 (d, $^{3}J_{P-H}$ = 14.4 Hz, 9H), 1.36 (d, $^{3}J_{P-H}$ = 14.4 Hz, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 166.9 (d, $^{3}J_{P-C}$ = 9.2 Hz), 149.5 (d, $^{2}J_{P-C}$ = 9.8 Hz), 132.4 (d, $^{1}J_{P-C}$ = 12.8 Hz), 119.6 (d, $^{2}J_{P-C}$ = 5.6 Hz), 82.4 (d, $^{2}J_{P-C}$ = 26.7 Hz), 65.4, 56.6, 38.6 (d, $^{1}J_{P-C}$ = 10.9 Hz), 38.6 (d, $^{1}J_{P-C}$ = 11.3 Hz), 34.4 (d, $^{2}J_{P-C}$ = 9.5 Hz), 32.4 (d, $^{3}J_{P-C}$ = 2.1 Hz), 31.9 (d, $^{2}J_{P-C}$ = 6.2 Hz), 31.7 (d, $^{2}J_{P-C}$ = 6.5 Hz), 30.7, 22.7 (d, $^{3}J_{P-C}$ = 2.3 Hz), 21.5; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 75.37; IR 2926 (s), 2854 (s), 1462 (s), 1379 (m), 1265 (m), 1145 (w), 1031 (w), 798 (w), 720 (w), 637 (m) cm^{-1}. Anal. Calcd for $C_{23}H_{41}F_3NO_3PPdS$: C, 45.59; H, 6.82; N, 2.31. Found: C, 45.65; H, 6.85; N, 2.51.

[(2-Di-*tert*-butylphosphinocycloheptene-1-(*tert*-butyl)-imine)Pd(allyl)]OTf (9Pd): light yellow solid (0.322 g, 62.0%); mp 149−154 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.07 (d, $^{4}J_{P-H}$ = 2.4 Hz, 1H), 5.63−5.57 (m, 1H), 5.22−5.19 (m, 1H), 3.93 (d, $^{3}J_{H-H}$ = 7.2 Hz, 1H), 3.89−3.85 (m, 1H), 2.98−2.88 (m, 2H), 2.79−2.68 (m, 3H), 1.92−1.88 (m, 1H), 1.86−1.81 (m, 1H), 1.78−1.72 (m, 2H), 1.55−1.48 (m, 2H), 1.45 (s, 9H), 1.43 (d, $^{3}J_{P-H}$ = 14.4 Hz, 9H), 1.33 (d, $^{3}J_{P-H}$ = 15.0 Hz, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 167.8 (d, $^{3}J_{P-C}$ = 10.0 Hz), 156.8 (d, $^{2}J_{P-C}$ = 9.8 Hz), 156.1 (d, $^{1}J_{P-C}$ = 13.7 Hz), 119.7 (d, $^{2}J_{P-C}$ = 5.4 Hz), 85.1 (d, $^{2}J_{P-C}$ = 26.1 Hz), 65.7, 54.2 (d, $^{2}J_{P-C}$ = 4.1 Hz), 39.4 (d, $^{1}J_{P-C}$ = 13.3 Hz), 38.8 (d, $^{1}J_{P-C}$ = 10.9 Hz), 38.6 (d, $^{2}J_{P-C}$ = 11.6 Hz), 34.5 (d, $^{3}J_{P-C}$ = 2.0 Hz), 31.6, 31.61 (d, $^{2}J_{P-C}$ = 6.2 Hz), 31.3 (d, $^{2}J_{P-C}$ = 6.8 Hz), 30.9, 27.5 (d, $^{3}J_{P-C}$ = 2.4 Hz), 25.2 (d, $^{4}J_{P-C}$ = 2.0 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 80.64; IR: 2937 (s), 2854 (s), 1623 (w), 1545 (w), 1462 (s), 1374 (s), 1265 (s), 1223 (m), 1145 (m), 1031 (m), 964 (w), 922 (w), 865 (w), 803 (w), 751 (w), 720 (w), 637 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{43}F_3NO_3PPdS$: C, 46.49; H, 7.00; N, 2.26. Found: C, 46.58; H, 7.00; N, 2.27.

[(2-Di-*tert*-butylphosphinocyclobutene-1-(*tert*-butyl)imine)-Pd(allyl)]OTf (10Pd): sticky brown solid (0.415 g, 71.4%); ^{1}H NMR ($CDCl_3$) δ 7.94 (d, $^{4}J_{P-H}$ = 1.8 Hz, 1H), 5.60−5.58 (m, 1H), 5.38−5.35 (m, 1H), 4.19−4.16 (m, 1H), 3.99 (d, $^{3}J_{H-H}$ = 6.6 Hz, 1H), 3.13−3.02 (m, 4H), 2.54 (d, $^{3}J_{H-H}$ = 12.0 Hz, 1H), 1.42 (d, $^{3}J_{P-H}$ = 15.0 Hz, 9H), 1.42 (s, 9H), 1.26 (d, $^{3}J_{P-H}$ = 15.0 Hz, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ 160.3 (d, $^{1}J_{P-C}$ = 10.7 Hz), 157.5 (d, $^{3}J_{P-C}$ = 3.9 Hz), 140.5 (d, $^{2}J_{P-C}$ = 8.6 Hz), 118.5 (d, $^{2}J_{P-C}$ = 5.3 Hz), 92.3 (d, $^{2}J_{P-C}$ = 25.6 Hz), 65.1, 45.2, 39.9 (d, $^{1}J_{P-C}$ = 14.6 Hz), 37.6 (d, $^{1}J_{P-C}$ = 19.2 Hz), 35.3 (d, $^{3}J_{P-C}$ = 5.3 Hz), 32.1 (d, $^{2}J_{P-C}$ = 16.6 Hz), 30.6 (d, $^{2}J_{P-C}$ = 5.7 Hz), 30.5, 30.3 (d, $^{2}J_{P-C}$ = 4.5 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) δ 55.18; IR 2916 (s), 2854 (s), 2719 (m), 2293 (w), 1602 (w), 1457 (s), 1374 (s), 1259 (s), 1151 (m), 1088 (m), 1026 (s), 933 (m), 876 (w), 803 (m), 720 (m), 632 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{37}F_3NO_3PPdS$: C, 43.64; H, 6.45, N, 2.42. Found: C, 43.00; H, 6.26; N, 2.21.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Summary of crystal data, collection parameters, and ORTEP diagrams for crystal structures of **1Pd**, **8Pd**, and **9Pd**. CIF files providing additional crystallographic data, including bond lengths and angles, for compounds **1Pd**, **8Pd**, and **9Pd**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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