Reactivity of (3-Iminophosphine)palladium(II) Complexes: Evidence of Hemilability

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Several palladium(II) 3-iminophosphine complexes were synthesized in moderate to high yield. With relevance to many palladium-catalyzed coupling reactions, these complexes incorporate a wide variety of ligands, including amines, alkyls, allyls, and triflates. The presence of both η^1- and η^2-coordination modes demonstrates the hemilability of the 3-iminophosphine ligand class, as determined by X-ray crystallography and NMR spectroscopy.

Introduction

In the last century, research involving palladium has revealed an amazingly diverse reactivity for this metal. With access to reaction pathways involving oxidative addition, reductive elimination, insertion, transmetalation, and β-elimination (hydride, carbon, or other heteroatoms), palladium proves to be among the most versatile of transition metals.[1] Furthermore, palladium complexes have shown broad utility in catalytic coupling reactions and are often tolerant to a wide range of substrate functional groups.[1] This balance of stability and reactivity is ideal for building a catalyst system. Thus far, a wide variety of palladium catalysts have been developed and commercialized.[2] The primary limitations of currently available palladium catalysts involve electronic factors, often reducing substrate scope. This difficulty is not due to catalyst instability, but is a result of both catalytic activity (kinetics) and selectivity. In an effort to improve existing catalyst technology while broadening substrate applicability, our research has focused on the development of new palladium-based catalyst systems.

For over a decade, it has been recognized that ligands capable of hemilability play a special role in catalysis.[3−8] The term hemilability refers to a chelating ligand's ability to partially decoordinate from a metal center, freeing binding sites for further reactivity while remaining attached to the transition metal. This can be especially useful in stabilizing catalytic intermediates, as the proximity of the ligand's unutilized donor atoms can help to prevent decomposition of highly reactive intermediates within a catalytic cycle. Key aspects in the design of hemilabile ligands include reduced ligand symmetry and steric or electronic factors that favor one donor atom over another within the ligand framework.

In an effort to couple the stability and reactivity of palladium complexes with the benefits of a robust hemilabile ligand framework, we recently reported the development of a new class of chelating ligands known as 3-iminophosphines (3IP).[9] These ligands have significant electronic asymmetry, utilizing a soft tertiary phosphine that exhibits a high affinity for palladium in tandem with a much more weakly coordinating aldimine. The difference in binding strength of these donor atoms makes these ligands likely candidates to display hemilability within their reaction manifolds. Palladium complexes have been shown to be effective catalysts for the hydroamination of alkenes, alkynes, and dienes.[9−29] Despite the significant work done in this field, a general mechanism for hydroamination via a group 10 catalyst

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remains ambiguous. One plausible mechanism entails the presence of a palladium-amido intermediate, with a rate-determining step likely involving the breakage of a nitrogen−hydrogen bond. Alternatively, Hartwig and co-workers have suggested a catalytic cycle utilizing a metal-hydride intermediate with nucleophilic attack of an allylic species by an amine as the rate-limiting step.[30,31] Intriguingly, in our initial report, we note that the hydroamination catalysis observed displays reactivity trends that are orthogonal to those observed in Hartwig's study.[9] Specifically, the correlation between amine basicity and catalytic activity observed was inverse to what had been previously reported. Given the uniqueness of our system, we set out to produce a series of target palladium complexes relevant to the study of this hydroamination mechanism and, moreover, to investigate the stoichiometric reactivity of these new 3-iminophosphine palladium complexes.

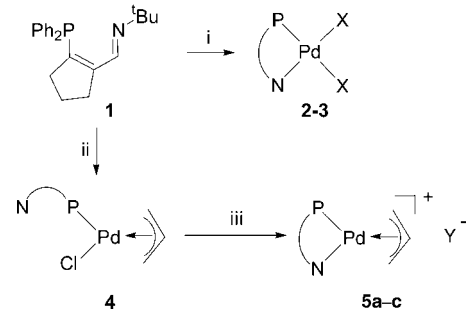
Results and Discussion

As a means to initiate a detailed study into the mechanism of hydroamination using 3-iminophosphine palladium species, we first set out to synthesize and isolate several discrete complexes bearing substituents that were plausible intermediates in its catalytic cycles. Additionally, due to the reasonably weak bonding of imines to palladium, we hypothesized that hemilabile characteristics in this ligand set could play a very important role in its chemistry. Thus, we investigated relevant reactions targeted at establishing the hemilabile nature of the 3-iminophosphine ligand set. Herein, the synthesis of several palladium(II) complexes using classical organometallic routes from commercially available palladium(II) sources is presented. In general, these complexes were produced in moderate yields by first coordination of a 3-iminophosphine ligand to a palladium(II) precursor, followed by an alkylation and/or salt metathesis reaction to yield the functionalized palladium complexes. The resulting species are potentially useful as precatalysts for a variety of palladium-catalyzed coupling reactions, including the intermolecular hydroamination of unsaturated carbon−carbon bonds. In this contribution, we focus exclusively on the synthesis and isolation of a wide variety of functionalized 3-iminophosphine palladium(II) complexes.

We presented the synthesis of the 3-iminophosphine ligand (**1**) used throughout this work previously.[9] The coordination complexes (3IP)PdX_2 (**2** and **3**) were readily produced by reacting 1 equiv of anhydrous PdX_2, where X = Cl (**2**) or Br (**3**), with an equimolar amount of **1** (Scheme 1). The chloro complex (**2**) displayed η^2-ligand coordination, as evident by the upfield shift of the imine proton and downfield shift of the phosphorus resonance and was confirmed by X-ray crystallography.[9] The related bromo complex (**3**) showed similar NMR resonances to that of **2**, consistent with η^2 ligation. An alternate route to **3** involved the reaction of **2** with 2 equiv of lithium bromide. This reaction proceeded rapidly with quantitative conversion of **2** to **3**. The driving force for this reaction likely derives from the high lattice energy of the byproduct, lithium chloride, as well as improved orbital overlap between the palladium and the bromide ligands compared to that observed with chloride ligands.

The 3IP ligand also readily coordinates to palladium supplied as the (allyl)palladium chloride dimer.[9] The resulting complex

Scheme 1. Metal Complexation[a]



[a] (i) PdX_2 (X = Cl (**2**), Br (**3**)), CH_3CN, 14 h. (ii) 0.5 $[(allyl)PdCl]_2$, CH_2Cl_2, 14 h. (iii) AgOTf, CH_2Cl_2, 2 h; or $Li[B(C_6F_5)_4]$, Et_2O, 14 h; or NH_4PF_6, CH_2Cl_2, 14 h; Y = OTf (**5a**), $B(C_6F_5)$ (**5b**), PF_6 (**5c**).

(**4**) was found to contain an η^1-3IP ligand coordinated through its phosphorus donor atom, with the remainder of the palladium's coordination sphere fulfilled by chloro and η^3-allyl ligands.[9] Treatment of **4** with silver triflate readily produced [(3IP)Pd(allyl)][OTf] (**5a**), containing an η^2-3IP ligand and an outer-sphere triflate ligand.[9] In a similar fashion, the reaction of **4** with $Li[B(C_6F_5)_4]$ also results in salt elimination and the formation of $[(3IP)Pd(allyl)][B(C_6F_5)_4]$ (**5b**). On the basis of the strong similarities in the NMR spectra, we postulate an analogous coordination environment at the palladium center in this complex. We have recently found a more attractive route to similar complexes through the treatment of **4** with ammonium salts.[32,33] The reaction of **4** with ammonium hexafluorophosphate yielded the ionic species $[(3IP)Pd(allyl)][PF_6]$ (**5c**) (Scheme 1). Again, similar NMR shifts were observed for **5c**; however, two isomers were present in a 10:3 ratio. These isomers were a result of the geometric arrangement of the allylic substituent with respect to the cyclopentenyl ring. The allyl group can be considered to point in a certain direction, as indicated by the C→H vector of its central carbon atom. In addition, the five-membered chelate ring of the 3IP ligand is not planar, but rather puckered with the cyclopentenyl ring centered above or below the palladium coordination plane. Thus, two distinct isomers exist, denoted *cis* and *trans*, indicating that the C→H vector and the cyclopentenyl ring are on the same or opposite sides of the square plane of palladium coordination. The isomer assignment was supported by 2D NMR experiments. The solid state structure of **5c** was obtained and revealed that the two distinctive isomers cocrystallized, confirming these conclusions (Figure 1).

Given that **5a** was previously shown to be active for the catalytic hydroamination of dienes and alkynes,[9] we were curious about the affinity of 3IP complexes for amine ligands. Specifically, we sought to establish a positive correlation between amine coordination to the palladium center and catalytic activity. As a means to probe this, we investigated the reactions of complex **2** with a wide variety of primary and secondary amines. Also, this amine coordination could be an important step in the mechanism for catalytic aryl amination.[34] Therefore, a variety of amines were reacted with **2** to yield the corresponding (3IP)$PdCl_2$(amine) complexes (**6a**−**l**) (Scheme 2). The reaction proceeded readily in almost any solvent, including

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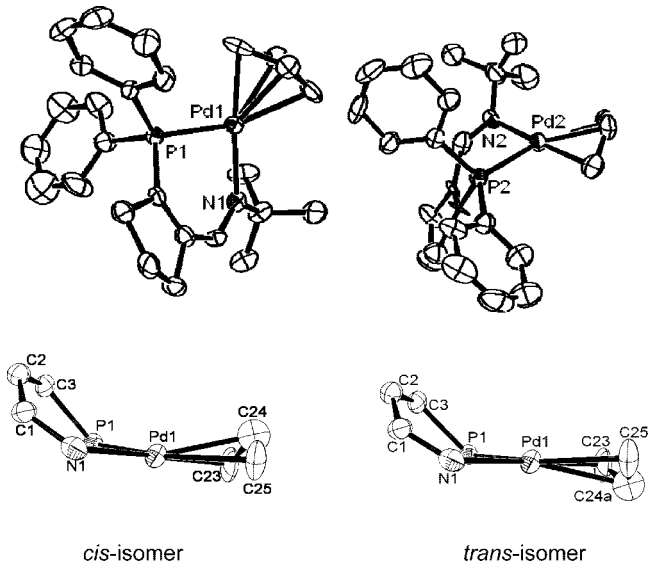
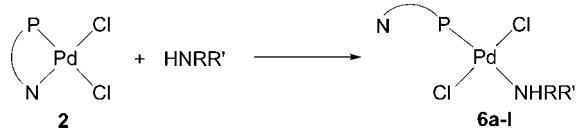


Figure 1. ORTEP diagram (50% thermal ellipsoids) of the cationic portions of **5c**. The central carbon of the allyl group bound to Pd1 is disordered over two positions in a 1:1 ratio, giving a 1:1 ratio of *cis/trans* isomers in this half of the asymmetric unit. Hydrogen atoms and hexafluorophosphate ions have been omitted for clarity. Bond lengths (in Å): Pd1−P1 = 2.267(2), Pd1−N1 = 2.160(5), Pd2−P2 = 2.262(2), Pd2−N2 = 2.144(6). Bond angles (in deg): P1−Pd1−N1 = 90.2(1), P2−Pd2−N2 = 87.7(2).

Scheme 2. Amine Coordination[a]



[a] HNRR′ = diethylamine (**6a**), morpholine (**6b**), piperidine (**6c**), *N*-methylbutylamine (**6d**), di-*n*-butylamine (**6e**), dibenzylamine (**6f**), pyrrolidine (**6g**), diisopropylamine (**6h**), cyclohexylamine (**6i**), *tert*-butylamine (**6j**), *p*-toluidine (**6k**), or benzylamine (**6l**).

chloroform, dichloromethane, tetrahydrofuran, diethyl ether, and toluene; however, the reaction rate is correlated to the solubility of the initial palladium complex in the reaction solvent. The observed NMR spectra were suggestive of η^1 coordination by the 3IP ligand in the product complexes, as evidenced by the significant downfield shift of the imine proton, while the phosphorus shift moved only slightly upfield. The solid state structure of **6a** confirmed the suspected coordination environment of the palladium, revealing *trans* chloride ligands, a coordinated diethylamine, and the η^1-3IP ligand bound only through the phosphorus donor atom (Figure 2). Ultimately, it was found that this reaction was general to virtually every amine tested, and so a series of these complexes with differing electronic and steric properties were synthesized, all displaying similar NMR shifts. In general, for aliphatic amines, coordination appeared to be independent of amine basicity and steric bulk. It is perhaps most revealing to discuss those amines that did not undergo this reaction readily, specifically aryl amines. Two representative aryl amines, *p*-toluidine and 2,6-diethylaniline, were used to investigate this coordination reaction. The coordination of *p*-toluidine proceeded very slowly, only achieving 51% completion, even after extensive heating at 100 °C. No reaction at all was observed for 2,6-diethylaniline even when the reaction was heated to 60 °C for several days. The reduced basicity of these aryl amines clearly hampers their ability to coordinate to the palladium center. In the case of the 2,6-

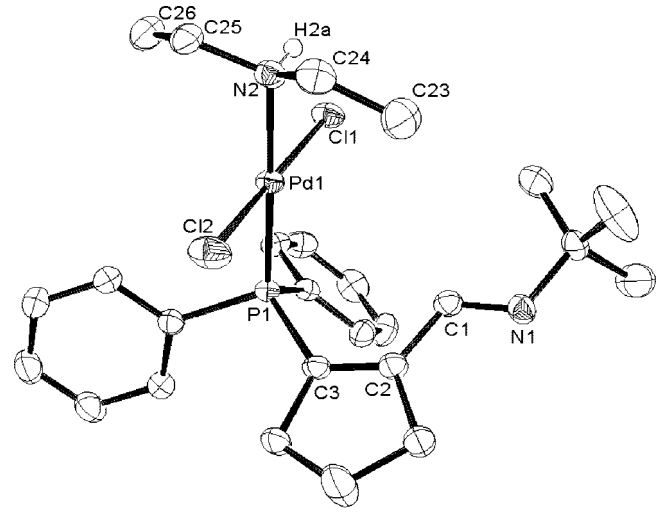
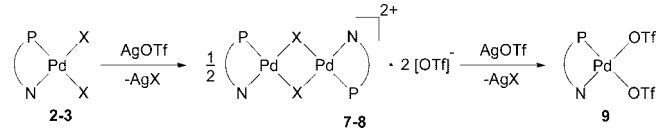


Figure 2. ORTEP diagram (50% thermal ellipsoids) of **6a**. Other than the amine, hydrogen atoms have been omitted for clarity. Bond lengths (in Å): Pd1−P1 = 2.246(1), Pd1−Cl1 = 2.298(1), Pd1−Cl2 = 2.306(1), Pd1−N2 = 2.211(2), N1−C1 = 1.267(3), C1−C2 = 1.460(3), C2−C3 = 1.338(3), N2−C24 = 1.479(3), N2−C25 = 1.476(3). Bond angles (in deg): P1−Pd1−N2 = 177.0(1), P1−Pd1−Cl1 = 95.3(1), P1−Pd1−Cl2 = 86.6(1), Cl1−Pd1−Cl2 = 177.4(1), N1−C1−C2 = 121.3(2), C1−C2−C3 = 126.8(2), C2−C3−P1 = 124.1(2), C23−C24−N2 = 111.9(2), C24−N2−C25 = 111.2(2), N2−C25−C26 = 111.9(2).

Scheme 3. Salt Metathesis of 2[a]



[a] X = Cl (**2**, **7**), Br (**3**, **8**).

diethylaniline, the lower basicity, coupled to its extensive steric bulk, completely prohibits its coordination.

Next, we set out to produce a set of highly electrophilic (3IP)Pd(II) complexes for future catalytic screening. The synthesis of a monochloro, monotriflato palladium complex (**7**) was achieved by the reaction of **2** with 1 equiv of silver triflate (Scheme 3). This reaction proceeds through a standard salt metathesis reaction pathway, where the silver cation removes a chloride from the palladium. There are significant downfield shifts in the ^{1}H NMR spectrum for all the protons except for those associated with the methylene bridge of the cyclopentenyl ring. Moreover, the phosphorus resonance is also shifted downfield significantly. The solid state structure of **7** revealed a dimer with two chlorides bridging two palladium centers, along with two outer-sphere triflate anions (Figure 3).[35] The analogous monobromo, monotriflato palladium complex (**8**) was synthesized in a similar fashion and displayed very similar spectroscopic data to that of **7**, consistent with a similar dimeric structure. To further enhance the electrophilicity of these complexes, we replaced the remaining halide ligand with another triflate counterion. Amazingly, the resultant complex proved to

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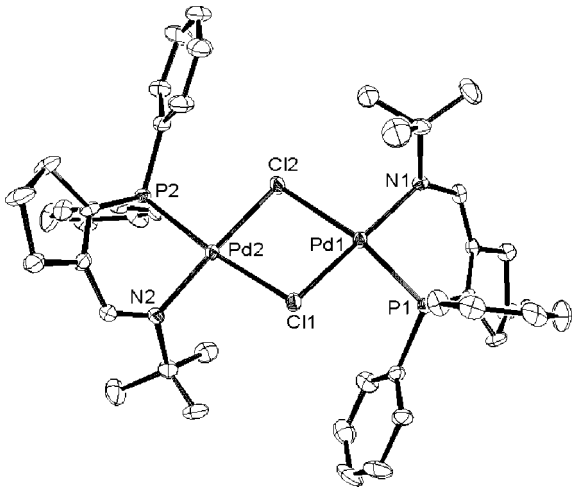


Figure 3. ORTEP diagram (50% thermal ellipsoids) of the cationic portion of **7**. Hydrogen atoms, disordered ^{t}Bu carbon atoms, CH_2Cl_2 molecule, and triflate ions have been omitted for clarity. Bond lengths (in Å): Pd1−P1 = 2.215(2), Pd1−N1 = 2.080(5), Pd−Cl1 = 2.326(2), Pd1−Cl2 = 2.468(2), Pd2−P2 = 2.020(2), Pd2−N2 = 2.045(5), Pd2−Cl1 = 2.446(2), Pd2−Cl2 = 2.327(2). Bond angles (in deg): P1−Pd1−N1 = 89.4(1), P1−Pd1−Cl1 = 89.9(1), P1−Pd1−Cl2 = 165.6(1), N1−Pd1−Cl1 = 172.7(1), N1−Pd1−Cl2 = 99.4(1), P2−Pd2−N2 = 88.3(2), P2−Pd2−Cl1 = 166.1(1), P2−Pd2−Cl2 = 93.0 (1), N2−Pd2−Cl1 = 97.1(2), N2−Pd2−Cl2 = 172.7(2).

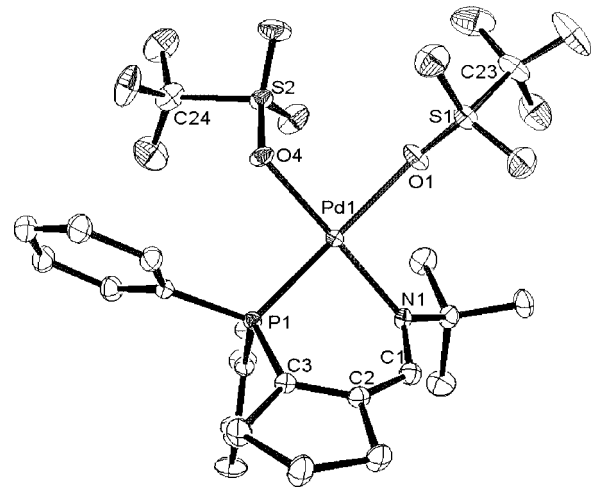


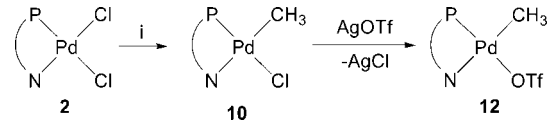
Figure 4. ORTEP diagram (50% thermal ellipsoids) of **9**. Hydrogen atoms have been omitted for clarity. Bond lengths (in Å): Pd1−P1 = 2.194(1), Pd1−N1 = 2.016(2), Pd1−O1 = 2.155(2), Pd1−O4 = 2.064(2), N1−C1 = 1.288(3), C1−C2 = 1.452(3), C2−C3 = 1.341(3). Bond angles (in deg): P1−Pd1−N1 = 86.1(1), P1−Pd1−O1 = 174.4(1), P1−Pd1−O4 = 92.4(1), O1−Pd1−O4 = 86.9(1), O1−Pd1−N1 = 94.7(1), N1−C1−C2 = 125.7(2), C1−C2−C3 = 125.0(2), C2−C3−P1 = 120.2(2).

be isolable, with no evidence of decomposition to palladium black or other likely byproducts. The product, $(3IP)Pd(OTf)_2$ (**9**), can be synthesized by either adding 1 equiv of silver triflate to **7** or adding 2 equiv to **2**. Initially, we noted that **9** had very similar NMR resonances to **2**, which was suggestive of a similar coordination environment. To confirm this assertion, X-ray quality crystals were grown and the solid state structure confirmed the η^2 coordination of the 3-iminophosphine ligand as well as two *inner-sphere* triflate anions (Figure 4).[36]

The versatility and stability of halogenated palladium(II) compounds are excellent attributes for their synthesis and isolation. However, we expect that the incorporation of triflate anion(s) will enhance the reactivity of the 3IP-palladium complexes because of the increased electrophilicity of the metal, which allows for stronger binding to substrates. Moreover, we suspect that compound **9** will display similar amine coordination chemistry to that of compound **2**, although it is unclear how the amine binding will affect the coordination environment of the palladium. The investigation of this amine coordination chemistry remains a topic of current pursuit in our laboratory.

One final class of compounds of interest herein are those in which palladium−alkyl bonds are present. Palladium−alkyl complexes are relevant to a wide variety of cross-coupling reactions commonly catalyzed by palladium species.[1,37−40] In addition, palladium−alkyls often undergo insertion reactions, leading to the production of alternative functional groups such as acyls and carboxylates.[1] Moreover, the weaker palladium−carbon bond is more susceptible to cleavage than the corresponding palladium−chloride bond. Alkylation of **2** was readily achieved using two different synthetic routes (Scheme 4). $(3IP)Pd(CH_3)Cl$

Scheme 4. Alkylation of 2[a]



[a] (i) $Sn(CH_3)_4$, CH_2Cl_2, 30 h or CH_3Li, THF, −78°C → 22°C, 14 h.

(**10**) was synthesized by reacting **2** with either methyllithium or tetramethyltin. The appearance of a doublet in the ^{1}H NMR spectrum, as well as a significant shift in the phosphorus resonance, was indicative of alkylation. Also, the imine proton displayed a chemical shift less than 8.00 ppm, suggestive of η^2 coordination. The solid state structure of **10** confirmed the η^2 coordination of the 3-iminophosphine ligand and showed that the methyl group was located *trans* to the nitrogen donor atom (Figure 5). In contrast, when the methylating agent used was methyllithium complexed with lithium bromide, an anion exchange was observed, ultimately leading to the isolation of $(3IP)Pd(CH_3)Br$ (**11**). A more straightforward synthesis of **11** was achieved similarly by reacting **3** with either methyllithium or tetramethyltin (Scheme 5). Furthermore, **11** was also produced by the reaction of **10** with 1 equiv of lithium bromide, which is believed to be the reaction that occurs if methylation of **2** is attempted with methyllithium complexed with lithium bromide. These reaction pathways are very similar to the alternative synthesis of **3** from **2** using lithium bromide. With these alkylated species isolated, our final goal was to combine the traits of the alkyl complexes with weakly coordinating counterions to produce a highly electrophilic palladium−alkyl

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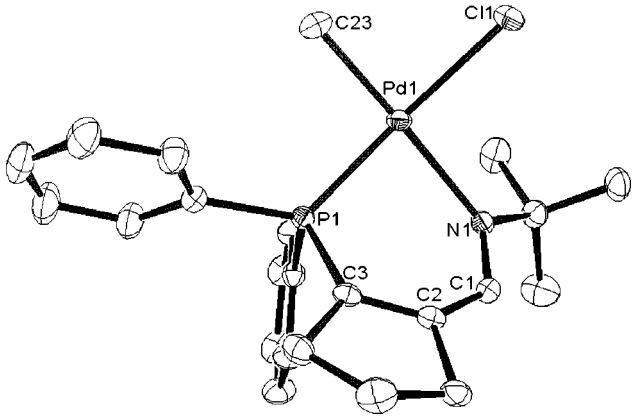
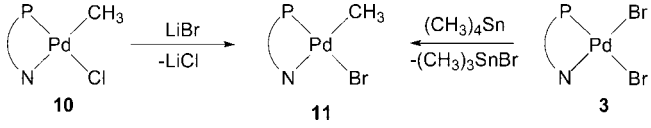


Figure 5. ORTEP diagram (50% thermal ellipsoids) of **10**. Hydrogen atoms have been omitted for clarity. Bond lengths (in Å): Pd1−P1 = 2.196(1), Pd1−N1 = 2.212(2), Pd1−Cl1 = 2.389(1), Pd1−C23 = 2.034(2), N1−C1 = 1.274(3), C1−C2 = 1.463(3), C2−C3 = 1.346(3). Bond angles (in deg): P1−Pd1−N1 = 84.9(1), P1−Pd1−C23 = 93.3(1), C23−Pd1−Cl1 = 87.3(1), Cl1−Pd1−N1 = 95.1(1), N1−C1−C2 = 124.8(2), C1−C2−C3 = 126.4(2), C2−C3−P1 = 121.3(2).

Scheme 5. Synthesis of 11



complex. Substitution of the chloride for a weakly coordinating triflate anion was accomplished by reacting **10** with 1 equiv of silver triflate in a standard salt metathesis reaction to produce (3IP)Pd(Me)OTf (**12**) (Scheme 4). The NMR assignment of the observed resonances was consistent with η^2 coordination of the ligand and showed very little shift in the resonance associated with the methyl bound to the palladium center. Therefore, it was determined that the triflate was coordinated to the palladium center, and the solid state crystal structure confirmed that assessment (Figure 6).[41]

As shown above, 3IP ligands adopt η^1 or η^2 coordination dependent on the coordinative requirements of the palladium center. Clearly, the imine is a much weaker donor atom than the phosphorus in this type of ligand. We hypothesize that the hemilabile nature of this ligand plays a key role in the catalytic activity previously displayed by its palladium complexes.[9] Interestingly, we found that the solid state structure of compound **11** depends on the recrystallization solvents used, where two distinct structures were observed. Crystals that yielded a monomeric solid state structure with an η^2-3IP ligand (Figure 7) were produced from a layered solution of CH_2Cl_2 and Et_2O. This monomeric structure is completely isomorphous to that observed for **10**, its chloro counterpart. However, when the solid state structure was obtained from crystals produced from a layered solution of THF and pentane, the 3-iminophosphine adopted an η^1 coordination mode, binding to the palladium through only the phosphorus atom, resulting in a dimeric structure (Figure 8). The NMR spectra for each set of crystals were identical, supporting that the hemilability of the 3-iminophosphine ligand is entirely solvent dependent. These results represent the first evidence of hemilabile structural isomers in 3-iminophosphine palladium complexes and suggest that a complex solution behavior is operable.

(41) Methylpalladium(II) complexes with inner-sphere triflate ligands have been observed in several reports: (a) Burger, P.; Baumeister, J. M. *J. Organomet. Chem.* **1999**, *575*, 214–222. (b) Burrows, A. D.; Mahon, M. F.; Varrone, M. *Dalton Trans.* **2003**, 4718–4730. (c) Scarel, A.; Durand, J.; Franchi, D.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Mosca, L.; Seraglia, R.; Consiglio, G.; Milani, B. *Chem.−Eur. J.* **2005**, *11*, 6014–6023. (d) Grotjahn, D. B.; Gong, Y.; Zakharov, L.; Golen, J. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **2006**, *128*, 438–453. (e) Yamashita, M.; Takamiya, I.; Jin, K.; Nozaki, K *J. Organomet. Chem.* **2006**, *691*, 3189–3195. (f) Yamashita, M.; Takamiya, I.; Jin, K.; Nozaki, K. *Organometallics* **2006**, *25*, 4588–4595. (g) Agostinho, M.; Braunstein, P. *Chem. Commun.* **2007**, 58–60. (h) Agostinho, M.; Braunstein, P.; Welter, R. *Dalton Trans.* **2007**, 759–770.

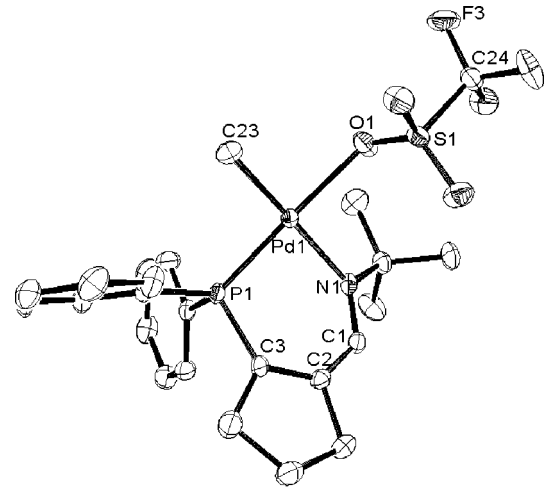


Figure 6. ORTEP diagram (50% thermal ellipsoids) of **12**. Hydrogen atoms have been omitted for clarity. Bond lengths (in Å): Pd1−P1 = 2.173(1), Pd1−N1 = 2.188(2), Pd1−O1 = 2.182(2), Pd1−C23 = 2.022(3), N1−C1 = 1.281(4), C1−C2 = 1.461(4), C2−C3 = 1.336(4). Bond angles (in deg): P1−Pd1−N1 = 87.9(1), P1−Pd1−C23 = 91.3(1), P1−Pd1−O1 = 172.5(1), C23−Pd1−O1 = 86.9(1), O1−Pd1−N1 = 94.3(91), N1−C1−C2 = 125.3(3), C1−C2−C3 =126.7(2), C2−C3−P1 = 123.6(2).

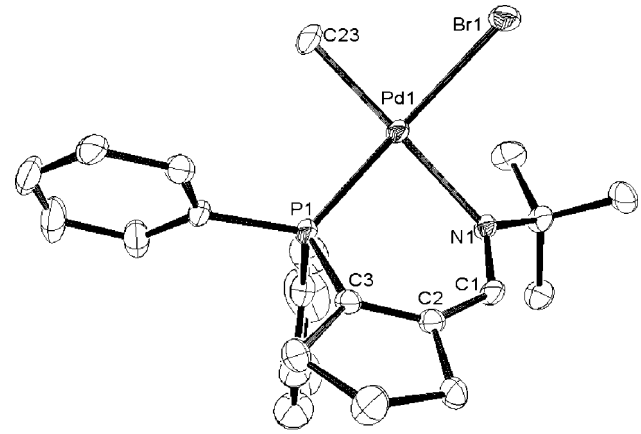


Figure 7. ORTEP diagram (50% thermal ellipsoids) of **11a**. Hydrogen atoms have been omitted for clarity. Bond lengths (in Å): Pd1−P1 = 2.208(1), Pd1−N1 = 2.154(4), Pd1−Br1 = 2.530(1), Pd1−C23 = 2.087(6), N1−C1 = 1.275(6), C1−C2 = 1.463(6), C2−C3 = 1.344(7). Bond angles (in deg): P1−Pd1−N1 = 85.8(1), P1−Pd1−C23 = 93.9(2), P1−Pd1−Br1 = 164.4(1), Br1−Pd1−C23 = 87.9(2), Br1−Pd1−N1 = 94.7(1), N1−C1−C2 = 125.2(4), C1−C2−C3 = 125.6(5), C2−C3−P1 = 122.2(4).

Conclusions

In this article, we described the synthesis and isolation of a wide variety of 3-iminophosphine palladium complexes. Specifically, we focused on compounds most relevant to catalytic hydroamination and similar cross-coupling reactions. The

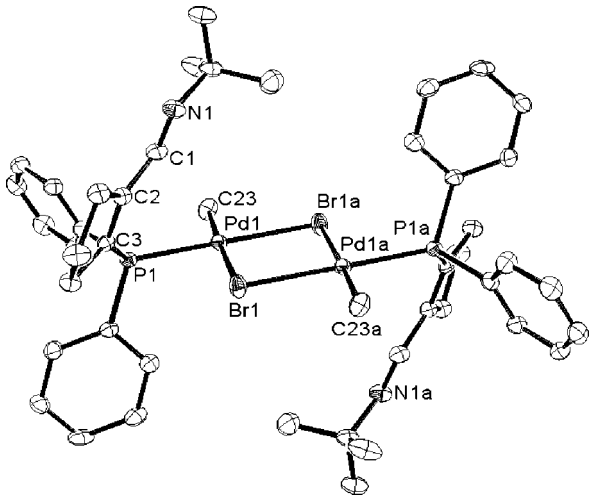


Figure 8. ORTEP diagram (50% thermal ellipsoids) of **11b**. Hydrogen atoms have been omitted for clarity. Bond lengths (in Å): Pd1−P1 = 2.372(1), Pd1−Br1 = 2.584(1), Pd1−Br1a = 2.656(1), Pd1−C23 = 2.031(3), N1−C1 = 1.225(4), C1−C2 = 1.585(4), C2−C3 = 1.304(4). Bond angles (in deg): P1−Pd1−C23 = 94.0(1), P1−Pd1−Br1 = 88.2(1), P1−Pd1−Br1a = 178.2(1), Br1−Pd1−Br1a = 90.0(1), Br1−Pd1−C23 = 177.7(1), N1−C1−C2 = 127.9(2), C1−C2−C3 = 131.4(2), C2−C3−P1 = 115.1(2). Atoms labeled with an "a" are generated by an inversion symmetry operator: $-x$, $-y+1$, $-z+1$.

halogenated and alkylated palladium complexes synthesized were readily converted to highly electrophilic complexes through the use of weakly coordinating counterions. Additionally, we demonstrated that these halide species have a strong affinity for amine ligands. Numerous examples of both η^1- and η^2-coordinated 3IP ligands support that hemilabile traits are quite common in this ligand set. With these results, we continue to investigate the catalytic mechanism involved in hydroamination using our 3IP palladium complexes while applying these unique catalysts to a wide variety of other cross-coupling reactions.

Experimental Section

General Considerations. Compounds **5**−**12** were prepared using standard Schlenk and drybox techniques. Palladium(II) chloride, palladium(II) bromide, (allyl)palladium(II) chloride dimer, methyllithium complexed with lithium bromide (1.5 M in diethyl ether), and silver triflate were purchased from Strem and used without further purification. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and for air-sensitive applications, was dried over calcium hydride, freeze−pump−thawed three times, vacuum transferred, and stored in a nitrogen atmosphere. All other solvents were purchased from either VWR or Fisher. Pentane, toluene, tetrahydrofuran, and dichloromethane were purified by passage through a column of activated 4 Å molecular sieves and degassed prior to use. Diethyl ether was purified by passage through a column of activated alumina and degassed prior to use. Acetonitrile was dried over calcium hydride at reflux, distilled and degassed with nitrogen prior to use. NH_4PF_6 was purchased from Acros and used without further purification. Diethylamine, dibenzylamine, morpholine, piperidine, *N*-methyl-*n*-butylamine, di-*n*-butylamine, *p*-toluidine, cyclohexylamine, *tert*-butylamine, pyrrolidine, diisopropylamine, benzylamine, and 2,6-diethylaniline used for coordination reactions were purchased from Acros and dried over by calcium hydride, freeze−pump−thawed three times, distilled, and stored under nitrogen. Methyllithium (3.0 M in hexanes) and tetramethyltin were purchased from Aldrich and used without further purification. Lithium bromide was purchased from Fisher and used without further purification. All ^{1}H and ^{13}C NMR data were obtained on a 600 MHz Inova NMR spectrometer at ambient temperature at 599.9 and 150.2 MHz, respectively. ^{31}P and ^{19}F NMR data were obtained on a 400 MHz Varian NMR spectrometer at ambient temperature at 161.9 and 376.3 MHz, respectively. ^{1}H NMR shifts are given relative to $CHCl_3$ (7.26 ppm), and ^{13}C NMR shifts are given relative to $CDCl_3$ (77.3 ppm). Phosphorus and fluorine NMR were externally referenced to 0.00 ppm with 5% H_3PO_4 in D_2O and $CFCl_3$, respectively. 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 Mel-Temp apparatus in sealed capillary tubes under nitrogen for compounds **5**−**12** and are uncorrected. Elemental analyses were determined by Columbia Analytics, Tucson, AZ, and Galbraith Laboratories, Knoxville, TN. Single-crystal X-ray structure determinations were performed at The University of Toledo. Compounds **1**, **2**, **4**, and **5a** were prepared as described previously.[9] $Li[B(C_6F_5)_4]$ was prepared according to literature.[42,43]

(3IP)PdBr$_2$ (3). Method A: To a slurry of $PdBr_2$ (0.442 g, 1.66 mmol) in acetonitrile (30 mL), a solution of **1** (0.613 g, 1.83 mmol) in an acetonitrile/dichloromethane mixture (20 mL:5 mL) was added, and the reaction was stirred at ambient temperature for 14 h. Solvent was removed, and the red solid was washed with diethyl ether (3 × 30 mL) to remove excess **1**. The solid was dissolved in dichloromethane and precipitated with diethyl ether (0.913 g, 91.3%); **Method B**: Lithium bromide (0.009 g, 0.1 mmol) and **2** (0.017 g, 0.033 mmol) were added to two vials in a drybox, $CDCl_3$ was added to each, and the contents of the vials were mixed. Quantitative formation of **3** was observed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy; mp 185 °C (dec); ^{1}H NMR δ 7.53−7.57 (m, 6H), 7.45−7.48 (m, 4H), 7.41 (s, 1H), 2.87−2.91 (m, 2H), 2.46−2.52 (m, 2H), 2.14 (pent, $^3J_{HH}$ = 7.8 Hz, 2H), 1.43 (s, 9H); ^{13}C{^{1}H} NMR δ 163.2 (d, $^1J_{PC}$ = 73.5 Hz), 159.9 (d, $^3J_{PC}$ = 9.5 Hz), 156.1 (d, $^2J_{PC}$ = 15.3 Hz), 133.7 (d, $^3J_{PC}$ = 11.0 Hz), 132.5 (d, $^4J_{PC}$ = 2.9 Hz), 129.1 (d, $^2J_{PC}$ = 11.9 Hz), 126.4 (d, $^1J_{PC}$ = 56.5 Hz), 67.2, 37.1 (d, $^3J_{PC}$ = 2.6 Hz), 36.6 (d, $^2J_{PC}$ = 11.6 Hz), 32.2, 23.5 (d, $^3J_{PC}$ = 6.4 Hz); ^{31}P{^{1}H} NMR δ 23.7; IR 2923 (s), 2850 (s), 2722 (w), 2676 (w), 1614 (w), 1578 (w), 1458 (m), 1371 (m), 1307 (w), 1271 (w), 1220 (w), 1183 (w), 1156 (w), 1097 (w), 1028 (w), 1000 (w), 987 (w), 890 (w), 744 (w), 689 (w). Anal. Calcd for $C_{22}H_{26}Br_2NPPd\cdot CH_2Cl_2$: C, 40.24; H, 4.11; N, 2.04. Found: C, 39.85; H, 4.05; N, 1.90.

[(3IP)Pd(allyl)][B(C$_6$F$_5$)$_4$] (5b). To a stirring slurry of lithium tetrakis(pentafluorophenyl)borate (0.354 g, 0.516 mmol) in diethyl ether (20 mL) was added a solution of **4** (0.223 g, 0.430 mmol) in diethyl ether (20 mL), and the mixture was stirred for 14 h. Solvent was removed, resulting in a yellow powder, which was washed with pentane (3 × 20 mL), dissolved in diethyl ether, and precipitated with pentane (0.234 g, 46.8%); mp 147−148 °C; ^{1}H NMR δ 8.02 (s, 1H), 7.54 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 7.47 (pseudo t, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.8 Hz, 4H), 7.41 (dd, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 8.4 Hz, 4H), 5.57−5.64 (m, 1H), 4.93−4.96 (m, 1H), 3.77−3.81 (m, 1H), 2.82−2.96 (m, 4H), 2.51−2.55 (m, 2H), 2.01 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.25 (s, 9H); ^{13}C{^{1}H} NMR δ 154.3 (d, $^3J_{PC}$ = 15.9 Hz), 151.6 (d, $^2J_{PC}$ = 9.2 Hz), 149.2 (br s), 147.6 (br s), 137.3 (br s), 136.1 (d, $^1J_{PC}$ = 34.0 Hz), 135.7 (br s), 134.0 (d, $^1J_{PC}$ = 26.2 Hz), 132.9 (d, $^2J_{PC}$ = 12.2 Hz), 132.2, 129.7 (d, $^3J_{PC}$ = 11.0 Hz), 120.1 (d, $^3J_{PC}$ = 6.0 Hz), 83.1 (d, $^2J_{PC}$ = 27.9 Hz), 66.5, 57.4, 37.6 (d, $^2J_{PC}$ = 9.9 Hz), 37.3, 29.8, 22.6 (d, $^3J_{PC}$ = 6.2 Hz); ^{31}P{^{1}H} NMR δ 16.0; ^{19}F{^{1}H} NMR δ −133.0 (br s, 8F), −163.6 (t, $^3J_{FF}$ = 18.4 Hz, 4F), −167.2 (br t, $^3J_{FF}$ = 18.4 Hz, 8F); IR 2955 (s), 2914 (s), 2853 (s), 2731 (w), 2344 (w), 1760 (w), 1638 (w), 1582 (w), 1505 (m), 1454 (s), 1372 (m), 1300

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(43) Massay, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245–250.

(w), 1259 (w), 1223 (w), 1187 (w), 1151 (w), 1084 (m), 1023 (w), 977 (m), 864 (w), 797 (w), 771 (w), 740 (w), 720 (w), 689 (w), 663 (w). Anal. Calcd for $C_{49}H_{31}BF_{20}NPPd$: C, 50.64; H, 2.69; N, 1.21. Found: C, 50.97; H, 2.81; N, 1.18.

[(3IP)Pd(allyl)][PF$_6$] (5c). To a stirring slurry of ammonium hexafluorophosphate (0.136 g, 0.833 mmol) in dichloromethane (20 mL), **4** (0.360 g, 0.694 mmol) in dichloromethane (20 mL) was added, and the mixture was allowed to stir at ambient temperature for 14 h. Solvent was removed, and the solid was washed with diethyl ether to remove any unreacted **4**, to yield a mixture of *cis* and *trans* isomers in a 3:10 ratio as a yellow solid (0.436 g, 87.2%); mp 169−174 °C; *cis* isomer: ^{1}H NMR δ 8.50 (d, $^4J_{PH}$ = 3.0 Hz, 1H), 7.48−7.56 (m, 6H), 7.35−7.43 (m, 4H), 5.62−5.68 (m, 1H), 5.18−5.21 (m, 1H), 3.83−3.87 (m, 1H), 3.56−3.58 (m, 1H), 2.88−3.03 (m, 2H), 2.57−2.64 (m, 2H), 2.44−2.49 (m, 1H), 1.99−2.11 (m, 2H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR δ 164.9 (d, $^3J_{PC}$ = 9.2 Hz), 153.6 (d, $^2J_{PC}$ = 16.2 Hz), 136.3 (d, $^1J_{PC}$ = 31.6 Hz), 133.2 (d, $^2J_{PC}$ = 13.2 Hz), 132.6 (d, $^2J_{PC}$ = 12.6 Hz), 132.3 (d, $^4J_{PC}$ = 2.7 Hz), 132.0 (d, $^4J_{PC}$ = 2.7 Hz), 129.9 (d, $^3J_{PC}$ = 10.5 Hz), 129.8 (d, $^3J_{PC}$ = 10.0 Hz), 128.4 (d, $^1J_{PC}$ = 47.8 Hz, 2C), 122.7 (d, $^3J_{PC}$ = 5.6 Hz), 81.9 (d, $^2J_{PC}$ = 27.9 Hz), 68.3, 56.1 (d, $^2J_{PC}$ = 3.2 Hz), 38.6 (d, $^2J_{PC}$ = 11.4 Hz), 35.8 (bs), 30.0, 22.3 (d, $^3J_{PC}$ = 5.4 Hz); ^{31}P{^{1}H} NMR δ 11.0, −143.2 (sept, $^1J_{PF}$ = 713.4 Hz); ^{19}F{^{1}H} NMR δ −73.2 (d, $^1J_{PF}$ = 713.4 Hz); *trans* isomer: ^{1}H NMR δ 7.88 (d, $^4J_{PH}$ = 3.6 Hz, 1H), 7.48−7.56 (m, 6H), 7.35−7.43 (m, 4H), 5.67−5.74 (m, 1H), 4.99−5.01 (m, 1H), 3.94−3.98 (m, 1H), 3.25−3.26 (m, 1H), 2.88−3.03 (m, 2H), 2.57−2.64 (m, 2H), 2.44−2.49 (m, 1H), 1.99−2.11 (m, 2H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR δ 159.8 (d, $^3J_{PC}$ = 7.6 Hz), 155.3 (d, $^2J_{PC}$ = 17.4 Hz), 134.5 (d, $^1J_{PC}$ = 34.2 Hz), 133.3 (d, $^2J_{PC}$ = 13.4 Hz), 132.4 (d, $^2J_{PC}$ = 12.6 Hz), 132.3 (d, $^4J_{PC}$ = 2.7 Hz), 131.8 (d, $^4J_{PC}$ = 2.7 Hz), 129.9 (d, $^3J_{PC}$ = 11.1 Hz), 129.7 (d, $^3J_{PC}$ = 11.6 Hz), 128.8 (d, $^1J_{PC}$ = 49.8 Hz, 2C), 120.7 (d, $^3J_{PC}$ = 6.3 Hz), 84.0 (d, $^2J_{PC}$ = 30.0 Hz), 68.3, 56.0 (d, $^2J_{PC}$ = 3.9 Hz), 38.2 (d, $^2J_{PC}$ = 11.7 Hz), 36.9 (bs), 30.0, 22.8 (d, $^3J_{PC}$ = 6.0 Hz); ^{31}P{^{1}H} NMR δ 17.5, −143.2 (sept, $^1J_{PF}$ = 713.4 Hz); ^{19}F{^{1}H} NMR δ −73.2 (d, $^1J_{PF}$ = 713.4 Hz); IR 3319 (w), 2962 (s), 2927 (s), 2847 (s), 2731 (w), 2678 (w), 1619 (w), 1579 (w), 1437 (m), 1403 (m), 1374 (w), 1307 (w), 1259 (w), 1192 (w), 1152 (w), 1094 (w), 1076 (w), 1023 (w), 996 (w), 974 (w), 921 (w), 836 (s), 801 (w), 743 (w), 721 (w), 694 (w), 552 (s). Anal. Calcd for $C_{25}H_{31}F_6NP_2Pd$: C, 47.82; H, 4.98; N, 2.23. Found: C, 48.29; H, 5.07; N, 2.33.

(3IP)PdCl$_2$(HN(C$_2$H$_6$)$_2$) (6a). To a stirring solution of **2** (0.438 g, 0.853 mmol) in dichloromethane (25 mL) was added diethylamine (0.062 g, 0.85 mmol) in dichloromethane (10 mL), and the mixture was allowed to stir at ambient temperature for 4 h. Solvent was removed, and the solid was triturated with diethyl ether. The red solid was recrystallized from diethyl ether at −25 °C (0.321 g, 64%); mp 124−126 °C; ^{1}H NMR[44] δ 8.50 (s, 1H), 7.80−7.81 (m, 4H), 7.42−7.45 (m, 2H), 7.37−7.40 (m, 4H), 3.15−3.17 (m, 2H), 2.88−2.91 (m, 2H), 2.60 (q, $^3J_{HH}$ = 6.6 Hz, 4H), 2.09 (pent, $^3J_{HH}$ = 7.2 Hz, 2H), 1.54 (t, $^3J_{HH}$ = 6.6 Hz, 6H), 1.03 (s, 9H); ^{13}C{^{1}H} NMR δ 153.5 (d, $^2J_{PC}$ = 4.9 Hz), 153.4 (d, $^3J_{PC}$ = 8.6 Hz), 136.4 (d, $^1J_{PC}$ = 45.7 Hz), 135.0 (d, $^3J_{PC}$ = 10.8 Hz), 131.1 (d, $^4J_{PC}$ = 2.9 Hz), 129.8 (d, $^1J_{PC}$ = 56.4 Hz), 128.4 (d, $^2J_{PC}$ = 11.2 Hz), 58.3, 46.9 (d, $^3J_{PC}$ = 2.8 Hz), 40.8 (d, $^3J_{PC}$ = 6.6 Hz), 35.0 (d, $^2J_{PC}$ = 12.1 Hz), 29.8, 22.9 (d, $^3J_{PC}$ = 8.6 Hz), 15.6; ^{31}P{^{1}H} NMR δ 15.6; IR 3236 (w), 2957 (s), 2920 (s), 2847 (s), 2728 (w), 2673 (w), 1617 (w), 1576 (w), 1457 (m), 1374 (m), 1306 (w), 1260 (w), 1181 (w), 1150 (w), 1090 (w), 1068 (w), 1022 (w), 948 (w), 893 (w), 825 (w), 802 (w), 742 (w), 719 (w), 692 (w). Anal. Calcd for $C_{26}H_{37}Cl_2N_2PPd$: C, 53.30; H, 6.37; N, 4.78. Found: C, 53.52; H, 6.48; N, 4.56.

General Procedure for NMR Scale Imine Displacement Reactions. In a drybox, a solution of amine (0.039 mmol) in 0.6 mL of $CDCl_3$ was added to a vial containing **2** (0.020 g, 0.039 mmol). The solutions were allowed to stand for 10 min before the spectra were obtained.

(3IP)PdCl$_2$(HN(C$_2$H$_4$)$_2$O) (6b). ^{1}H NMR δ 8.89 (s, 1H), 7.72−7.76 (m, 4H), 7.44−7.46 (m, 2H), 7.36−7.39 (m, 4H), 3.86 (d, $^3J_{HH}$ = 10.8 Hz, 4H), 3.33 (d, $^3J_{PH}$ = 7.2 Hz, 1H), 3.01 (d, $^3J_{HH}$ = 10.8 Hz, 4H), 2.90−2.93 (m, 2H), 2.52−2.55 (m, 2H), 1.90 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.10 (s, 9H); ^{13}C{^{1}H} NMR δ 154.1 (d, $^2J_{PC}$ = 6.9 Hz), 153.5 (d, $^3J_{PC}$ = 9.4 Hz), 136.1 (d, $^1J_{PC}$ = 46.8 Hz), 135.1 (d, $^3J_{PC}$ = 10.6 Hz), 131.3 (d, $^4J_{PC}$ = 2.8 Hz), 129.2 (d, $^1J_{PC}$ = 57.2 Hz), 128.3 (d, $^2J_{PC}$ = 11.4 Hz), 68.2 (d, $^4J_{HH}$ = 3.2 Hz), 58.4, 48.2 (d, $^3J_{PC}$ = 3.2 Hz), 40.6 (d, $^3J_{PC}$ = 5.8 Hz), 35.0 (d, $^2J_{PC}$ = 12.3 Hz), 30.1, 22.8 (d, $^3J_{PC}$ = 8.7 Hz); ^{31}P{^{1}H} NMR δ 16.7.

(3IP)PdCl$_2$(HN(C$_5$H$_{10}$)) (6c). ^{1}H NMR δ 8.90 (s, 1H), 7.72−7.76 (m, 4H), 7.42−7.45 (m, 2H), 7.35−7.38 (m, 4H), 3.22−3.24 (m, 2H), 3.12−3.16 (m, 2H), 3.04−3.10 (m, 1H), 2.89−2.92 (m, 2H), 2.50−2.54 (m, 2H), 1.89 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.68−1.74 (m, 3H), 1.50−1.55 (m, 3H), 1.11 (s, 9H); ^{13}C{^{1}H} NMR δ 153.8 (d, $^2J_{PC}$ = 7.2 Hz), 153.6 (d, $^3J_{PC}$ = 9.4 Hz), 136.3 (d, $^1J_{PC}$ = 45.9 Hz), 135.1 (d, $^2J_{PC}$ = 10.5 Hz), 131.1 (d, $^4J_{PC}$ = 3.0 Hz), 129.4 (d, $^1J_{PC}$ = 56.0 Hz), 128.2 (d, $^3J_{PC}$ = 11.2 Hz), 58.3, 49.3 (d, $^3J_{PC}$ = 3.4 Hz), 40.6 (d, $^3J_{PC}$ = 5.7 Hz), 35.0 (d, $^2J_{PC}$ = 12.0 Hz), 30.0, 27.4 (d, $^4J_{PC}$ = 3.4 Hz), 24.0, 22.8 (d, $^3J_{PC}$ = 8.6 Hz); ^{31}P{^{1}H} NMR δ 16.2.

(3IP)PdCl$_2$(HN(Me)^{n}Bu) (6d). ^{1}H NMR δ 8.74 (s, 1H), 7.76−7.79 (m, 4H), 7.43−7.46 (m, 2H), 7.37−7.40 (m, 4H), 3.27−3.32 (m, 1H), 3.13−3.20 (m, 1H), 2.89−2.92 (m, 2H), 2.64 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 4.2 Hz, 3H), 2.52−2.56 (m, 2H), 2.38−2.45 (m, 1H), 2.04−2.10 (m, 1H), 1.90 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.79−1.86 (m, 1H), 1.44−1.50 (m, 1H), 1.37−1.42 (m, 1H), 1.08 (s, 9H), 0.97 (t, $^3J_{HH}$ = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR δ 153.7 (d, $^2J_{PC}$ = 6.9 Hz), 153.6 (d, $^3J_{PC}$ = 9.2 Hz), 136.3 (d, $^1J_{PC}$ = 45.9 Hz), 135.1 (d, $^2J_{PC}$ = 10.5 Hz), 131.2 (d, $^4J_{PC}$ = 2.7 Hz), 129.6 (d, $^1J_{PC}$ = 56.0 Hz), 128.5 (d, $^3J_{PC}$ = 11.4 Hz), 58.3, 53.4 (d, $^3J_{PC}$ = 2.8 Hz), 40.6 (d, $^3J_{PC}$ = 6.0 Hz), 39.1 (d, $^3J_{PC}$ = 3.6 Hz), 36.0 (d, $^2J_{PC}$ = 12.2 Hz), 31.7, 30.0, 22.8 (d, $^3J_{PC}$ = 8.6 Hz), 20.5, 14.3; ^{31}P{^{1}H} NMR δ 16.0.

(3IP)PdCl$_2$(HN^{n}Bu$_2$) (6e). ^{1}H NMR δ 8.43 (s, 1H), 7.80−7.84 (m, 4H), 7.42−7.46 (m, 2H), 7.37−7.40 (m, 4H), 3.26−3.31 (m, 1H), 3.10−3.17 (m, 2H), 2.86−2.89 (m, 2H), 2.55−2.58 (m, 2H), 2.46−2.53 (m, 2H), 2.14−2.22 (m, 2H), 1.90 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.82−1.88 (m, 2H), 1.43−1.51 (m, 2H), 1.34−1.41 (m, 2H), 1.02 (s, 9H), 0.97 (t, $^3J_{HH}$ = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR δ 153.5 (d, $^3J_{PC}$ = 8.6 Hz), 153.4 (d, $^2J_{PC}$ = 6.2 Hz), 136.4 (d, $^1J_{PC}$ = 45.4 Hz), 135.0 (d, $^2J_{PC}$ = 10.8 Hz), 131.1 (d, $^4J_{PC}$ = 2.8 Hz), 129.8 (d, $^1J_{PC}$ = 55.8 Hz), 128.4 (d, $^3J_{PC}$ = 11.1 Hz), 58.2, 52.3 (d, $^3J_{PC}$ = 3.0 Hz), 40.7 (d, $^3J_{PC}$ = 6.9 Hz), 34.9 (d, $^2J_{PC}$ = 12.2 Hz), 32.2, 29.8, 22.8 (d, $^3J_{PC}$ = 8.6 Hz), 20.6, 14.3; ^{31}P{^{1}H} NMR δ 15.8.

(3IP)PdCl$_2$(HN(CH$_2$C$_6$H$_5$)$_2$) (6f). ^{1}H NMR δ 8.22 (s, 1H), 7.52−7.58 (m, 8H), 7.39−7.43 (m, 8H), 7.30−7.33 (m, 4H), 4.36−4.41 (m, 2H), 3.86−3.94 (m, 1H), 3.76−3.80 (m, 2H), 2.84−2.87 (m, 2H), 2.42−2.45 (m, 2H), 1.86 (pseudo t, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR δ 153.8 (d, $^3J_{PC}$ = 8.1 Hz), 153.4 (d, $^2J_{PC}$ = 5.2 Hz), 136.4, 135.7 (d, $^1J_{PC}$ = 46.2 Hz), 135.1 (d, $^2J_{PC}$ = 11.0 Hz), 131.1 (d, $^4J_{PC}$ = 2.7 Hz), 130.3, 129.7 (d, $^1J_{PC}$ = 56.6 Hz), 129.1, 128.4, 128.3 (d, $^3J_{PC}$ = 11.2 Hz), 58.1, 54.7 (d, $^3J_{PC}$ = 2.7 Hz), 40.4 (d, $^3J_{PC}$ = 7.8 Hz), 35.0 (d, $^2J_{PC}$ = 12.2 Hz), 29.8, 22.7 (d, $^3J_{PC}$ = 8.7 Hz); ^{31}P{^{1}H} NMR δ 17.2.

(3IP)PdCl$_2$(HN(C$_4$H$_8$)) (6g). ^{1}H NMR δ 9.08 (s, 1H), 7.72−7.76 (m, 4H), 7.42−7.45 (m, 2H), 7.36−7.38 (m, 4H), 3.34−3.37 (m, 1H), 3.14−3.17 (m, 4H), 2.90−2.93 (m, 2H), 2.49−2.52 (m, 2H), 1.89 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.83−1.88 (m, 2H), 1.62−1.64 (m, 2H), 1.14 (s, 9H); ^{13}C{^{1}H} NMR δ 153.9 (d, $^3J_{PC}$ = 7.0 Hz), 153.7 (d, $^2J_{PC}$ = 9.6 Hz), 136.3 (d, $^1J_{PC}$ = 46.0 Hz), 135.2 (d, $^2J_{PC}$ = 10.5 Hz), 131.2 (d, $^4J_{PC}$ = 2.8 Hz), 129.3 (d,

(44) The ^{1}H NMR signal for the N-*H* proton was not observed.

$^1J_{PC}$ = 56.2 Hz), 128.2 (d, $^3J_{PC}$ = 11.2 Hz), 58.4, 49.1 (d, $^3J_{PC}$ = 2.2 Hz), 40.5 (d, $^3J_{PC}$ = 5.2 Hz), 35.0 (d, $^2J_{PC}$ = 12.0 Hz), 30.1, 24.6 (d, $^4J_{PC}$ = 4.2 Hz), 22.8 (d, $^3J_{PC}$ = 8.2 Hz); $^{31}P\{^1H\}$ NMR δ 15.7.

(3IP)PdCl$_2$(HN^{i}Pr$_2$) (6h). ^{1}H NMR δ 8.36 (s, 1H), 7.77−7.81 (m, 4H), 7.41−7.43 (m, 2H), 7.35−7.38 (m, 4H), 3.28−3.34 (m, 2H), 3.23−3.27 (m, 1H), 2.84−2.88 (m, 2H), 2.57−2.60 (m, 2H), 1.88 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.58 (d, $^3J_{HH}$ = 6.0 Hz, 6H), 1.40 (d, $^3J_{HH}$ = 6.6 Hz, 6H), 0.99 (s, 9H); $^{13}C\{^1H\}$ NMR δ 153.4 (d, $^2J_{PC}$ = 8.4 Hz), 153.1 (d, $^3J_{PC}$ = 5.8 Hz), 136.6 (d, $^1J_{PC}$ = 46.0 Hz), 135.0 (d, $^2J_{PC}$ = 10.6 Hz), 131.0 (d, $^4J_{PC}$ = 2.7 Hz), 130.0 (d, $^1J_{PC}$ = 56.1 Hz), 128.3 (d, $^3J_{PC}$ = 11.2 Hz), 58.1, 49.2 (d, $^3J_{PC}$ = 2.7 Hz), 41.0 (d, $^3J_{PC}$ = 5.2 Hz), 34.9 (d, $^2J_{PC}$ = 12.2 Hz), 29.7, 23.6 (bs), 23.4 (d, $^4J_{PC}$ = 2.7 Hz), 22.8 (d, $^3J_{PC}$ = 8.8 Hz); $^{31}P\{^1H\}$ NMR δ 15.4.

(3IP)PdCl$_2$(H$_2$NCy) (6i). ^{1}H NMR δ 8.78 (s, 1H), 7.76−7.80 (m, 4H), 7.43−7.46 (m, 2H), 7.37−7.40 (m, 4H), 3.06−3.11 (m, 1H), 2.89−2.92 (m, 2H), 2.66 (pseudo t, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 6.0 Hz, 2H), 2.53−2.56 (m, 2H), 2.26−2.28 (m, 2H), 1.90 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.74−1.78 (m, 2H), 1.60−1.63 (m, 1H), 1.29−1.34 (m, 2H), 1.21−1.27 (m, 2H), 1.10−1.15 (m, 1H), 1.08 (s, 9H); $^{13}C\{^1H\}$ NMR δ 153.9 (d, $^2J_{PC}$ = 6.8 Hz), 153.5 (d, $^3J_{PC}$ = 9.2 Hz), 136.0 (d, $^1J_{PC}$ = 46.2 Hz), 135.1 (d, $^2J_{PC}$ = 10.6 Hz), 131.2 (d, $^4J_{PC}$ = 2.8 Hz), 129.4 (d, $^1J_{PC}$ = 56.6 Hz), 128.4 (d, $^3J_{PC}$ = 11.4 Hz), 58.3, 52.8 (d, $^3J_{PC}$ = 2.2 Hz), 40.6 (d, $^3J_{PC}$ = 6.2 Hz), 36.1 (d, $^4J_{PC}$ = 2.4 Hz), 35.0 (d, $^2J_{PC}$ = 12.3 Hz), 29.9, 25.5, 25.2, 22.7 (d, $^3J_{PC}$ = 8.4 Hz); $^{31}P\{^1H\}$ NMR δ 15.5.

(3IP)PdCl$_2$(H$_2$N^{t}Bu) (6j). ^{1}H NMR δ 8.67 (s, 1H), 7.78−7.82 (m, 4H), 7.43−7.44 (m, 2H), 7.37−7.40 (m, 4H), 2.87−2.90 (m, 2H), 2.86 (d, $^3J_{PH}$ = 6.0 Hz, 2H), 2.55−2.58 (m, 2H), 1.89 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.45 (s, 9H), 1.05 (s, 9H); $^{13}C\{^1H\}$ NMR δ 153.8 (d, $^2J_{PC}$ = 6.6 Hz), 153.5 (d, $^3J_{PC}$ = 8.8 Hz), 136.0 (d, $^1J_{PC}$ = 47.1 Hz), 135.1 (d, $^2J_{PC}$ = 10.5 Hz), 131.2 (d, $^4J_{PC}$ = 2.8 Hz), 129.5 (d, $^1J_{PC}$ = 57.0 Hz), 128.4 (d, $^3J_{PC}$ = 11.2 Hz), 58.3, 53.7 (d, $^3J_{PC}$ = 1.4 Hz), 40.7 (d, $^3J_{PC}$ = 6.4 Hz), 35.0 (d, $^2J_{PC}$ = 12.2 Hz), 32.5 (d, $^4J_{PC}$ = 2.2 Hz), 29.9, 22.8 (d, $^3J_{PC}$ = 8.6 Hz); $^{31}P\{^1H\}$ NMR δ 15.8.

(3IP)PdCl$_2$(H$_2$N-*p*-CH$_3$C$_6$H$_4$) (6k). Reaction time was 120 h at ambient temperature, 24 h at 50 °C, then 24 h at 100 °C (51% conversion based on ^{1}H NMR); ^{1}H NMR δ 8.68 (s, 1H), 7.79−7.82 (m, 4H), 7.43−7.44 (m, 2H), 7.37−7.40 (m, 4H), 7.21 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.01 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 2.94−2.96 (m, 2H), 2.88−2.90 (m, 2H), 2.55−2.58 (m, 2H), 2.31 (s, 3H), 1.89 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.06 (s, 9H); $^{13}C\{^1H\}$ NMR δ 153.6 (d, $^2J_{PC}$ = 8.6 Hz), 153.5 (d, $^3J_{PC}$ = 5.8 Hz), 143.9, 135.1 (d, $^2J_{PC}$ = 10.5 Hz), 135.0 (d, $^1J_{PC}$ = 47.2 Hz), 131.2 (d, $^4J_{PC}$ = 2.8 Hz), 129.2, 129.1, 128.6 (d, $^3J_{PC}$ = 11.4 Hz), 125.3 (d, $^1J_{PC}$ = 57.4 Hz), 123.1, 58.3, 40.7 (d, $^3J_{PC}$ = 6.4 Hz), 36.6 (d, $^2J_{PC}$ = 11.6 Hz), 32.5, 29.9, 22.8 (d, $^3J_{PC}$ = 8.6 Hz); $^{31}P\{^1H\}$ NMR δ 17.3.

(3IP)PdCl$_2$(H$_2$NCH$_2$C$_6$H$_5$) (6l). ^{1}H NMR δ 8.87 (s, 1H), 7.76−7.80 (m, 4H), 7.45−7.48 (m, 2H), 7.38−7.41 (m, 4H), 7.36−7.38 (m, 2H), 7.33−7.35 (m, 3H), 4.10−4.13 (m, 2H), 2.95−2.98 (m, 2H), 2.91−2.94 (m, 2H), 2.54−2.56 (m, 2H), 1.91 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.10 (s, 9H); $^{13}C\{^1H\}$ NMR δ 154.2 (d, $^3J_{PC}$ = 6.8 Hz), 153.6 (d, $^2J_{PC}$ = 9.0 Hz), 139.1 (d, $^4J_{PC}$ = 3.4 Hz), 135.7 (d, $^1J_{PC}$ = 47.0 Hz), 135.1 (d, $^2J_{PC}$ = 10.8 Hz), 131.3 (d, $^4J_{PC}$ = 2.8 Hz), 129.4, 129.1 (d, $^1J_{PC}$ = 57.2 Hz), 128.5, 128.45, 128.39 (d, $^3J_{PC}$ = 11.4 Hz), 58.5, 48.1 (d, $^3J_{PC}$ = 2.6 Hz), 40.4 (d, $^3J_{PC}$ = 6.3 Hz), 35.1 (d, $^2J_{PC}$ = 12.3 Hz), 30.0, 22.8 (d, $^3J_{PC}$ = 8.6 Hz); $^{31}P\{^1H\}$ NMR δ 16.4.

[(3IP)Pd(Cl)]$_2$[OTf]$_2$ (7). To a stirring slurry of silver triflate (0.410 g, 1.60 mmol) in dichloromethane (20 mL) was added **2** (0.819 g, 1.60 mmol) in dichloromethane (20 mL), and the mixture was stirred at ambient temperature for 14 h in the absence of light. Solvent was removed, and the orange solid was dissolved in THF and precipitated with pentane at −25 °C (0.621 g, 62.1%); mp 156−158 °C; ^{1}H NMR δ 10.36 (d, $^4J_{PH}$ = 16.8 Hz, 1H), 7.64−7.69 (m, 6H), 7.56−7.59 (m, 4H), 3.19−3.22 (m, 2H), 2.63−2.66 (m, 2H), 2.13 (pent, $^3J_{HH}$ = 7.8 Hz, 2H), 1.61 (s, 9H); $^{13}C\{^1H\}$ NMR[45] δ 163.4 (d, $^1J_{PC}$ = 81.8 Hz), 161.6 (d, $^3J_{PC}$ = 2.0 Hz), 150.0 (d, $^2J_{PC}$ = 5.0 Hz), 133.7 (d, $^4J_{PC}$ = 2.8 Hz), 132.0 (d, $^3J_{PC}$ = 10.5 Hz), 129.6 (d, $^2J_{PC}$ = 12.6 Hz), 129.6 (d, $^1J_{PC}$ = 107.4 Hz), 63.0, 39.8 (d, $^3J_{PC}$ = 9.6 Hz), 34.0 (d, $^2J_{PC}$ = 10.6 Hz), 28.2, 23.5 (d, $^3J_{PC}$ = 8.8 Hz); $^{31}P\{^1H\}$ NMR δ 27.5; $^{19}F\{^1H\}$ NMR δ −78.7; IR 3152 (w), 2960 (s), 2923 (s), 2850 (s), 2731 (w), 1651 (w), 1586 (w), 1458 (m), 1375 (m), 1288 (m), 1261 (m), 1224 (w), 1188 (w), 1151 (w), 1114 (w), 1096 (w), 1064 (w), 1032 (m), 958 (w), 798 (w), 752 (w), 720 (w), 697 (w), 633 (m). Anal. Calcd for $C_{44}H_{52}Cl_2N_2P_2Pd_2$:[46] C, 55.35; H, 5.50; N, 2.93. Found: C, 55.31; H, 5.20; N, 2.82.

[(3IP)Pd(Br)]$_2$[OTf]$_2$ (8). To a stirring slurry of silver triflate (0.192 g, 0.745 mmol) in dichloromethane (20 mL) was added **3** (0.448 g, 0.745 mmol) in dichloromethane (20 mL), and the mixture was stirred at ambient temperature for 14 h in the absence of light. Solvent was removed, and the orange solid was dissolved in THF and precipitated with pentane at −25 °C (0.273 g, 54.6%); mp 159−160 °C; ^{1}H NMR δ 10.35 (d, $^4J_{PH}$ = 17.4 Hz, 1H), 7.64−7.68 (m, 6H), 7.56−7.59 (m, 4H), 3.18−3.21 (m, 2H), 2.64−2.67 (m, 2H), 2.12 (pseudo pent, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.61 (s, 9H); $^{13}C\{^1H\}$ NMR[45] δ 163.5 (d, $^1J_{PC}$ = 56.1 Hz), 161.6, 150.1 (d, $^2J_{PC}$ = 15.4 Hz), 133.7 (d, $^4J_{PC}$ = 2.7 Hz), 133.0 (d, $^3J_{PC}$ = 10.5 Hz), 129.6 (d, $^2J_{PC}$ = 12.4 Hz), 129.4 (d, $^1J_{PC}$ = 60.3 Hz), 63.0, 39.8 (d, $^3J_{PC}$ = 9.8 Hz), 34.0 (d, $^2J_{PC}$ = 11.0 Hz), 28.2, 23.5 (d, $^3J_{PC}$ = 8.7 Hz); $^{31}P\{^1H\}$ NMR δ 27.9; $^{19}F\{^1H\}$ NMR δ −78.7; IR 3155 (w), 3120 (w), 3041 (w), 2916 (s), 2854 (s), 2729 (w), 1649 (m), 1586 (w), 1457 (m), 1436 (m), 1400 (w), 1379 (m), 1332 (w), 1285 (m), 1259 (m), 1223 (m), 1192 (m), 1156 (m), 1114 (m), 1099 (w), 1062 (w), 1031 (m), 995 (w), 953 (w), 901 (w), 824 (w), 792 (w), 751 (m), 720 (m), 694 (m), 632 (m). Anal. Calcd for $C_{44}H_{52}Br_2N_2P_2Pd_2$:[46] C, 50.65; H, 5.02; N, 2.68. Found: C, 50.78; H, 5.12; N, 2.55.

(3IP)Pd(OTf)$_2$ (9). Method A: To a stirring slurry of silver triflate (0.365 g, 1.42 mmol) in dichloromethane (20 mL) was added **2** (0.346 g, 0.676 mmol) in dichloromethane (20 mL), and the mixture was stirred at ambient temperature for 14 h in the absence of light. Solvent was removed, and the orange solid was dissolved in THF and precipitated with pentane at −25 °C (0.287 g, 57.4%). **Method B**: To a stirring slurry of silver triflate (0.038 g, 0.15 mmol) in dichloromethane (10 mL) was added **7** (0.085 g, 0.14 mmol) in dichloromethane (10 mL), and the mixture was stirred at ambient temperature for 14 h in the absence of light. Solvent was removed, and the orange solid was dissolved in THF and precipitated with pentane at −25 °C (0.073 g, 73%); mp 160−161 °C; ^{1}H NMR δ 7.68−7.70 (m, 6H), 7.56−7.59 (m, 4H), 7.23 (bs, 1H), 3.02−3.05 (m, 2H), 2.69−2.72 (m, 2H), 2.31 (pent, $^3J_{HH}$ = 7.8 Hz, 2H), 1.45 (s, 9H); $^{13}C\{^1H\}$ NMR[45] δ 164.1 (d, $^2J_{PC}$ = 14.4 Hz), 160.9 (d, $^1J_{PC}$ = 62.4 Hz), 159.6 (d, $^3J_{PC}$ = 9.4 Hz), 134.1 (bs), 133.6 (d, $^3J_{PC}$ = 9.0 Hz), 130.1 (d, $^2J_{PC}$ = 13.2 Hz), 121.4 (d, $^1J_{PC}$ = 65.1 Hz), 53.7, 39.8 (d, $^2J_{PC}$ = 10.5 Hz), 36.1 (bs), 31.0, 23.8 (d, $^3J_{PC}$ = 9.2 Hz); $^{31}P\{^1H\}$ NMR δ 22.3; $^{19}F\{^1H\}$ NMR δ −77.8; IR 3051 (w), 2958 (s), 2916 (s), 2843 (s), 1618 (w), 1581 (w), 1457 (m), 1435 (m), 1389 (w), 1368 (m), 1301 (s), 1228 (s), 1207 (s), 1166 (s), 1099 (m), 1068 (w), 1021 (s), 964 (w), 891 (w), 751 (m), 694 (m), 632 (m). Anal. Calcd for $C_{24}H_{26}F_6NO_6PPdS_2$: C, 38.96; H, 3.54; N, 1.89. Found: C, 38.93; H, 3.01; N, 1.81.

(3IP)Pd(CH$_3$)Cl (10). Method A: To a stirring solution of **2** (0.521 g, 1.02 mmol) in THF (40 mL) at 0 °C was added methyllithium (0.37 mL, 1.1 mmol) via syringe. The reaction was

(45) The $^{13}C\{^1H\}$ NMR signal for the carbon atom of the triflate anion was unobserved.

(46) Compounds **7** and **8** undergo loss of the triflate anions and a two-electron reduction, resulting in palladium(I), prior to analysis.

Table 1. Crystal Data and Collection Parameters

	5c	6a	7	9	10	11a	11b	12
formula	$C_{50}H_{62}F_{12}N_2P_4Pd_2$	$C_{26}H_{37}Cl_2N_2PPd$	$C_{46}H_{52}Cl_2F_6N_2O_6P_2Pd_2S_2 \cdot 0.5\ CH_2Cl_2$	$C_{24}H_{26}F_6NO_6PPdS_2$	$C_{23}H_{29}ClNPPd$	$C_{23}H_{29}BrNPPd$	$C_{23}H_{29}BrNPPd$	$C_{24}H_{29}F_3NO_3PPdS$
fw	1255.86	585.85	1337.72	739.95	492.29	536.75	536.75	605.99
space group	*Iba*2 (#45)	*Pbcn* (#60)	$P2_1$ (#4)	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P2_12_12_1$ (#19)
temperature (K)	140	140	140	140	140	140	140	140
a (Å)	21.604(1)	28.334(1)	9.485(1)	18.658(1)	8.830(1)	13.944(1)	9.480(1)	10.079(1)
b (Å)	27.913(1)	10.179(1)	10.534(1)	10.556(1)	16.792(1)	9.840(1)	9.936(1)	15.819(1)
c (Å)	17.792(2)	19.203(1)	26.883(1)	14.722(1)	15.270(1)	17.190(1)	12.549(1)	15.947(1)
α (deg)	90.000	90.000	90.000	90.000	90.000	90.000	73.030(1)	90.000
β (deg)	90.000	90.000	90.804(1)	106.146(2)	93.184(1)	95.697(2)	79.326(1)	90.000
γ (deg)	90.000	90.000	90.000	90.000	90.000	90.000	86.795(1)	90.000
V (Å^3)	10729(1)	5538.4(1)	2685.9(1)	2785.1(1)	2260.6(1)	2346.9(3)	1110.9(1)	2542.4(1)
Z	8	8	2	4	4	4	2	4
density$_{calc}$ (g/cm^3)	1.555	1.405	1.646	1.765	1.446	1.519	1.605	1.588
diffractometer	Siemens SMART	Siemens SMART	Siemens SMART	Siemens SMART	Siemens SMART	Siemens SMART	Siemens SMART	Siemens SMART
radiation	Mo Kα (*λ* = 0.71069 Å)	Mo Kα (*λ* = 0.71069 Å)	Mo Kα (*λ* = 0.71069 Å)	Mo Kα (*λ* = 0.71069 Å)	Mo Kα (*λ* = 0.71069 Å)	Mo Kα (*λ* = 0.71069 Å)	Mo Kα (*λ* = 0.71069 Å)	Mo Kα (*λ* = 0.71069 Å)
monochromator	graphite	graphite	graphite	graphite	graphite	graphite	graphite	graphite
detector	CCD area detector	CCD area detector	CCD area detector	CCD area detector	CCD area detector	CCD area detector	CCD area detector	CCD area detector
scan type, width	*ω*, 0.3°	*ω*, 0.3°	*ω*, 0.3°	*ω*, 0.3°	*ω*, 0.3°	*ω*, 0.3°	*ω*, 0.3°	*ω*, 0.3°
scan speed	20.0 s/frame	20.0 s/frame	20.0 s/frame	20.0 s/frame	20.0 s/frame	20.0 s/frame	20.0 s/frame	20.0 s/frame
no. of reflns measd	hemisphere	hemisphere	hemisphere	hemisphere	hemisphere	hemisphere	hemisphere	hemisphere
2*θ* range (deg)	4.6−48.2	4.5−56.6	4.5−56.5	5.0−56.6	5.2−56.6	4.8−56.5	4.3−56.7	4.8−56.6
cryst dimens (mm)	0.30 × 0.15 × 0.02	0.32 × 0.28 × 0.04	0.48 × 0.22 × 0.04	0.68 × 0.15 × 0.15	0.38 × 0.10 × 0.08	0.16 × 0.14 × 0.06	0.32 × 0.10 × 0.04	0.42 × 0.09 × 0.06
no. of reflns measd	113 063	63 537	61 781	31 988	25 894	26 518	12 552	29 311
no. of unique reflns	13 318	6902	13 270	6933	5629	5838	5504	6343
no. of observations	13 318	6902	13 270	6933	5629	5838	5504	6343
no. of params	653	293	623	370	244	244	244	307
R, R_w, R_{all}	0.0494, 0.1199, 0.0844	0.0296, 0.0827, 0.0436	0.0576, 0.1452, 0.0594	0.0322, 0.0878, 0.0394	0.0306, 0.0785, 0.0328	0.0516, 0.1717, 0.0677	0.0367, 0.0852, 0.0464	0.0319, 0.0777, 0.0335
GOF	0.867	0.995	1.152	1.021	1.108	1.067	0.960	1.091

warmed to ambient temperature over 14 h. Solvent was removed, and the yellow solid was washed with diethyl ether. The solid was dissolved in dichloromethane and precipitated with diethyl ether (0.241 g, 48.2%). **Method B**: To a stirring solution of **2** (0.521 g, 1.02 mmol) in dichloromethane (40 mL) was added tetramethyltin (0.28 mL, 2.03 mmol) via syringe. The reaction was stirred at ambient temperature for 40 h. Solvent was removed, and the yellow solid was washed with pentane (3 × 30 mL) to remove any leftover tetramethyltin. The solid was dissolved in dichloromethane and precipitated with diethyl ether (0.363 g, 72.6%); mp 139−141 °C; ^{1}H NMR δ 7.70 (d, $^4J_{PH}$ = 3.0 Hz, 1H), 7.47−7.50 (m, 2H), 7.39−7.44 (m, 8H), 2.75−2.79 (m, 2H), 2.40−2.44 (m, 2H), 2.01 (pent, $^3J_{HH}$ = 7.8 Hz, 2H), 1.43 (s, 9H), 0.64 (d, $^3J_{PH}$ = 3.0 Hz, 3H); ^{13}C{^{1}H} NMR δ 157.5 (d, $^3J_{PC}$ = 6.0 Hz), 152.2 (d, $^2J_{PC}$ = 15.2 Hz), 135.8 (d, $^1J_{PC}$ = 38.8 Hz), 133.5 (d, $^2J_{PC}$ = 12.0 Hz), 131.3 (d, $^4J_{PC}$ = 2.6 Hz), 129.0 (d, $^3J_{PC}$ = 11.0 Hz), 128.9 (d, $^1J_{PC}$ = 51.0 Hz), 63.6, 38.1 (d, $^3J_{PC}$ = 1.8 Hz), 37.3 (d, $^2J_{PC}$ = 11.3 Hz), 31.3, 23.2 (d, $^3J_{PC}$ = 6.0 Hz), 3.6 (d, $^2J_{PC}$ = 0.4 Hz); ^{31}P{^{1}H} NMR δ 28.2; IR 3051 (w), 2926 (s), 2852 (s), 2724 (w), 2678 (w), 1620 (w), 1574 (w), 1460 (m), 1437 (m), 1377 (m), 1308 (w), 1231 (w), 1198 (w), 1157 (w), 1098 (w), 1070 (w), 1024 (w), 1000 (w), 992 (w), 942 (w), 892 (w), 791 (w), 759 (w), 735 (w), 717 (w), 690 (m). Anal. Calcd for $C_{23}H_{29}ClNPPd$: C, 56.11; H, 5.94; N, 2.84. Found: C, 56.13; H, 5.62; N, 2.78.

(3IP)Pd(CH$_3$)Br (11). Method A: To a stirring solution of **2** (0.478 g, 0.931 mmol) in THF (40 mL) at 0 °C was added slowly via syringe methyllithium complexed with lithium bromide (0.68 mL, 1.0 mmol). The reaction was allowed to warm to ambient temperature over the course of 1 h. Solvent was removed to afford a red-orange powder. The powder was dissolved in dichloromethane and precipitated with diethyl ether (0.278 g, 55.6%). **Method B**: To a stirring solution of **3** (0.560 g, 0.931 mmol) in dichloromethane (40 mL) was added tetramethyltin (0.26 mL, 2.0 mmol) via syringe. The reaction was stirred at ambient temperature for 40 h. Solvent was removed, and the yellow solid was washed with pentane (3 × 30 mL) to remove any leftover tetramethyltin. The solid was dissolved in dichloromethane and precipitated with diethyl ether (0.314 g, 62.8%). **Method C**: Lithium bromide (0.011 g, 0.12 mmol) and **10** (0.020 g, 0.041 mmol) were added to vials in the drybox, followed by the addition of $CDCl_3$ (0.5 mL) to each vial. The contents of the vials were mixed and placed into a NMR tube. Quantitative formation of **11** was observed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy; mp 155−157 °C; ^{1}H NMR δ 7.66 (d, $^4J_{PH}$ = 3.0 Hz, 1H), 7.48−7.50 (m, 2H), 7.39−7.45 (m, 8H), 2.76−2.78 (m, 2H), 2.41−2.43 (m, 2H), 2.01 (pent, $^3J_{HH}$ = 7.8 Hz, 2H), 1.40 (s, 9H), 0.71 (d, $^3J_{PH}$ = 3.0 Hz, 3H); ^{13}C{^{1}H} NMR δ 158.0 (d, $^3J_{PC}$ = 6.3 Hz), 152.2 (d, $^2J_{PC}$ = 14.6 Hz), 136.0 (d, $^1J_{PC}$ = 38.7 Hz), 133.4 (d, $^2J_{PC}$ = 12.0 Hz), 131.3 (d, $^4J_{PC}$ = 2.4 Hz), 129.0 (d, $^3J_{PC}$ = 10.8 Hz), 128.9 (d, $^1J_{PC}$ = 67.5 Hz), 63.6, 38.1 (bs), 37.3 (d, $^2J_{PC}$ = 11.1 Hz), 31.3, 23.1 (d, $^3J_{PC}$ = 6.0 Hz), 2.0 (d, $^2J_{PC}$ = 0.4 Hz); ^{31}P{^{1}H} NMR δ 28.5; IR 3050 (w), 2960 (s), 2923 (s), 2850 (s), 2722 (w), 2676 (w), 2199 (w), 1957 (w), 1884 (w), 1811 (w), 1699 (w), 1582 (w), 1463 (m), 1436 (m), 1380 (m), 1371 (m), 1307 (w), 1257 (w), 1225 (w), 1197 (w), 1161 (m), 1097 (m), 1023 (w), 987 (w), 964 (w), 913 (m), 890 (w), 845 (w), 794 (w), 730 (m), 693 (m), 643 (m). Anal. Calcd for $C_{23}H_{29}BrNPPd$: C, 51.46; H, 5.45; N, 2.61. Found: C, 51.70; H, 5.51; N, 2.29.

(3IP)Pd(CH$_3$)OTf (12). Method A: To a stirring slurry of silver triflate (0.233 g, 0.908 mmol) in dichloromethane (20 mL) was added a solution of **10** (0.406 g, 0.825 mmol) in dichloromethane (20 mL), and the mixture was stirred at ambient temperature for 4 h in the absence of light. Solvent was removed, and the yellow solid was dissolved in dichloromethane and precipitated with pentane (0.378 g, 75.6%). **Method B**: To a stirring slurry of silver triflate (0.233 g, 0.908 mmol) in dichloromethane (20 mL) was added a solution of **11** (0.443 g, 0.825 mmol) in dichloromethane (20 mL), and the mixture was stirred at ambient temperature for 4 h in the absence of light. Solvent was removed, and the yellow solid was dissolved in dichloromethane and precipitated with pentane (0.343 g, 68.6%); mp 153−154 °C; ^{1}H NMR δ 7.75 (d, $^4J_{PH}$ = 2.4 Hz, 1H), 7.51−7.53 (m, 2H), 7.42−7.48 (m, 8H), 2.82−2.84 (m, 2H), 2.39−2.42 (m, 2H), 2.03 (pent, $^3J_{HH}$ = 7.2 Hz, 2H), 1.37 (s, 9H), 0.70 (bs, 3H); ^{13}C{^{1}H} NMR[45] δ 157.2 (d, $^3J_{PC}$ = 5.7 Hz), 152.9 (d, $^2J_{PC}$ = 14.1 Hz), 134.4 (d, $^1J_{PC}$ = 6.3 Hz), 133.2 (d, $^2J_{PC}$ = 12.0 Hz), 131.9 (d, $^4J_{PC}$ = 2.6 Hz), 129.2 (d, $^3J_{PC}$ = 11.7 Hz), 128.0 (d, $^1J_{PC}$ = 57.8 Hz), 64.0, 38.0 (d, $^3J_{PC}$ = 2.6 Hz), 37.7 (d, $^2J_{PC}$ = 12.3 Hz), 30.3, 23.1 (d, $^3J_{PC}$ = 6.2 Hz), 6.6; ^{31}P{^{1}H} NMR δ 30.0; ^{19}F{^{1}H} NMR δ −78.2; IR 3053 (w), 2956 (s), 2920 (s), 2849 (s), 2724 (w), 2687 (w), 2314 (w), 1680 (w), 1622 (w), 1584 (m), 1530 (w), 1463 (s), 1438 (s), 1375 (m), 1337 (w), 1300 (s), 1258 (m), 1233 (s), 1208 (s), 1170 (s), 1103 (m), 1070 (m), 1019 (s), 994 (m), 961 (m), 894 (w), 798 (m), 748 (m), 697 (m), 635 (s). Anal. Calcd for $C_{24}H_{29}F_3NO_3PPdS \cdot 0.3\ CH_2Cl_2$: C, 46.22; H, 4.73; N, 2.22. Found: C, 46.38; H, 4.30; N, 2.60.

Crystallography. Summaries of crystal data and collection parameters for crystal structures of **5**, **6a**, **7**, and **9**−**12** are provided in Table 1. Detailed descriptions of data collection, as well as data solution, are provided below. ORTEP diagrams were generated with the ORTEP-3 software package.[47] For each sample, a suitable crystal was mounted on a pulled glass fiber using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART[48] diffractometer with a CCD area detector, centered in the X-ray beam, and cooled to 140 K using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected using 0.3° ω scans, and the data were integrated by the program SAINT.[49] The final unit cell parameters were determined by a least-squares refinement of the reflections with $I > 10\sigma(I)$. Data analysis using Siemens XPREP[50] and the successful solution and refinement of the structure determined the space group. An empirical absorption correction was applied using SADABS.[51] Equivalent reflections were averaged, and the structures were solved by direct methods using the SHELXTL software package.[52] Unless otherwise noted, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as fixed atoms but not refined.

5: X-ray quality crystals were grown from a layered solution of THF and pentane at ambient temperature. The asymmetric unit contains two independent [(3IP)Pd(allyl)]$^+$ cations. One is fully ordered as the *trans* isomer, while the second has an allyl group with a disordered central carbon atom, giving a 1:1 *cis/trans* ratio. Thus, the overall crystal structure contains a 3:1 *trans:cis* ratio of isomers. Additionally, the 2 equiv of PF_6^- necessary for charge balance are present as one fully occupied PF_6^- (with one disordered fluorine) and two $P_{0.5}F_3$ units located at special positions: 0, 0, *z* and 1/2, 0, *z*. The final cycle of full-matrix least-squares refinement was based on 13 318 observed reflections and 653 variable parameters and converged yielding final residuals: $R = 0.0494$, $R_{all} = 0.0844$, and GOF = 0.867.

6a: X-ray quality crystals were grown from a saturated solution of diethyl ether at −25 °C. The final cycle of full-matrix least-squares refinement was based on 6902 observed reflections and 293 variable parameters and converged, yielding final residuals: $R = 0.0296$, $R_{all} = 0.0436$, and GOF = 0.995.

(47) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(48) *SMART: Area-Detector Software Package*, v5.625; Bruker AXS, Inc.: Madison, WI, 1997−2001.
(49) *SAINT: SAX Area-Detector Integration Program, V6.22*; Bruker AXS, Inc.: Madison, WI, 1997−2001.
(50) *XPREP: Reciprocal Space Exploration Program, V6.12*; Bruker AXS, Inc.: Madison, WI, 2001.
(51) *SADABS: Bruker/Siemens Area Detector Absorption Program, V2.03*; Bruker AXS, Inc.: Madison, WI, 2001.
(52) *SHELXL-97: Structure Solution Program, V6.10*; Bruker AXS, Inc.: Madison, WI, 2000.

7: X-ray quality crystals were grown from a layered solution of THF and pentane at ambient temperature. The asymmetric unit contained 1 equiv of CH_2Cl_2 in addition to dimeric **7**. One ^{t}Bu group was disordered over two rotational positions. The final cycle of full-matrix least-squares refinement was based on 13 270 observed reflections and 623 variable parameters and converged, yielding final residuals: $R = 0.0576$, $R_{all} = 0.0594$, and GOF $= 1.152$.

9: X-ray quality crystals were grown from a layered solution of THF and pentane at ambient temperature. The final cycle of full-matrix least-squares refinement was based on 6933 observed reflections and 370 variable parameters and converged, yielding final residuals: $R = 0.0322$, $R_{all} = 0.0394$, and GOF 1.021.

10: X-ray quality crystals were grown from a saturated solution of diethyl ether at ambient temperature. The final cycle of full-matrix least-squares refinement was based on 5629 observed reflections and 244 variable parameters and converged, yielding final residuals: $R = 0.0306$, $R_{all} = 0.0328$, and GOF $= 1.108$.

11a: X-ray quality crystals were grown from a layered solution of dichloromethane and diethyl ether at ambient temperature. The final cycle of full-matrix least-squares refinement was based on 5838 observed reflections and 244 variable parameters and converged, yielding final residuals: $R = 0.0516$, $R_{all} = 0.0677$, and GOF $=$ 1.067.

11b: X-ray quality crystals were grown from a layered solution of THF and pentane at ambient temperature. The final cycle of full-matrix least-squares refinement was based on 5504 observed reflections and 244 variable parameters and converged, yielding final residuals: $R = 0.0367$, $R_{all} = 0.0464$, and GOF $= 0.960$.

12: X-ray quality crystals were grown from a layered solution of dichloromethane and diethyl ether at ambient temperature. The final cycle of full-matrix least-squares refinement was based on 6343 observed reflections and 307 variable parameters and converged, yielding final residuals: $R = 0.0319$, $R_{all} = 0.0335$, and GOF $=$ 1.091.

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Supporting Information Available: CIF files providing additional crystallographic data, including bond lengths and angles, for compounds **5**, **6a**, **7**, and **9**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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