Palladium(II) 3-Iminophosphine Complexes as Intermolecular Hydroamination Catalysts for the Formation of Imines and Enamines

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Received November 2, 2007

Palladium(II) 3-iminophosphine derivatives were screened as intermolecular hydroamination catalysts, with (3-iminophosphine)(allyl)palladium triflate determined to be the most active for the hydroamination of 1,3-cyclohexadiene and phenylacetylene. The iminophosphine ligands were synthesized by a three-step process and coordinated in an η^2 and η^1 manner to palladium(II) chloride and (allyl)palladium(II) chloride, respectively.

Introduction

The wide use of amines and their derivatives across many fields of chemistry has led to considerable interest concerning the synthesis of C−N bonds. One of the most attractive routes for C−N bond formation is through the hydroamination of unsaturated carbon−carbon double and triple bonds by primary or secondary amines, due in part to its 100% atom efficiency. The formation of C−N bonds via hydroamination can occur through intramolecular or intermolecular processes,[1–4] although the latter are generally preferred due to the large array of commercially available, low-cost substrates. Typically, intermolecular hydroamination is harder to achieve due to the higher entropic demands and slower reaction kinetics, thus requiring a more active and selective catalyst than intramolecular hydroamination. The products generated by intermolecular hydroamination include secondary and tertiary amines, diamines, imines, and enamines. There are several reports of the intermolecular hydroamination of alkenes,[5–9] dienes,[9–15] vinyl arenes,[9,16–20] and alkynes[5,6,21–28] but few examples involving cyclic dienes[29–33] as substrates.

Imines and enamines are very useful compounds because they function as reagents for the introduction of nitrogen-containing moieties into a synthetic sequence. Specifically, imines are commonly employed in carbon−carbon bond formation, as seen in Mannich reactions and aza Diels–Alder cycloadditions.[34] Additionally, they are readily reduced to the corresponding secondary amines.[34] Ketimines are commonly targeted as hydroamination products because alternative synthetic pathways often involve the need for elevated temperatures, an acid catalyst and/or a water scavenger, imposing functional group limitations, and/or a lack of regio- and stereochemical control. Second, enamines are other important synthetic targets due to the subsequent reactivity of their double bonds, often employed as

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10.1021/om701106q CCC: $40.75
Publication on Web 02/27/2008

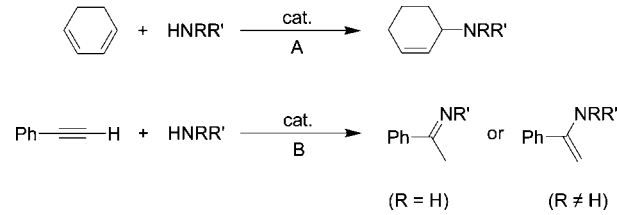
substrates for addition or redox reactions.[35,36] Currently, enamine synthesis involves allylic amination[36] or Buchwald−Hartwig coupling.[37,38] Only a few studies have shown the catalytic addition of amines to cyclic dienes,[29–32] and thus a more thorough investigation of catalysts for this reaction is necessary in order to develop an efficient route to enamines that has substrate tolerance without compromising catalytic activity.

3-Iminophosphine ligands containing an *o*-phenylene backbone have been investigated previously, and their palladium complexes serve as catalysts for the polymerization of ethylene,[39] Stille reactions,[40,41] Heck coupling,[42,43] and other bond-forming reactions.[44–46] The new type of 3-iminophosphine framework employed herein has been constructed around an alicyclic (cyclopentenyl) backbone and contains features similar to those of two prominent ligand classes: β-diketiminates and phosphinooxazolines. β-Diketiminates, when used as ancillary ligands in late-transition-metal catalysis, employ steric bulk to help shield reactive metal centers and provide stability for reactive intermediates.[47] Phosphinooxazolines use an asymmetric and rigid backbone to facilitate several catalytic processes, such as asymmetric allylic substitution,[30] Heck coupling,[34] and hydrogenation.[36,48,49] Phosphinooxazolines help stabilize reactive intermediates and reactive metal centers through a combination of steric protection and strong σ-donation from the phosphorus donor atom. There has been only minimal investigation of the effect of ligand rigidity on hydroamination catalysis using bidentate ligands containing at least one phosphorus donor atom.[31] Our research efforts have focused on a new variety of 3-iminophosphine ligand with an alicyclic (cyclopentenyl) backbone, employing soft phosphorus and hard imine nitrogen donor atoms. It was postulated that these ligands would have many of the favorable characteristics generally associated with β-diketiminate and phosphinooxazoline ligands. Herein, we report the palladium-catalyzed intermolecular hydroamination of the terminal alkyne phenylacetylene, as well as the cyclic diene 1,3-cyclohexadiene, with a variety of amines using ancillary 3-iminophosphine ligands (Scheme 1).

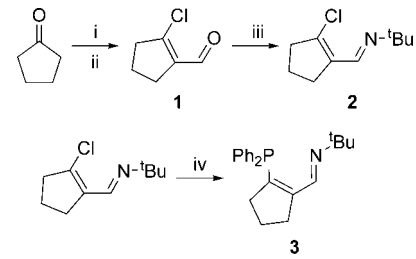
Results and Discussion

The 3-iminophosphine (3IP) ligand (**3**) was synthesized in 52% yield through a three-step synthesis (Scheme 2). First, a Vilsmeier–Haack reagent was combined with cyclopentanone to generate a β-chlorovinyl aldehyde (**1**) after basic workup. Application of a Vilsmeier–Haack reagent results in the conversion of the enol tautomer of ketones to β-chloroaldehydes by formylation of the α-carbon in tandem with chlorination of the hydroxyl group.[50,51] In the ^{1}H NMR spectrum of 2-chlorocyclopentenecarboxaldehyde (**1**), the aldehyde proton appears as a singlet at 10.00 ppm, whereas the protons from the cyclopentenyl ring appear as two sets of overlapping triplets of doublets at 2.81 and 2.58 ppm as well as a pentet at 2.01 ppm. The subsequent Schiff-base condensation of **1** with *tert*-butylamine yields the corresponding imine (**2**). The aldimine proton shifts upfield significantly to 8.24 ppm, while the cyclopentenyl protons show little change, appearing as overlapping triplets of doublets at 2.70 and 2.63 ppm and a pentet at 1.96 ppm. The cyclopentenyl imine, once isolated, is thermally unstable, decomposing in 8 h at 22 °C or 96 h at −25 °C. Synthesis of the 3IP ligand (**3**) is completed when **2** undergoes a Michael addition with either sodium or lithium diphenylphosphide, followed by chloride elimination. The imine proton of **3** is shifted slightly to 8.72 ppm and now exhibits phosphorus−proton coupling: $^4J_{P-H} = 2.0$ Hz (Table 1). The cyclopentenyl ring protons undergo minimal changes and are observed as broad triplets of doublets at 2.83 and 2.36 ppm and a pentet at 1.85 ppm. The ^{31}P NMR spectrum reveals a single resonance at −24.7 ppm. X-ray-quality crystals of **3** were produced by

Scheme 1. Hydroamination of 1,3-Cyclohexadiene (A) and Phenylacetylene (B)



Scheme 2. Synthesis of the 3-Iminophosphine Ligand[a]



[a] Legend: (i) $POCl_3$, DMF, 0 °C, 40 min; (ii) ice, $NaHCO_3$; (iii) H_2N^tBu, Et_2O, 0 °C, 14 h; (iv) Ph_2PM (M = Li, Na), toluene, 0 °C, 14 h.

Table 1. ^{31}P NMR Shifts, ^{1}H Coupling Constants, and ^{13}C Coupling Constants

compd	^{31}P NMR shift (δ)[a]	$^4J_{P-H}$ (Hz)[b]	$^1J_{P-C}$ (Hz)[c]
3IP (**3**)	−24.7	2.0	25.6
(3IP)$PdCl_2$ (**4**)	21.5	3.0	44.1
(3IP)Pd(allyl)Cl (**5**)	7.6	n/a[d]	32.6
[(3IP)Pd(allyl)][OTf] (**6**)	16.9	3.0	34.2

[a] Relative to 5% H_3PO_4 in D_2O. [b] Coupling of phosphorus to aldimine proton. [c] Coupling of phosphorus to adjacent cyclopentyl carbon. [d] Broad singlet observed.

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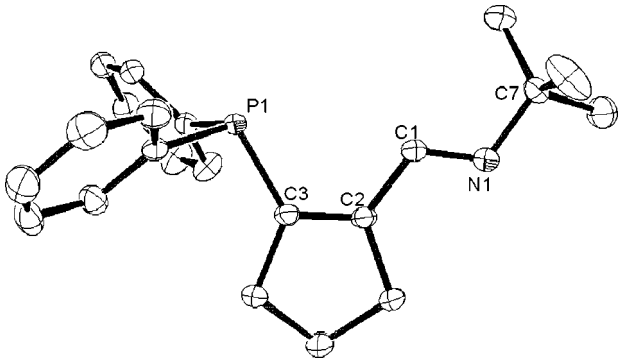
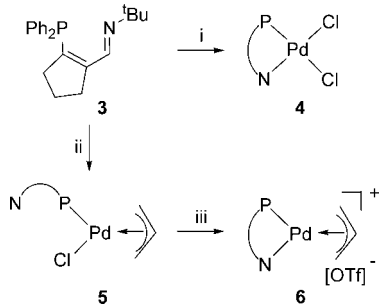


Figure 1. ORTEP diagram (50% thermal ellipsoids) of 3IP (**3**). Hydrogen atoms are omitted for clarity. Bond lengths (in Å): C1−C2 = 1.460(6), C2−C3 = 1.354(8), C3−P1 = 1.817(7). Bond angles (in deg): C1−N1−C7 = 119.5(5), C2−C1−N1 = 120.6(1), C3−C2−C1 = 125.5(3), P1−C3−C2 = 122.7(2).

Scheme 3. Metal Complexation[a]



[a] Legend: (i) $PdCl_2$, MeCN, 14 h; (ii) 0.5 $[(allyl)PdCl]_2$, CH_2Cl_2, 14 h; (iii) AgOTf, Et_2O, 4 h.

layering diethyl ether with pentane at −25 °C, and the crystal structure confirms the connectivity in this species (Figure 1). The carbon−carbon single- and double-bond distances and angles as well as the phosphorus−carbon and imine bond distances and angles are similar to those observed in related compounds.[52,53]

The complex (3IP)$PdCl_2$ (**4**) was synthesized by treating anhydrous $PdCl_2$ with **3** in acetonitrile at ambient temperature and isolated as a yellow solid in 90% yield (Scheme 3). There is a significant shift in the ^{31}P NMR resonance to 21.5 ppm, 46 ppm downfield compared to the free ligand (Table 1). The imine doublet also has a larger coupling constant, $^4J_{P-H} = 3.0$ Hz, in comparison to the value for the free ligand, and shifts to 7.48 ppm, indicative of coordination of the imine nitrogen to the palladium center. X-ray-quality crystals of **4** were grown from methylene chloride layered with diethyl ether at 22 °C, and the resulting crystal structure (Figure 2) shows that palladium adopts a square-planar configuration with a ligand bite angle of 85.7° (P−Pd−N). The related complex (3IP)Pd(allyl)Cl (**5**) was synthesized in a manner similar to that for **4**, except for the use of methylene chloride as solvent, and was isolated as an orange-yellow solid in 74% yield (Scheme 3). Once again, the ^{31}P NMR resonance from compound **5** is significantly shifted upon ligand coordination, appearing at δ 7.6—more than 32 ppm downfield from the free ligand resonance (Table 1). X-ray-quality crystals of **5** were obtained from a saturated solution of diethyl ether at

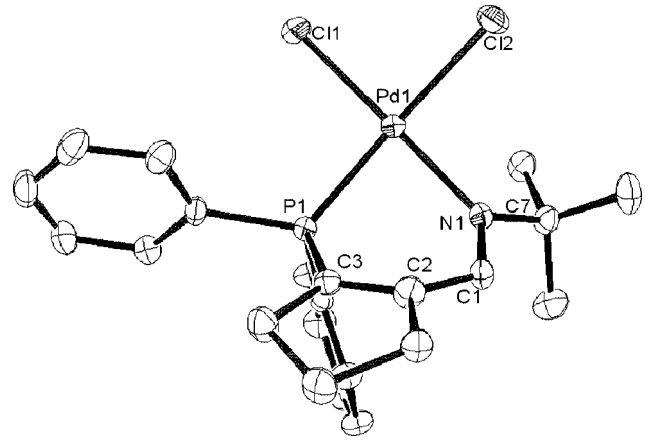


Figure 2. ORTEP diagram (50% thermal ellipsoids) of (3IP)$PdCl_2$ (**4**). Hydrogen atoms and disordered methylene chloride molecules are omitted for clarity. Bond lengths (in Å): Pd1−N1 = 2.065(4), Pd1−P1 = 2.22(1), C1−N1 = 1.285(6), C2−C1 = 1.463(6), C3−C2 = 1.351(6), P1−C3 = 1.804(4). Bond angles (in deg): P1−Pd1−N1 = 85.3(7), P1−Pd1−Cl1 = 93.4(6), P1−Pd1−Cl2 = 166.7(7), Cl1−Pd1−Cl2 = 90.9(7), N1−Pd1−Cl1 = 176.0(7), N1−Pd1−Cl2 = 90.9(9), Pd1−P1−C3 = 100.2(2), C3−C2−C1 = 124.1(9), C2−C1−N1 = 123.6(2), C1−N1−Pd1 = 123.1(2), C1−N1−C7 = 116.6(5).

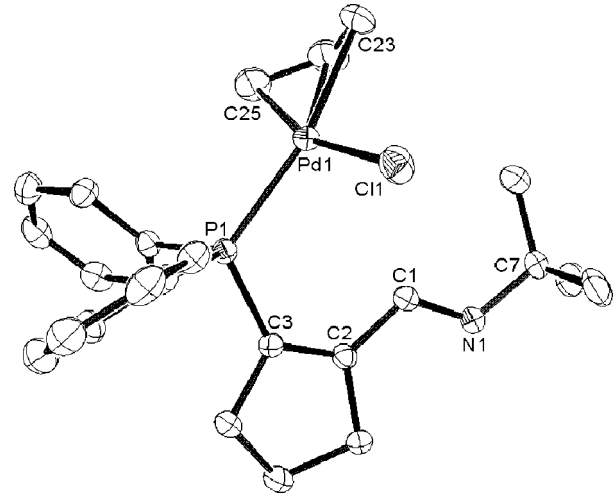


Figure 3. ORTEP diagram (50% thermal ellipsoids) of (3IP)Pd(allyl)Cl (**5**). Hydrogen atoms are omitted for clarity. Bond lengths (in Å): Pd1−Cl1 = 2.378(5), Pd1−P1 = 2.308(8), Pd1−C23 = 2.202(3), Pd1−C25 = 2.101(4), C1−N1 = 1.269(7), C2−C1 = 1.460(4), C3−C2 = 1.346(6), P1−C3 = 1.81(1). Bond angles (in deg): P1−Pd1−Cl1 = 101.7(2), C23−Pd1−C25 = 67.7(3), P1−Pd1−C23 = 163.4(3), P1−Pd1−C25 = 95.9(3), C3−P1−Pd1 = 117.2(7), C3−C2−C1 = 127.5(6), C2−C1−N1 = 119.7(5), C1−N1−C7 = 120.4(4).

−25 °C, and the crystal structure indicates a monodentate coordination of the 3IP ligand through the phosphorus to palladium, as well as the presence of a chloride ligand (Figure 3). Treatment of **5** with silver triflate in diethyl ether results in loss of silver chloride and concomitant formation of the ionic species [(3IP)Pd(allyl)][OTf] (**6**) in 90% yield (Scheme 3). Pronounced shifts in the imine proton resonance to 7.94 ppm and the ^{31}P NMR signal to 16.9 ppm indicate bidentate ligand coordination (Table 1). Layering of a tetrahydrofuran solution of **6** with pentane yielded crystals suitable for X-ray structure determination. The resulting solid-state structure reveals an ionic species, in which square-planar palladium is coordinated by an η^2-3IP and an η^2-allyl ligand with an outer-sphere triflate anion

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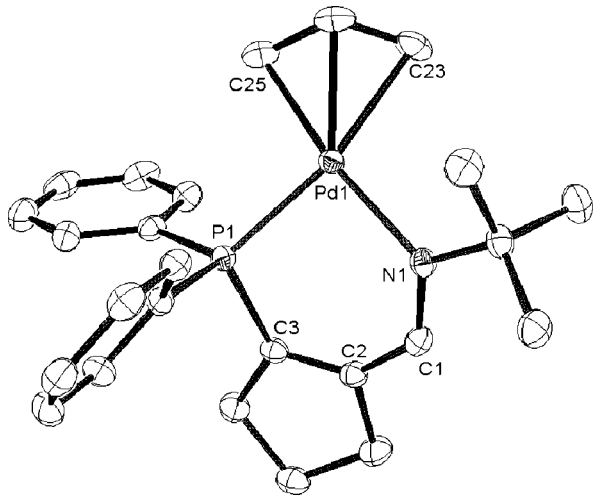


Figure 4. ORTEP diagram (50% thermal ellipsoids) of [(3IP)Pd(allyl)][OTf] (**6**). Triflate anion and hydrogen atoms are omitted for clarity. Bond lengths (in Å): Pd1−P1 = 2.267(5), Pd1−N1 = 2.141(3), Pd1−C23 = 2.238(5), Pd1−C25 = 2.102(4), P1−C3 = 1.81(1), C3−C2 = 1.342(3), C2−C1 = 1.465(4), C1−N1 = 1.284(1). Bond angles (in deg): P1−Pd1−N1 = 92.9(5), C23−Pd1−C25 = 67.0(6), C23−Pd1−N1 = 104.6(7), C25−Pd1−N1 = 171.6(2), C23−Pd1−P1 = 157.7(8), C25−Pd1−P1 = 95.3(4), Pd1−P1−C3 = 105.6(9), P1−C3−C2 = 123.4(2), C3−C2−C1 = 129.8(2), C2−C1−N1 = 127.8(9), C1−N1−Pd1 = 123.5(8).

present (Figure 4). The ligand bite angle in **6** is 92.9° (P−Pd−N), nearly 7° larger than that observed in compound **4**. This can be attributed to a substantial decrease in the steric demands of the other ligands, as the angle between the terminal allylic carbons is 67.0° (C23−Pd−C25) compared to 91.0° in the dichloride complex (Cl1−Pd−Cl2).

Analysis of the NMR spectroscopic data from this series of compounds (**3**–**6**) reveals excellent correlation between the chemical shifts of the imine and phosphorus resonances and the ligand coordination mode (Table 1). Compounds **4** and **6**, with η^2 coordination of the ligand, show substantial shifts in the imine ^{1}H resonance (∼1 ppm) and the ^{31}P resonance (>40 ppm downfield) compared to the related signals in the free ligand (**3**). In contrast, only the phosphorus resonance for **5** is shifted significantly (32 ppm downfield), correlating with the observed η^1 coordination of the phosphorus donor atom in the solid-state structure. Additionally, by comparison of **4** with **6**, it is clear that the allyl group is a better σ-donor ligand than chloride because of the lengthening of both the Pd−P (0.05 Å longer than in **4**) and Pd−N (0.13 Å longer than in **4**) bond distances. This is further evident in **5**, where the Pd−P bond is even longer (0.09 Å longer than in **4** and 0.04 Å longer than in **6**), due to both the trans effect of the allyl group and the lack of coordinative constraints imposed by chelation.

Compounds **3**–**6** were screened for activity as hydroamination catalysts using the following procedure. A solution of 3.6 mmol of 1,3-cyclohexadiene, 0.60 mmol of the selected amine, and 1.0 mL of methylene chloride was added to a reaction vial equipped with a magnetic stir bar that had been preloaded with 0.030 mmol of the catalyst under nitrogen. After the mixture was heated to 50 °C for 22 h, 100 μL of dodecane was added to the reaction vial as an internal standard and product distribution was determined via gas chromatography. ^{1}H and ^{13}C NMR spectra were obtained after column chromatography. The hydroamination of 1,3-cyclohexadiene with primary and secondary amines using catalysts **3**–**6** (Scheme 1A) is summarized in Table 2. Entries 1–4 show that compounds **3**–**5** display almost no catalytic activity, while compound **6** does catalyze the hydroamination. Entries 4–6 show that compound **6** readily converts morpholine and piperidine into the corresponding 1,4-hydroamination products, while the activity is much lower for benzylamine. The relative activities are less than those observed previously using related diphosphine complexes.[30,31] However, it should be noted that a catalytic amount of triflic acid was used in the previously reported cases, while we have not investigated its effect on our catalysts. Extending the reaction time to 72 h results in significant increases in conversion to product, although it does not result in successful hydroamination using other amines such as aniline, cyclohexylamine, and diethylamine.

Table 2. Hydroamination of 1,3-Cyclohexadiene using 3–6[a]

entry	amine	catalyst	yield (%)[b]
1	morpholine	3IP (**3**)	0
2	morpholine	(3IP)$PdCl_2$ (**4**)	0
3	morpholine	(3IP)Pd(allyl)Cl (**5**)	4
4	morpholine	[(3IP)Pd(allyl)][OTf] (**6**)	52
5	piperidine	[(3IP)Pd(allyl)][OTf] (**6**)	31
6	benzylamine	[(3IP)Pd(allyl)][OTf] (**6**)	9

[a] Reaction conditions: 3.6 mmol of 1,3-cyclohexadiene, 0.60 mmol of amine, 0.030 mmol of catalyst, 50 °C, CH_2Cl_2, 22 h. [b] Determined by average of two GC runs.

Table 3. Effect of 1,3-Cyclohexadiene to Morpholine Ratio and Solvent Effects[a]

entry	diene:amine	solvent	yield (%)[b]
1	1:1	CH_2Cl_2	25
2	2:1	CH_2Cl_2	35
3	4:1	CH_2Cl_2	41
4	6:1	CH_2Cl_2	52
5	8:1	CH_2Cl_2	58
6	10:1	CH_2Cl_2	62
7	4:1	THF	2
8	4:1	dioxane	2
9	4:1	toluene	1
10	4:1	chloroform	30

[a] Reaction conditions: 0.030 mmol of **6** (5 mol %), 50 °C, 22 h. [b] Determined by average of two GC runs.

The effects of the 1,3-cyclohexadiene to morpholine ratio and the reaction solvent on catalytic hydroamination using compound **6** are represented in Table 3. Entries 1–6 demonstrate a direct correspondence between the ratio of diene to amine and the percent conversion with the catalytic rate increasing as a result of higher substrate (diene) concentration. We have observed that a byproduct of this catalysis is benzene, the dehydrogenation product of 1,3-cyclohexadiene. To the best of our knowledge, we are the first to report this phenomenon in the hydroamination of 1,3-cyclohexadiene. Entries 7–10 show the effect of different solvents on this catalysis. The Lewis bases tetrahydrofuran and dioxane most likely function as competitive inhibitors, due to their ability to coordinate to the palladium center, leading to substantially less conversion to the product. The very low solubility of compound **6** leads to its virtual inactivity in toluene. The use of chloroform provides moderate conversion to the 1,4-hydroamination product at 50 °C, although with somewhat slower rates than those observed in methylene chloride. Increasing the reaction temperature when using chloroform, tetrahydrofuran, or dioxane as solvent improves product yields, but with lower conversion when compared to that observed in methylene chloride at 50 °C.

The effects of the amount of solvent used for the hydroamination of 1,3-cyclohexadiene with morpholine are illustrated in terms of amine concentration in Figure 5. The data clearly indicate that increasing the molar concentration increases the

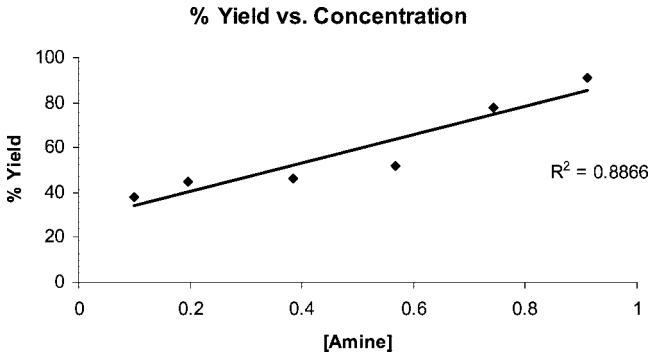
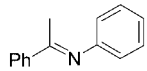
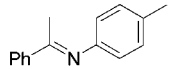
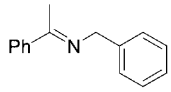
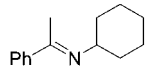
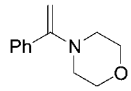
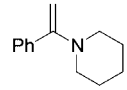


Figure 5. Effect of concentration on the hydroamination of 1,3-cyclohexadiene with morpholine in the presence of **6**. Reaction conditions: 6:1:0.05 ratio of 1,3-cyclohexadiene to morpholine to **6**. The percent yield was determined by the average of two GC runs.

Table 4. Hydroamination of Phenylacetylene[a]

Entry	Amine	pK_b[b]	Product	Yield[c]
1	aniline	9.37		75%
2	*p*- toluidine	8.92		67%
3	benzylamine	4.67		12%
4	cyclohexylamine	3.34		6%
5	morpholine	5.67		62%
6	piperidine	2.88		38%

[a] Reaction conditions: 6.0 mmol of phenylacetylene, 0.60 mmol of amine, 0.030 mmol of **6**, 70 °C, THF, 22 h. [b] Reference 55. [c] Determined by average of two GC runs.

overall conversion. At these higher substrate concentrations, our catalytic hydroamination of 1,3-cyclohexadiene with morpholine is quite comparable to that in previous reports, although our system does not require the necessity of an acid cocatalyst.[29–31]

The hydroamination of phenylacetylene, to form enamines and imines, is also an important transformation (Scheme 1B). As such, we have employed our catalyst system for the hydroamination of phenylacetylene employing a number of amines (Table 4). This reaction proved to be quite versatile, with successful catalysis using both primary and secondary amines. The primary amines (entries 1–4) tautomerize to the Markovnikov imine, while the secondary amines (entries 5 and 6) yield the Markovnikov enamine. The observed catalytic activity is similar to other catalysts.[52,54] A large excess of phenylacetylene (10 equiv) was necessary for the catalysis due to the competing cyclotrimerization of phenylacetylene to form 1,2,4- and 1,3,5-triphenylbenzene. Finally, within each group (primary/secondary amines), the hydroamination using catalyst **6** is fastest with the amines having the highest pK_b values (lowest basicity).[55]

Conclusions

3-Iminophosphine ligands (**3**) and their palladium(II) chloride (**4**), (allyl)palladium(II) chloride (**5**), and (allyl)palladium(II) triflate (**6**) complexes have been successfully synthesized, isolated, and characterized. The triflate complex (**6**) shows moderate catalytic activity for the intermolecular hydroamination of 1,3-cyclohexadiene and phenylacetylene. Currently, we are investigating additional substrates, including internal alkynes, dienes, alkenes, and amine−alkene tethered compounds. Also, we are in the process of synthesizing alternative palladium(II) complexes that do not contain an allyl functionality, as well as the related palladium(0) derivatives. Finally, we are exploring the electronic effects of the 3-iminophosphine ligand on the rate and product distribution of hydroamination.

Experimental Section

General Considerations. Compounds **1** and **2** were synthesized under the ambient atmosphere. All other reactions were performed with standard Schlenk and drybox techniques. *n*-Butyllithium (1.6 M in hexanes), palladium(II) chloride, (allyl)palladium(II) chloride dimer, diphenylchlorophosphine, and silver triflate were purchased from Strem and used without further purification. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and vacuum-transferred from CaH_2. Pentane, toluene, tetrahydrofuran, and methylene chloride were purified by passage through a column of activated 4 Å molecular sieves and degassed with nitrogen prior to use. Diethyl ether was purified by passage through a column of activated alumina and degassed with nitrogen prior to use. Acetonitrile was purified by vacuum transfer from CaH_2. 1,4-Dioxane was refluxed over sodium and distilled under nitrogen. Cyclopentanone, $POCl_3$, *tert*-butylamine, sodium, phenylacetylene, 1,3-cyclohexadiene, aniline, piperidine, benzylamine, morpholine, cyclohexylamine, and *p*-toluidine were purchased from Acros. All amines used for hydroamination were dried by vacuum transfer or distillation from CaH_2, unless otherwise noted. Morpholine was purified by distillation from sodium. 1,3-Cyclohexadiene was vacuum-transferred from $NaBH_4$. Phenylacetylene was purified by passage through a column of alumina and further vacuum-transferred from CaH_2. ^1H NMR data was obtained on a 600 MHz Inova NMR spectrometer at ambient temperature. ^{13}C, ^{31}P, and ^{19}F NMR data were obtained on a 400 MHz Varian NMR spectrometer at ambient temperature at 100.580, 161.910, and 376.288 MHz, respectively. ^1H 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 spectra 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 Mel-Temp apparatus in sealed capillary tubes and are uncorrected. Gas chromatography was performed on a Varian CP-3800 gas chromatograph equipped with an FID detector. Elemental analyses were determined by Desert Analytics, Tucson, AZ. X-ray structure determinations were performed at the Ohio Crystallographic Consortium housed at The University of Toledo. Sodium diphenylphosphide was prepared

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(55) *CRC Handbook of Chemistry and Physics*; CRC Press: Ann Arbor, MI, 1991.

according to the literature procedure.[56] Diphenylphosphine was prepared according to a literature procedure for diisopropylphosphine.[57]

2-Chlorocyclopentenecarboxaldehyde (1). The procedure used was a slight modification of that reported by Benson and Pohland.[50] $POCl_3$ (18.315 g, 119.30 mmol) was added to a flask containing dimethylformamide (10.896 g, 149.10 mmol) in an ice bath and the mixture stirred for 7 min. The ice bath was replaced with an ambient-temperature water bath and stirred for an additional 8 min. The mixture was cooled to 0 °C, and cyclopentanone (6.249 g, 74.54 mmol) was added and stirred for 15 min. The ice bath was replaced with an ambient-temperature water bath and the mixture stirred for an additional 15 min. The yellowish red solution was poured into an Erlenmeyer flask containing ice (150 g). The solution was made basic using sodium bicarbonate. After extraction with diethyl ether (3 × 100 mL), the combined organic extracts were washed with 100 mL of saturated sodium bicarbonate solution, 100 mL of brine, and 100 mL of water. The organic layer was dried over magnesium sulfate for 5 min and filtered, and the solvent was evaporated, yielding a yellow liquid (7.397 g, 76.00%): bp 61 °C (12 mm); ^{1}H NMR (600 MHz) δ 10.00 (s, 1H), 2.82 (td, $^3J_{H-H}$ = 7.8 Hz, $^2J_{H-H}$ = 2.0 Hz, 1H), 2.81 (td, $^3J_{H-H}$ = 7.8 Hz, $^2J_{H-H}$ = 2.4 Hz, 1H), 2.59 (td, $^3J_{H-H}$ = 7.8 Hz, $^2J_{H-H}$ = 2.4 Hz, 1H), 2.58 (td, $^3J_{H-H}$ = 7.8 Hz, $^2J_{H-H}$ = 2.0 Hz, 1H), 2.01 (pent, 7.8 Hz, 2H); ^{13}C{^{1}H} NMR δ 187.8, 151.3, 137.3, 40.2, 28.6, 20.4; IR 2947 (s), 2719 (m), 1742 (m), 1674 (s), 1618 (s), 1430 (m), 1384 (m), 1332 (s), 1280 (w), 1244 (m), 1202 (w), 1093 (s), 943 (m) cm^{-1}.

2-Chlorocyclopentene-1-(*tert*-butyl)imine (2). 1 (7.397 g, 56.61 mmol) was dissolved in diethyl ether (20 mL) and cooled to 0 °C for 5 min. *tert*-Butylamine (4.558 g, 62.32 mmol) diluted with diethyl ether (10 mL) was added, and the mixture was stirred for 14 h and gradually warmed to room temperature. Magnesium sulfate was added to the round-bottom flask, the mixture filtered, and the solvent evaporated, yielding an orange-red liquid (10.247 g, 97.48%) that shows evidence of decomposition at room temperature after 8 h and at −25 °C after 96 h: bp 102–105 °C; ^{1}H NMR (600 MHz) δ 8.24 (s, 1H), 2.70 (td, $^3J_{H-H}$ = 7.8 Hz, $^2J_{H-H}$ = 2.4 Hz, 1H), 2.70 (td, $^3J_{H-H}$ = 7.8 Hz, $^2J_{H-H}$ = 2.0 Hz, 1H), 2.64 (td, $^3J_{H-H}$ = 7.8 Hz, $^2J_{H-H}$ = 2.4 Hz, 1H), 2.63 (td, $^3J_{H-H}$ = 7.8 Hz, $^2J_{H-H}$ = 2.0 Hz, 1H), 1.96 (pent, 7.8 Hz, 2H), 1.22 (s, 9H); ^{13}C{^{1}H} NMR δ 150.3, 137.8, 135.9, 57.6 39.3, 30.5, 29.7, 20.6; IR 2968 (s), 1628 (s), 1472 (w), 1363 (m), 1254 (w), 1213 (m), 1099 (m), 1026 (w), 948 (m) cm^{-1}.

Lithium Diphenylphosphide. A flask charged with diphenylphosphine (18.6 g, 17.4 mL, 0.100 mol) and pentane (300 mL) under nitrogen was cooled to 0 °C for 15 min. n-Butyllithium (1.6 M in hexanes, 75.0 mL, 0.12 mol) was added dropwise via an addition funnel. The addition funnel was rinsed with an additional 40 mL of pentane. The reaction was stirred overnight, gradually warming to ambient temperature, and then placed into a refrigerator overnight to maximize precipitation. The supernatant solution was filtered off, leaving behind a yellow semicrystalline solid (16.907 g, 88%) which was used without further characterization.

2-Diphenylphosphinocyclopentene-1-(*tert*-butyl)imine (3). Method A. Freshly prepared **2** (1.829 g, 9.852 mmol) was diluted with 10 mL of toluene and cooled to 0 °C. The solution was added to a slurry of lithium diphenylphosphide (1.893 g, 9.852 mmol) in 10 mL of toluene at 0 °C. The reaction was stirred at 0 °C for 1 h and at room temperature for 2 h. Volatiles were removed in vacuo. The resulting orange-yellow residue was triturated with pentane twice (5 mL each), and extraction with diethyl ether (100 mL) yielded an orange-red solution. The solution was concentrated under vacuum and cooled to −25 °C, resulting in the formation of yellow-orange crystals in two crops (2.313 g combined, 70.00%).

Method B. Freshly prepared **2** (1.829 g, 9.852 mmol) diluted with 10 mL of tetrahydrofuran was cooled in an ice bath and added to a previously prepared slurry of sodium diphenylphosphide (2.666 g, 12.81 mmol), 20 mL of tetrahydrofuran, and 90 mL of 1,4-dioxane. The reaction was stirred at room temperature for 3 h. A workup identical with that in method A resulted in the formation of yellow-orange crystals in two crops (2.034 g combined, 61.55%): mp 105–107 °C; ^{1}H NMR δ 8.72 (d, $^4J_{P-H}$ = 2.0 Hz, 1H), 7.40–7.31 (m, 10H), 2.83 (m, 2H), 2.36 (m, 2H), 1.85 (pent, $^3J_{H-H}$ = 7.6 Hz, 2H), 1.19 (s, 9H); ^{13}C{^{1}H} NMR δ 152.8 (d, 20.2 Hz), 136.8 (d, 8.6 Hz), 134.6 (d, 25.6 Hz), 133.4 (d, 19.0 Hz), 129.1 (d, 37.2 Hz), 128.7 (d, 3.7 Hz), 128.6, 57.8, 37.5 (d, 3.7 Hz), 34.4 (d, 5.7 Hz), 30.0, 22.8 (d, 2.1 Hz); ^{31}P{^{1}H} NMR δ −24.7; IR 2719 (w), 2667 (w), 1887 (w), 1825 (w), 1773 (w), 1731 (w), 1700 (m), 1654 (m), 1618 (s), 1576 (m), 1560 (s), 1540 (m), 1431 (s), 1358 (s), 1306 (w), 1275 (w), 1208 (m), 1083 (m), 1026 (w), 995 (w), 964 (w), 891 (m), 824 (m), 787 (m), 746 (s), 694 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{26}NP$: C, 78.78; H, 7.81; N, 4.19. Found: C, 78.83; H, 7.95; N, 4.12.

(2-Diphenylphosphinocyclopentene-1-(*tert*-butyl)imine)palladium(II) Dichloride (4). 3 (3.271 g, 9.752 mmol) was dissolved in 5 mL of methylene chloride and 30 mL of acetonitrile and added to a slurry of palladium(II) chloride (1.729 g, 9.752 mmol) in 30 mL of acetonitrile. The mixture was stirred for 12 h at room temperature. Volatile materials were removed in vacuo. The yellow-red solid was triturated twice with 5 mL of pentane, washed with diethyl ether (3 × 10 mL), and extracted into methylene chloride (3 × 20 mL). The solution was concentrated to 40 mL, and pentane (40 mL) was added to precipitate the product. This process was repeated two times to maximize yield (4.512 g, 90.23%): mp 190 °C dec; ^{1}H NMR (600 MHz) δ 7.58–7.53 (m, 6H), 7.48 (d, $^4J_{P-H}$ = 3.0 Hz, 1H), 7.47–7.45 (m, 4H), 2.92–2.89 (m, 2H), 2.48–2.42 (m, 2H), 2.14 (pent, $^3J_{H-H}$ = 7.8 Hz, 2H), 1.45 (s, 9H); ^{13}C{^{1}H} NMR δ 159.9, 156.0 (d, 16.1 Hz), 135.6 (d, 44.1 Hz), 133.4 (d, 11.2 Hz), 132.2 (d, 5.8 Hz), 128.9 (d, 12.0 Hz), 125.0 (d, 57.8 Hz), 67.2, 36.5 (d, 2.0 Hz), 36.3 (d, 11.6 Hz), 31.8, 23.1 (d, 7.1 Hz); ^{31}P{^{1}H} NMR δ 21.5; IR 2252 (w), 1872 (w), 1830 (w), 1794 (w), 1773 (w), 1737 (w), 1700 (m), 1680 (w), 1649 (m), 1618 (w), 1576 (w), 1560 (m), 1534 (w), 1493 (w), 1436 (s), 1389 (m), 1316 (w), 1187 (m), 1166 (m), 1099 (s), 1052 (m), 995 (w), 876 (m), 756 (m), 699 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{26}Cl_2NPPd \cdot 2CH_2Cl_2$: C, 42.23; H, 4.43; N, 2.05. Found: C, 41.69; H, 4.22; N, 2.00.

(2-Diphenylphosphinocyclopentene-1-(*tert*-butyl)imine)(allyl)palladium(II) Chloride (5). 3 (647 mg, 1.93 mmol) was dissolved in 10 mL of methylene chloride and the mixture added to $[(allyl)PdCl]_2$ (372 mg, 0.965 mmol) in 10 mL of methylene chloride. The reaction mixture was stirred for 14 h. Volatile materials were removed in vacuo, and the residual solid was triturated with 5 mL of pentane twice. The yellow-orange solid was dissolved in 20 mL of diethyl ether and cooled to −25 °C overnight to yield yellow crystals (737 mg, 73.7%): mp 134 °C dec; ^{1}H NMR δ 8.66 (br s, 1H), 7.73–7.69 (m, 4H), 7.44–7.39 (m, 6H), 5.56 (pent, $^3J_{H-H}$ = 4.2 Hz, 1H), 4.71 (m, 1H), 3.69 (m, 1H), 2.99 (m, 2H), 2.95–2.92 (br t, $^3J_{H-H}$ = 7.8 Hz, 2H), 2.43–2.40 (m, 2H), 1.89 (pent, $^3J_{H-H}$ = 7.8 Hz, 2H), 1.05 (s, 9H); ^{13}C{^{1}H} NMR δ 153.5 (d, 2.3 Hz), 152.5 (d, 10.7 Hz), 137.8 (d, 32.6 Hz), 134.0 (d, 12.8 Hz), 132.0 (d, 10.7 Hz), 130.6, 128.8 (d, 2.6 Hz), 118.1 (d, 1.2 Hz), 79.5 (d, 1.0 Hz), 61.2, 58.1, 39.6 (d, 1.2 Hz), 35.1 (d, 2.5 Hz), 29.9, 22.6 (d, 1.8 Hz); ^{31}P{^{1}H} NMR δ 7.6; IR 1773 (w), 1747 (w), 1726 (w), 1700 (m), 1680 (w), 1648 (m), 1617 (w), 1576 (w), 1555 (m), 1539 (m), 1519 (w), 1488 (s), 1337 (w), 1306 (w), 1259 (w), 1207 (w), 1181 (w), 1156 (w), 1099 (s), 1041 (s), 969 (w), 860 (m), 829 (m), 767 (w), 741 (m), 694 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{31}ClNPPd$: C, 57.93; H, 6.03; N, 2.70. Found: C, 57.88; H, 6.30, N, 2.72.

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Table 5. Crystal Data and Collection Parameters

	3	4	5	6
formula	$C_{22}H_{26}NP$	$C_{22}H_{26}Cl_2NPPd \cdot 1.5CH_2Cl_2$	$C_{25}H_{31}ClNPPd$	$C_{26}H_{31}F_3NO_3PPdS$
fw	335.41	640.15	518.35	631.99
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
temp (K)	140	140	140	140
a (Å)	9.672(2)	12.669(1)	9.9685(6)	11.2833(5)
b (Å)	10.398(2)	15.035(1)	13.7786(9)	8.8106(4)
c (Å)	10.748(2)	14.120(1)	17.649(1)	26.981(1)
α (deg)	114.074(3)	90.000	90.000	90.000
β (deg)	91.190(3)	94.963(2)	97.424(1)	99.783(1)
γ (deg)	102.036(3)	90.000	90.000	90.000
V (Å^3)	958.5(3)	2679.5(5)	2403.9(3)	2643.3(2)
Z	2	4	4	4
calcd density (g/cm^3)	1.162	1.271	1.432	1.588
diffractometer	Siemens SMART			
radiation	Mo Kα (λ = 0.710 69 Å)			
monochromator	graphite			
detector	CCD area detector			
scan type, width	ω, 0.3°			
scan speed (s/frame)	10.0	20.0	10.0	20.0
no. of rflns measd	hemisphere	hemisphere	hemisphere	hemisphere
2θ range (deg)	4.6–56.7	4.5–57.1	4.6–56.6	4.9–56.3
cryst dimens (mm)	0.80 × 0.15 × 0.10	0.30 × 0.24 × 0.06	0.40 × 0.40 × 0.24	0.30 × 0.08 × 0.06
no. of rflns measd	6057	30 524	25 085	29 066
no. of unique rflns	3022	6817	5981	6557
no. of observns	3022	6817	5981	6557
no. of params	217	301	262	325
R, R_w, R_{all}	0.0431, 0.1181, 0.0504	0.0434, 0.1196, 0.0539	0.0269, 0.0682, 0.0311	0.0286, 0.0670, 0.0348
GOF	1.036	0.836	1.062	1.043

(2-Diphenylphosphinocyclopentene-1-(*tert*-butyl)imine)(allyl)palladium(II) Triflate (6). 5 (669 mg, 1.27 mmol) was dissolved in 10 mL of methylene chloride and added to a slurry of silver triflate (325 mg, 1.27 mmol) in 10 mL of methylene chloride and the mixture stirred in the absence of light for 2 h. Solvent was removed in vacuo, and the grayish red solid was triturated with 5 mL of pentane twice. The residue was extracted with tetrahydrofuran (3 × 15 mL), leaving behind a gray solid after filtration. Solvent was removed in vacuo, and the product was triturated with 5 mL of pentane twice to yield an orange-red solid (720 mg, 89.7%): mp 155 °C dec; ^{1}H NMR δ 7.94 (d, $^4J_{P-H}$ = 3.0 Hz, 1H), 7.53–7.50 (m, 6H), 7.42–7.37 (m, 4H), 5.76–5.69 (m, 1H), 5.00 (t, $^3J_{H-H}$ = 6.6 Hz, 1H), 3.99 (dd, $^3J_{P-H}$ = 14.4 Hz, $^3J_{H-H}$ = 9.6 Hz, 1H), 3.25 (d, $^3J_{H-H}$ = 4.8 Hz, 1H), 2.98 (dm, $^3J_{P-H}$ = 37.2 Hz, 2H), 2.63 (dm, $^3J_{P-H}$ = 12.0 Hz, 2H), 2.49–2.46 (m, 1H), 2.08–2.04 (m, 2H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR[58] δ 159.7 (d, 7.9 Hz), 154.9 (d, 17.3 Hz), 134.3 (d, 34.2 Hz), 133.0 (d, 13.6 Hz), 131.8 (d, 61.5 Hz), 129.6 (d, 17.3 Hz), 129.5, 120.4 (d, 6.6 Hz), 83.7 (d, 30.5 Hz), 64.3, 55.8 (d, 4.1 Hz), 38.0 (d, 11.6 Hz), 36.6, 29.7, 22.5 (d, 6.2 Hz); ^{31}P{^{1}H} NMR δ 16.9; ^{19}F{^{1}H} NMR δ −78.5; IR 1794 (w), 1768 (w), 1737 (w), 1716 (w), 1700 (w), 1685 (m), 1654 (m), 1618 (w), 1576 (w), 1560 (m), 1540 (m), 1519 (w), 1493 (m), 1265 (s), 1218 (m), 1187 (w), 1150 (s), 1099 (m), 1031 (s), 876 (w), 824 (w), 803 (w), 751 (w), 704 (w), 637 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{31}F_3NO_3PPdS$: C, 49.41; H, 4.94; N, 2.22. Found: C, 49.56; H, 4.99; N, 2.29.

General Procedure for Hydroamination of Cyclohexadiene. 1,3-Cyclohexadiene (3.6 mmol), amine (0.60 mmol), and 1.0 mL of methylene chloride were added to **6** (0.030 mmol) in a Teflon-capped 4 mL scintillation vial in a drybox. After the mixture was heated to 50 °C for 22 h, 100 μL of dodecane was added to the reaction vial as an internal standard and the product yield was determined via gas chromatography. Hydroamination products were readily isolated by column chromatography (silica gel) and removal of solvent via rotary evaporation. ^{1}H and ^{13}C NMR were obtained and compared to literature values.[30]

General Procedure for Hydroamination of Phenylacetylene. Phenylacetylene (6.0 mmol), amine (0.60 mmol), and 1.0 mL of tetrahydrofuran were added to **6** (0.030 mmol) in a Teflon-capped 4 mL scintillation vial in a drybox. After the mixture was heated to 70 °C for 22 h, 100 μL of dodecane was added to the reaction vial as an internal standard and product yield was determined via gas chromatography. Hydroamination products were readily isolated by column chromatography (silica gel) and removal of solvent via rotary evaporation. ^{1}H and ^{13}C NMR were obtained and compared to literature values.[59–61] Gas chromatography standards (entries 1–4, Table 4) were synthesized by a general procedure outlined by Bäckvall.[62]

Crystallography. A summary of crystal data and collection parameters for the crystal structures of **3–6** is provided in Table 5. Detailed descriptions of the data collection, as well as data solution, are provided below. ORTEP diagrams were generated with the ORTEP-3[63] software package. 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[64] 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.[65] 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[66] and the successful solution and refinement of the structure determined the space group. Empirical absorption corrections were applied using the program

(58) The CF_3 carbon of the triflate anion was not detected.

(59) Verkade, J. G.; Reddy, C.; Reddy, V.; Urgaonkar, S. *Org. Lett.* **2005**, *7*, 4427–4430.
(60) Lin, M.; Watson, W. H.; Kashyap, R. P.; le Noble, W. J. *J. Org. Chem.* **1990**, *55*, 3597–3602.
(61) Knettle, B. W.; Flowers, R. A. I. *Org. Lett.* **2001**, *3*, 2321–2324.
(62) Samec, J. S. M.; Backvall, J. E. *Chem. Eur. J.* **2002**, *8*, 2955–2961.
(63) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
(64) SMART: Area-Detector Software Package, v5.625; Bruker AXS, Inc., Madison, WI, 1997–2001.
(65) SAINT: SAX Area-Detector Integration Program, v6.22; Bruker AXS, Inc., Madison, WI, 1997–2001.
(66) XPREP: Reciprocal Space Exploration Program, v6.12; Bruker AXS, Inc., Madison, WI, 2001.

SADABS.[67] Equivalent reflections were averaged, and the structure was solved by direct methods using the SHELXTL[68] software package. Unless otherwise noted, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as fixed atoms but not refined.

Compound 3. X-ray-quality crystals were grown from a layered solution of diethyl ether and pentane which was cooled to −25 °C. The final cycle of full-matrix least-squares refinement was based on 3022 observed reflections and 217 variable parameters and converged yielding final residuals: $R = 0.0431$, $R_{all} = 0.0504$, and GOF = 1.036.

Compound 4. X-ray-quality crystals were grown from a layered solution of methylene chloride and diethyl ether at room temperature. One and a half molecules of disordered methylene chloride existed in the asymmetric unit and were refined isotropically. Hydrogen atoms were included for all ordered atoms. The final cycle of full-matrix least-squares refinement was based on 6817 observed reflections and 301 variable parameters and converged yielding final residuals: $R = 0.0434$, $R_{all} = 0.0539$, and GOF = 0.836.

(67) SADABS: Bruker/Siemens Area Detector Absorption Program, v2.03; Bruker AXS, Inc.:, Madison, WI, 2001.

(68) SHELXTL-97: Structure Solution Program, v6.10; Bruker AXS, Inc., Madison, WI, 2000.

Compound 5. 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 5981 observed reflections and 262 variable parameters and converged yielding final residuals: $R = 0.0269$, $R_{all} = 0.0311$, and GOF = 1.062.

Compound 6. X-ray-quality crystals were grown from a layered solution of tetrahydrofuran and pentane at ambient temperature. The final cycle of full-matrix least-squares refinement was based on 6557 observed reflections and 325 variable parameters and converged yielding final residuals: $R = 0.0286$, $R_{all} = 0.0348$, and GOF = 1.043.

Acknowledgment. We gratefully acknowledge the University of Toledo for generous start-up funding, as well as a University of Toledo Summer Research Fellowship (J.A.R.S.). Additionally, we thank Dr. Kristin Kirschbaum for X-ray crystallographic assistance.

Supporting Information Available: CIF files providing additional crystallographic data, including bond lengths and angles, for compounds **3**–**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701106Q