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Development of catalysts for the hydroamination of olefins*

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Abstract: Studies on the development of palladium, nickel, and rhodium catalysts for the hydroamination of dienes and vinylarenes are described. Enantioselective catalysts based on palladium have been developed for the addition of arylamines to dienes and for Markovnikov addition of arylamines to vinylarenes. In addition, nickel catalysts for the addition of aliphatic amines to dienes have been developed and rhodium catalysts for the first transition metal-catalyzed aminations of vinylarenes that generate terminal amines as the major product are described. Mechanistic data on the hydroamination of vinylarenes with palladium and rhodium is also provided.

INTRODUCTION

My group has been developing metal-catalyzed versions of fundamental organic transformations. For a number of years, much of our effort has been focused on metal-catalyzed aromatic substitution reactions that form carbon–nitrogen bonds in aromatic amines [1–3]. This paper will present recent developments on a new topic in my laboratory: the formation of carbon–nitrogen bonds in allylic, β-phenethyl, and α-phenethyl amines by hydroamination of dienes and vinylarenes. The hydroamination chemistry raises new mechanistic questions, creates issues of stereocontrol, and reveals the need to develop new elementary organometallic reactions.

A brief survey of the contributions of several groups to hydroamination processes is presented in Chart 1. The group of Tobin Marks has developed some highly active catalysts for intramolecular cyclizations [4–8], but intermolecular reactions have been slow [9]. Livinghouse [10] and Eisen [11] have also reported olefin amination with lanthanide and actinide complexes. One might prefer a late metal catalyst for these reactions because of the greater functional group tolerance of these metal complexes. In 1971, Coulson at Dupont [12] showed that rhodium trichloride catalyzed the addition of secondary amines to ethylene. Thus, the origins of homogeneous hydroamination chemistry can be traced to late metals. However, Coulson's report included reactions with only ethylene. Several hydroaminations of activated olefins have been reported. Casalnuovo at Dupont reported the addition of aniline to norbornene about 15 years after the Coulson paper [13], and Antonio Togni [14] reported about a decade after the Casalnuovo paper that fluoride accelerated the rate of these reactions and that the reactions could be conducted enantioselectively. Beller has reported the hydroamination of vinyl pyridine with morpholine [15], but the related reaction with styrene forms predominantly enamines from oxidative amination [16]. Finally, Bergman has reported the hydroamination of allenes to form imines, but simple olefins do not yet react [17,18]. Thus, progress on hydroamination is needed from the standpoint of activity as well as stereoselectivity.

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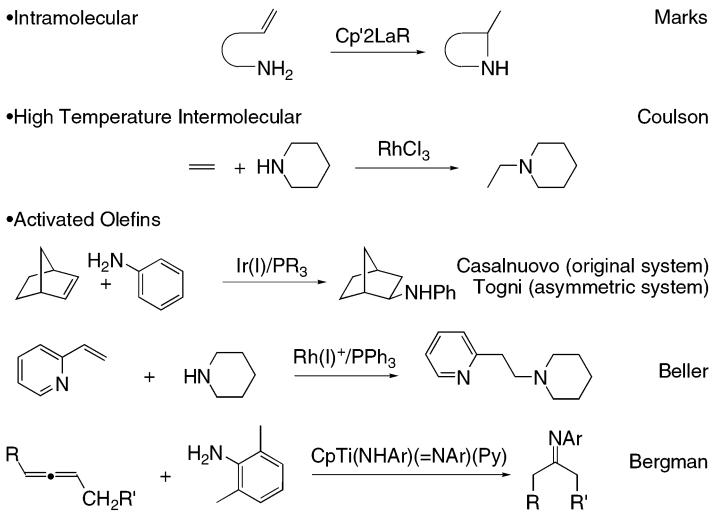


Chart 1 Summary of previous hydroamination of C=C bonds.

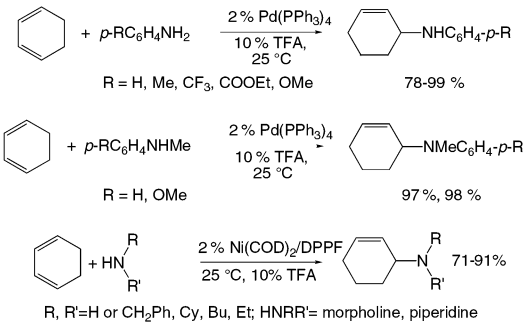
RESULTS AND DISCUSSION

Palladium- and nickel-catalyzed hydroamination of dienes

Several years ago, during the early stages of our search for catalysts for hydroamination, we began to investigate the addition of amines to dienes. Work on the telomerization of dienes with amines has been published over the past 20 years [19–27]. For example, the reaction of butadiene with a secondary amine and a nickel catalyst generates isomeric octenylamines. For complex molecule synthesis one would prefer to catalyze a 1:1 addition of an amine to a diene to generate an allylic amine [28]. If one could control the absolute stereochemistry, then a convenient route to nonracemic, chiral amines would result.

One experiment that we conducted during the early stages of this project was designed to scan a variety of different combinations of metals and ligands in a high-throughput manner. These experiments would reveal if a broad or narrow range of soluble complexes would catalyze the addition of aromatic and aliphatic amines to dienes to form allylic amines by a 1:1 addition process [29]. A variety of metal precursors were combined with a set of phosphines, many of which were commercially available, and an acid cocatalyst often used in telomerization processes [21,22,25]. These catalysts were tested for the addition of aniline to cyclohexadiene and piperidine to cyclohexadiene. The combination of furfural and acid provides a highly sensitive colorimetric assay for aromatic amines [30]. Thus, addition of these components to the reaction wells, followed by dilution to distinguish colors, showed the wells in which reactions of aniline occurred to fully consume the amine. The catalysts in these wells are then likely to be active for the addition process. GC analysis showed that the reaction formed the desired allylic amine. The simple combination of PPh_3 and the Pd(0) precursor $[Pd(allyl)Cl]_2$ was the most active of the catalysts tested for the addition of aniline to cyclohexadiene. A similar experiment that tested catalysts for the addition of piperidine to cyclohexadiene with basic ferricyanide as indicator showed that the combination of DPPF and $(COD)_2Ni$ was an active catalyst [31].

These additions of amines to dienes occurred with broad scope of aromatic and aliphatic amine as summarized in Scheme 1. Electron-neutral, -poor, and -rich anilines, as well as *N*-methylaniline, all added to cyclohexadiene in the presence of the palladium catalyst in good yield [29]. Primary and secondary aliphatic and benzylic amines that are both cyclic and acyclic as well as primary and secondary benzylic amines added to cyclohexadiene in the presence of DPPF and $(COD)_2Ni$ as catalyst [31]. In addition, palladium catalysts containing one of Trost's ligands developed for allylic substitution [32]



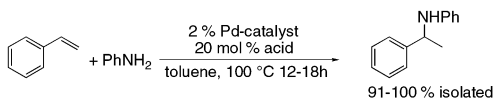
Scheme 1

catalyzed the addition of anilines to cyclohexadienes in high yields and enantioselectivitites in the absence of acid cocatalayst. However, reaction times were long in the absence of this acid cocatalyst. Mechanistic studies [31] showed that the product underwent racemization in the presence of palladium and acid; thus, reactions in the presence of acid cocatalyst occurred faster, but they gave nearly racemic product.

Palladium-catalyzed Markovnikov hydroamination of vinylarenes

As shown in Table 1, complexes similar to those that catalyze the addition of amine to cyclohexadiene catalyzed the addition of aromatic amines to vinylarenes [33]. Motoi Kawatsura, the postdoctoral associate who discovered a majority of the hydroamination processes described in this manuscript, simply evaluated for the addition of aniline to vinyarene the best catalyst and cocatalyst for the addition of aniline to cyclohexadiene. With the simple catalyst $Pd(PPh_3)_4$ or the combination of commercially available palladium trifluoroacetate and PPh_3 in the presence of an acid cocatalyst, the yields for the addition of aniline to styrene were high. In the absence of acid, the yields for reactions catalyzed by either $Pd(PPh_3)_4$ or the mixture of palladium trifluoroacetate and PPh_3 were low. In addition to palladium complexes of monophosphines, complexes of bisphosphines, such as DPPF, catalyzed the addition of aniline to styrene. In particular, $(DPPF)Pd(OTf)_2$ catalyzed this reaction in the absence of acid cocatalyst.

Table 1 Catalysts for the hydroamination of vinylarenes.



Palladium / Ligand	Acid	Yield
2 % $[Pd(PPh_3)_4]$		0 %
2 % $[Pd(PPh_3)_4]$	20 % TfOH	91 %
2 % $Pd(TFA)_2$ / 8 % PPh_3	20 % TfOH	68 %
2 % $[(DPPF)Pd(OTf)_2]$		100 %

The combination of $Pd(PPh_3)_4$ and triflic acid cocatalyst or the combination of DPPF, palladium trifluoroacetate and triflic acid catalyzed the additions of a variety of anilines to several types of vinylarenes. As outlined by the products in Chart 2, the reaction occurred with electron-rich anilines in high yields, but the reaction with an electron-poor aniline occurred in lower yield. The reaction of aniline occurred with vinylarenes containing ortho substituents on the aryl ring and with both electron-donating and -withdrawing groups on the vinylarene. Reactions with the electron-poor vinylarenes, such as trifluoromethylstyrene and vinylnaphthalene, occurred with the fastest rates and in the highest yields.

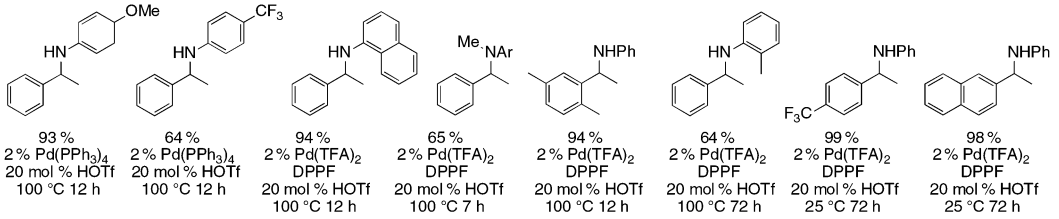
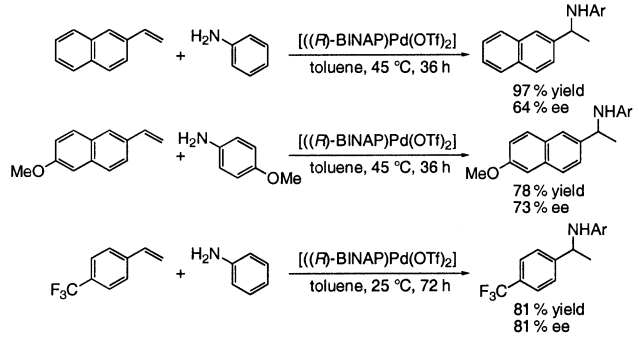


Chart 2

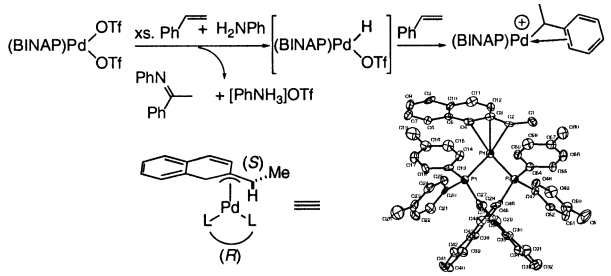
We have sought enantioselective versions of these C–N bond-forming reactions. In large part, our selectivities have been limited by temperature. Thus, we focused on the reactions in Scheme 2 of vinylnaphthalene and trifluoromethylstryene that occurred at or near room temperature. BINAP-ligated palladium is not as active as for these reactions as the PPh_3 or DPPF complexes, but the combination of resolved BINAP, palladium trifluoroacetate and triflic acid cocatalyst did lead to the addition of aniline to vinyl naphthalene and to trifluoromethylstyrene at modest temperatures. Under these conditions, the reaction yields were good, and enantioselectivities were significant for a new type of reaction. The reaction of aniline with trifluoromethylstyrene occurred in 81 % yield and 81 % enantioselectivity, and this combination of yield and enantioselectivity is the highest to date for a hydroamination reaction [34].



Scheme 2

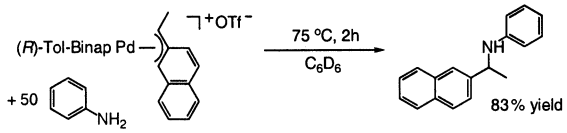
We have been particularly interested in determining the mechanism of these reactions to provide a basis for the selection and design of improved catalysts. The current data supports a mechanism that is distinct from the mechanisms of the reactions in Chart 1. One might expect that coordination of styrene and nucleophilic attack on the coordinated vinylarene would comprise a catalytic amination with palladium [35,36]. However, this sequence would lead to an aminoalkyl intermediate that should undergo β-hydrogen elimination to form an enamine by an oxidative amination reaction that would resemble the Wacker process [36]. Instead, the reactions summarized in Chart 1 and Table 1 provide the products of hydroamination.

Our data shows that the reaction occurs by generation of an η^3-phenethyl palladium complex as a reaction intermediate [37]. Reaction of BINAP- or DPPF-ligated palladium triflate complexes with the combination of vinylarene and arylamine generate palladium complexes of the general structure $L_2Pd(\eta^3\text{-}CH(Me)Ar)$, as outlined in Scheme 3. These compounds are formed by insertion of olefin into a palladium hydride, most likely generated from the palladium(II) precatalysts by the attack of aniline on a coordinated vinylarene and β-hydrogen elimination from the resulting aminoalkyl intermediate. The Tol-BINAP version of this complex formed by insertion of vinylnaphthalene was obtained as single crystals, and a structure of this material is shown in Scheme 3. The crystalline sample consists of a pure stereoisomer. Monitoring of catalytic reactions by ^{31}P NMR spectroscopy show that this η^3-phenethyl complex is the major palladium phosphine complex present in the catalytic solution.



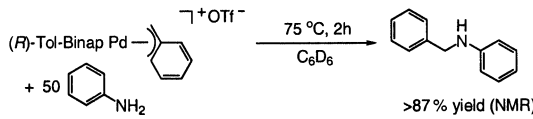
Scheme 3

The presence of this complex in the catalytic system, of course, does not require that it is an intermediate. Thus, we tested the chemical and kinetic competence of this complex to be an intermediate in the catalytic reaction by treating it with aniline and evaluating for the formation of the hydroamination product. Indeed, this complex formed the *N*-arylphenethylamine with yields and rates that were comparable to those of the overall catalytic process (eq. 1). Although these data provide strong evidence for the intermediacy of the η^3-phenethyl complex, generation of free vinylarene from this complex by deinsertion and subsequent reaction of this vinylarene with aniline catalyzed by the resulting palladium complex could form the hydroamination product by a pathway that begins with the η^3-phenethyl complex but forms the C–N bond with a different palladium species.



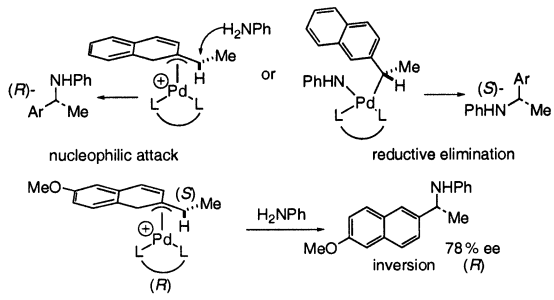
(1)

To test whether the product of the hydroamination process is formed directly from the η^3-phenethyl complex we evaluated the reaction chemistry of a related η^3-benzyl complex that cannot deinsert olefin. Consistent with the intermediacy of the η^3-phenethyl complexes, the η^3-benzyl complex ligated by BINAP reacted with aniline to form *N*-benzylaniline in high yield (eq. 2).



(2)

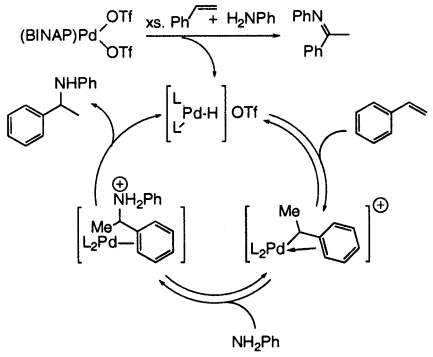
In addition, we tested the reaction of the η^3-phenethyl complex in the presence of a second vinylarene. If deinsertion of the vinylarene occurs on the reaction path, then reaction in the presence of an excess of vinylarene would form the amine containing the second vinylarene as the major product at low conversions. If the hydroamination product forms directly from the η^3-phenethyl complex, then reaction in the presence of an excess of vinylarene would form the amine containing the vinylarene unit of the η^3-phenethyl complex as the major product at low conversions. We evaluated the products from the reaction of aniline with a BINAP-ligated η^3-phenethyl complex containing a 6-methoxy substituent on the naphthyl ring in the presence of added free vinylnaphthalene. The major product at short reaction times was that containing the 6-methoxy substituent. Thus, the η^3-phenethyl complex reacts with aniline to form the hydroamination product without initial deinsertion to form free vinylarene.



Scheme 4

Two mechanisms shown in Scheme 1 could form the phenethylamine product from reaction of the η^3-phenethyl complex. One mechanism would occur by external attack of the amine on the benzylic carbon and the second would occur by internal attack of the amine at the metal and then C–N bond formation by reductive elimination after deprotonation of the coordinated amine. External attack would lead to inversion of configuration at the benzylic carbon, and internal attack would lead to retention of configuration. Because we had crystallized the enantiomerically pure Tol-BINAP-ligated η^3-phenethyl complex, the reaction of this complex with aniline can distinguish between these two mechanisms. Our experiments showed that this reaction occurred predominantly by inversion of configuration.

The catalytic mechanism in Scheme 5 is consistent with our mechanistic data. During a catalyst initiation phase, attack of aniline on coordinated styrene likely produces a palladium hydride and imine. Indeed, 1 equiv of imine per catalyst has been observed during catalytic reactions. Insertion of the olefin into this palladium hydride would lead to an η^3-phenethyl complex that reacts with amine by an external attack. Release of the coordinated product and proton transfer would regenerate the palladium hydride. This mechanism is distinct from that of the Casalnuovo and Milstein [13] or Togni [14] systems for the addition of aniline to norbornene catalyzed by iridium. It is also distinct from the mechanism by which Marks' lanthanide catalysts [5] or Bergman's zirconium catalysts undergo hydroamination [17,38]. Moreover, this mechanism departs from the stoichiometric amination chemistry of platinum and palladium η^2-olefin complexes [35].



Scheme 5

Rhodium-catalyzed anti-Markovnikov hydroamination of vinylarenes

In addition to control of stereochemistry, control of regiochemistry is an important problem in hydroamination. Recently, a visiting scholar in my group, Masaru Utsunomiya, developed some preliminary observations of previous postdoctorates into a process for the anti-Markovnikov addition of alkylamines to vinyl arenes [39]. The reaction scope and yields must be improved before the reaction is suitable for complex synthesis, but this process constitutes the first amination of an olefin to form the terminal

amine as the major product. Bis-diphenylphosphinobiphenyl ether, a ligand developed by Van Leeuwen for hydroformylation [40], is thus far unique for forming this anti-Markovnikov hydroamination product in good yield. Structurally related ligands, shown in Table 2, provide essentially no hydroamination product. As shown in Chart 3, a variety of combinations of aliphatic amines and vinylarenes generate terminal amines as the major reaction product. In all cases, the product from hydroamination is the major product, and the product from oxidative amination is the predominant nitrogen-containing side product. The ratios of hydroamination to oxidative amination product are provided in the Chart. Reactions of the electron-neutral or the electron-rich vinylarenes occurred with high ratios for formation of the hydroamination vs. oxidative amination product, although these reactions were slower than those with electron-poor vinylarenes. Reactions of electron-poor vinylarenes occurred to form lower ratios of hydroamination to oxidative amination products, but the β-phenethylamine remained the major product under optimized conditions.

Table 2 Effect of ligand on the rhodium-catalyzed anti-Markovnikov hydroamination of vinylarenes.

Entry	Ligand	Amine yield	Enamine yield
1	DPEphos	62 %	20 %
2	PPh_3	17 %	78 %
3	DPPE	0 %	1 %
4	DPPB	0 %	0 %
5	DPPPent	1 %	1 %
6	Xantphos (**1**)	trace	9 %
7	DBFphos (**2**)	3 %	40 %
8	BIPHEphos (**3**)	0 %	0 %

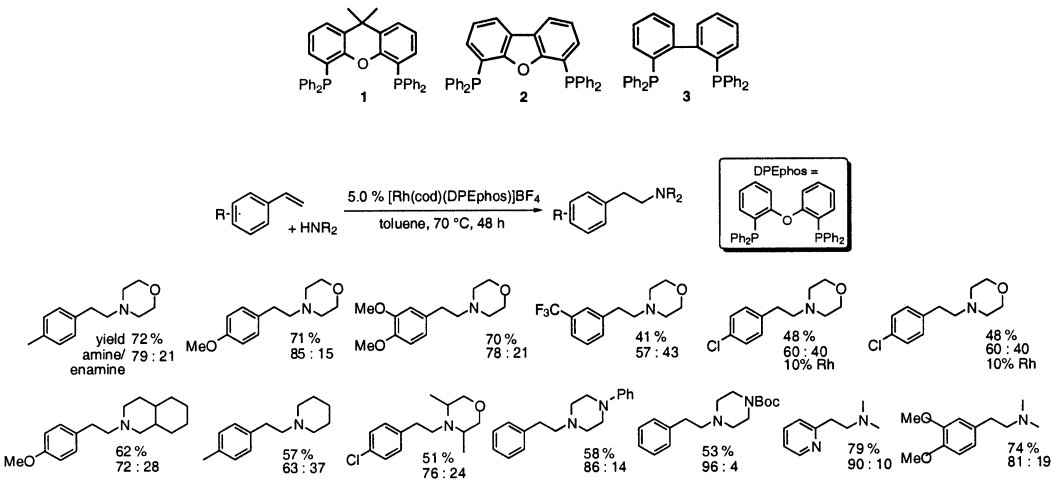
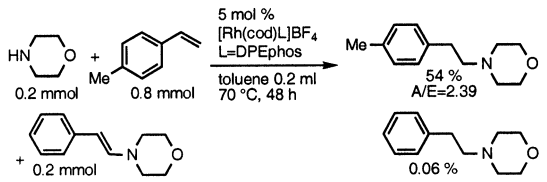


Chart 3

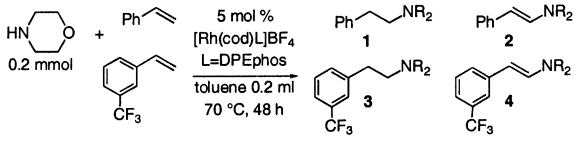
The amine product could form by hydrogenation of the oxidative amination product. To test for this scenario, we conducted the reaction of morpholine with styrene in the presence of the enamine bearing a *p*-tolyl group at the vinylarene, as outlined in eq. 3. If hydrogenation of an enamine product forms the amine, then the reaction with the added enamine would generate the amine bearing a *p*-tolyl group. Consistent with direct formation of the amine without a free enamine intermediate, the added enamine with a *p*-tolyl group remained unchanged during the reaction of aniline with styrene.



(3)

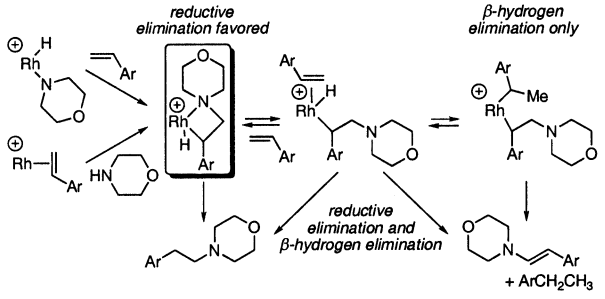
We have not obtained the structural detail about intermediates in the rhodium-catalyzed hydroamination process that we obtained on the palladium-catalyzed reaction. However, some mechanistic data has been obtained. The ratio of the hydroamination and oxidative amination product is constant throughout the reaction. Thus, a series of active catalysts do not seem to be generated during the catalytic process. Most interesting, our data suggests that two vinylarenes are present as part of the transition-state structure that forms the amine or the enamine or both. The ratio of amine to imine depended on the concentration of styrene. At high concentrations of styrene, the ratio of hydroamination to oxidative amination product decreased relative to the ratio formed at lower concentrations of styrene. In addition, the ratio of the two products from one type of vinylarene was altered by the presence of a second type of vinylarene. A comparison of product selectivities from three reactions with equal total concentrations of vinylarene is shown in Table 3. These data show that the ratio of amine to enamine from reaction of styrene alone was higher than the ratio generated from reaction of styrene in the presence of the electron-poor trifluoromethyl styrene. In addition, the ratio of products from reaction of trifluoromethylstyrene alone was lower than the ratio from reaction of this vinylarene in the presence of styrene. Thus, it appears two vinylarenes are present in the species that controls selectivity.

Table 3 Effect of one vinylarene on the hydroamination of another vinylarene.



Ph	F_3C	amine **1** : enamine **2**[a]	amine **3** : enamine **4**[a]
0.8 mmol	-	72 : 28	–
-	0.8 mmol	–	38 : 62
0.4 mmol	0.4 mmol	50 : 50	47 : 53

Scheme 6 provides a potential mechanism, which involves two vinylarenes. A complex containing an α-phenyl β-aminoalkyl intermediate may form by either N-H activation and olefin insertion or by external attack on a coordinated vinylarene. In this species, the β-hydrogens are positioned away



Scheme 6

from the metal, and this geometry makes β-hydrogen elimination slow. Reductive elimination from this complex would generate the hydroamination product. However, a high concentration of styrene could favor the generation of an acyclic aminoalkyl species formed by coordination of vinylarene and cleavage of the dative metal-nitrogen bond. If so, then β-hydrogen elimination to form an enamine product could become rapid and compete with reductive elimination to form amine. Alternatively, this second vinylarene could insert into the rhodium hydride. The resulting dialkylpalladium complex would then be unable to form amine. Instead, this species would undergo β-hydrogen elimination to form imine and subsequent reductive elimination to form the alkylarene.

SUMMARY

Our recent efforts to develop new hydroamination processes have led to a series of reactions that provide a broader reaction scope than previously observed for intermolecular hydroaminations and have begun to provide control over regio- and stereoselectivity. Studies on palladium-catalyzed reactions of alkylamines and other substrates with N–H bonds, additions of OH bonds across C=C bonds, and further mechanistic work on both palladium- and rhodium-catalyzed reactions are in progress.

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