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A General Nickel-Catalyzed Hydroamination of 1,3-Dienes by Alkylamines: Catalyst Selection, Scope, and Mechanism

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Abstract: A simple colorimetric assay of various transition-metal catalysts showed that the combination of DPPF, $Ni(COD)_2$, and acid is a highly active catalyst system for the hydroamination of dienes by alkylamines to form allylic amines. The scope of the reaction is broad; various primary and secondary alkylamines react with 1,3-dienes in the presence of these catalysts. Detailed mechanistic studies revealed the individual steps involved in the catalytic process. These studies uncovered unexpected thermodynamics for the addition of amines to π-allyl nickel complexes: instead of the thermodynamics favoring the reaction of a nickel allyl with an amine to form an allylic amine, the thermodynamics favored reaction of a nickel(0) complex with allylic amine in the presence of acid to form a Ni(II) allyl. The realization of these thermodynamics led us to the discovery that nickel and some palladium complexes in the presence or absence of acid catalyze the exchange of the amino groups of allylic amines with free amines. This exchange process was used to reveal the relative thermodynamic stabilities of various allylic amines. In addition, this exchange reaction leads to racemization of allylic amines. Therefore, the relative rate for C−N bond formation and cleavage influences the enantioselectivity of diene hydroaminations.

Introduction

The hydroamination of 1,3-dienes is an efficient route to allylic amines.[1] Reactions of amines with dienes catalyzed by transition-metal complexes have been studied extensively, but the simple formation of allylic amines is rare. The telomerization of butadiene in the presence of amines to form long-chain amines is well-known.[2−5] This chemistry has been developed with both nickel and palladium catalysts. Although some of these telomerization catalysts produce allylic amines by a 1:1 addition process, these 1:1 adducts are generally formed as a minor part of the reaction mixture. In only rare cases has the catalytic reaction between an amine and a diene occurred selectivity to form an allylic amine at low temperatures.[6] One previous study included a single example of the addition of morpholine to cyclohexadiene conducted with relatively high catalyst loadings.[7] Other studies were conducted with catalysts activated by alkylaluminum additives and were also limited in substrate scope.[8] Examples that give simple 1:1 adducts with primary alkylamines are rare or unknown.

Transition-metal complexes can catalyze not only the addition of amines to dienes, but the cleavage of allylic amines as well. Studies that have been published or patented have uncovered catalysts for the deamination of allylic amines to generate dienes.[9−15] Moreover, catalysts have been identified for the insertion of carbon monoxide into the C−N bond of allylic amines to form *N*-allyl amides.[16] This process certainly involves a metal-mediated C−N bond cleavage at some part of the catalytic cycle. Thus, there is a fine balance between C−N bond formation and C−N bond cleavage by group 10 metal catalysts.

We recently identified palladium catalysts for the 1:1 addition of aromatic amines to dienes, including catalysts that produced allylic amines with high enantioselectivity.[6] The catalysts tested were completely inactive toward the addition of either primary or secondary alkylamines to dienes. Thus, we sought a simple catalyst system that would induce the selective formation of 1:1 adducts at synthetically useful rates from reactions of dienes with both primary and secondary alkylamines.

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The catalysts that we had previously reported for the addition of aromatic amines to dienes were identified by a colorimetric assay. We had tested for the presence of aniline by adding furfural and acid to the reaction solutions. When aniline was present, a red color was observed. Thus, the solutions containing the most active catalysts displayed the least red color after addition of the stain. We envisioned a similar method that could screen catalysts for the addition of alkylamines to dienes. Nitroferricyanide(III) dihydrate reacts with secondary alkylamines in the presence of base and acetaldehyde to give a blue color.[17,18] Thus, we recently developed a similar procedure in which nitroferricyanide is used to indicate the consumption of a secondary alkylamine.[18]

In the present work, we have used this method to identify catalysts for the formation of allylic amines by the addition of either primary or secondary alkylamines to dienes with high selectivity for the 1:1 adducts. In addition to evaluating the scope for this process, we conducted a series of mechanistic experiments to identify the individual steps that compose the catalytic process. Considering the previous findings on catalytic formation and elimination of allylic amines mentioned above, the thermodynamics and reversibility of the individual steps in the catalytic cycle were unclear. These mechanistic experiments uncovered unexpected thermodynamics for the addition of amines to nickel allyl complexes and examples of directly observed oxidative addition of allylic amine C−N bonds. Moreover, these experiments showed that the nickel complexes catalyze the exchange of amines within allylic amines, and these exchange experiments uncovered the relative thermodynamics of allylic amines. Moreover, these exchange experiments revealed important information on enantioselective addition of nitrogen nucleophiles to metal allyl intermediates.

Results and Discussion

Identification of Catalysts for the Addition of Alkylamines to Dienes. We initially screened colorimetrically for complexes that would catalyze the addition of alkylamines to dienes at room temperature. Figure 1 shows the colors of a set of reactions between morpholine and cyclohexadiene (eq 1) after staining with basic nitroferricyanide and acetaldehyde. The reactions were conducted in the presence of benzoic acid cocatalyst and metal complexes that were generated from phosphines and one of several catalyst precursors. The reactions were conducted in a glass 96-well plate sealed with a glass slide. The coordination compounds on the left of the figure and the phosphine ligands at the top were added to the plate in a drybox as stock solutions using a multichannel pipet. After 48 h of reaction at room temperature in the drybox, the plate was removed from the box, and each reaction was treated with aqueous nitroferricyanide(III) dihydrate, aqueous NaOH, and neat acetaldehyde. The reactions with the palest blue color contain the lowest concentration of morpholine and, therefore, the most active catalysts. As shown in Figure 1, the combination of $Ni(COD)_2$ and DPPF with the acid cocatalyst in THF solvent led to almost complete consumption of morpholine with cyclohexadiene at room temperature after 48 h. After identifying the most active catalyst, we evaluated its selectivity for formation of a 1:1 adduct by GC methods. GC analysis of reactions that were not stained showed the formation of the 1:1 addition product in high yield.

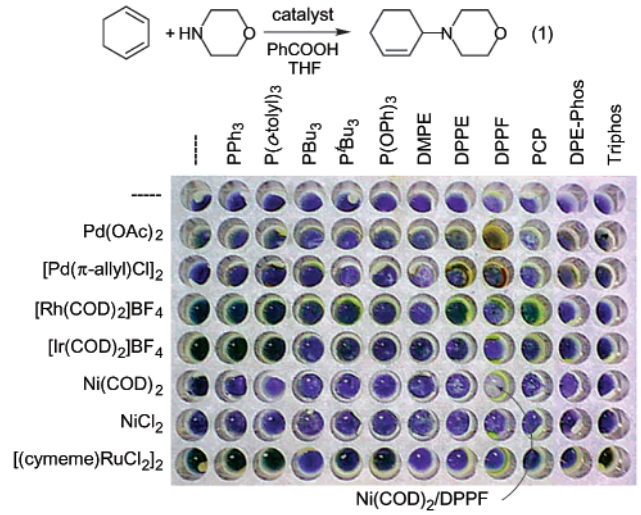

Figure 1. Evaluation of catalysts for eq 1, visualized by the combination of acetaldehyde, sodium nitroferricyanide(III) dihydrate ($Na_2Fe(CN)_5NO\cdot 2H_2O$), and NaOH. DPPF = 1,1′-bis(diphenylphosphino)ferrocene.

To optimize the process, we evaluated reactions that were conducted in the presence of catalysts generated from closely related ligands and under varied reaction conditions. These studies showed that the fastest rates were obtained with DPPF as ligand, with $Ni(COD)_2$ or $[(allyl)Ni(Cl)]_2$ as catalyst precursor and with trifluoroacetic acid (TFA) as cocatalyst. The resulting catalysts were much more active for this reaction than were the catalysts in previous reports.[7,8] In fact, we had difficulty obtaining even the modest reported turnover numbers when using phosphite ligands. Bisphosphines with larger or smaller bite angles (Xantphos, DPPB, and DPPE) and monophosphines or phosphites (PBu_3, PPh_3, or $P(OR)_3$ (R = Me, Ph)) gave low yields.[7] Reactions conducted with a 4:1, 2:1, or 1:1 ratio of ligand to metal occurred at comparable rates.

The reaction medium and acid cocatalyst was also varied. Reactions in benzene, THF, and ether occurred similarly but reactions in acetonitrile gave lower yields, and reactions in CH_2Cl_2 gave no product. Reactions in the presence of 2 mol % TFA gave the allylic amine in high yields, but they were slower than those conducted in the presence of 5−20 mol % acid. Reactions containing a large excess of acid relative to catalyst, such as 50 mol % TFA, occurred in lower yields. Reactions containing acetic acid and benzoic acid were slower than those containing TFA, while reactions containing pentafluorobenzoic acid gave rates similar to those of reactions containing TFA.[19] Reactions conducted in the presence of TFA-d_1 occurred at rates that were comparable to those of reactions conducted in the presence of TFA. Reactions in the absence of acid gave no product.

Reaction Scope. The hydroamination of dienes with alkylamines using the optimized conditions is summarized in Table 1. Aliphatic and benzylic secondary amines with modest steric properties (entries 1−4) all gave good isolated yields of the 1:1 addition products. Primary alkylamines (entries 5−9) also reacted in good yields, including those that provide access to

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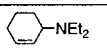
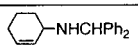
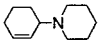
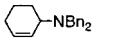
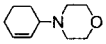
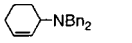
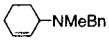
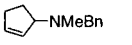
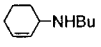
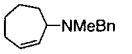
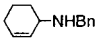
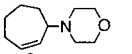
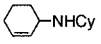
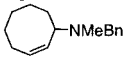
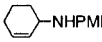
(19) Reaction half-lives at 20 °C: TFA, $C_6F_5CO_2H$: 3 h; $PhCO_2H$: 8 h; AcOH, 10 h.

Table 1. Nickel-Catalyzed Hydroamination of 1,3-Dienes

Entry	Product	Time (h)	Yield (%)	Entry	Product	Time (h)	Yield (%)
1		20	78	9		60	85
2		20	82	10		113	56
3		20	80	11		72[b]	71
4		20	89	12		43	91
5		7	89	13		60	94
6		6	93	14		60	83
7		37	82	15		84[b]	38[c]
8		30	87	16		0.5	83[d]

[a] Reaction conditions: 2.0 mmol amine, 4.0 mmol diene, 5.0 mol % DPPF, 5.0 mol % $Ni(COD)_2$, 20 mol % TFA, toluene, 25 °C. [b] At 60 °C. [c] Three regioisomers (GC/MS 14:4:7). [d] Isomer ratio by GC/MS: 27:2:2.

the formal ammonia addition product after deprotection.[20] The highly hindered dicyclohexylamine and 2,2,6,6-tetramethylpiperidine did not react. Although dibenzylamine reacted very slowly at room temperature (entry 10), it did react at 60 °C (entry 11) in good yield. Aromatic amines, which added to 1,3-cyclohexadiene using palladium catalysts,[6] were unreactive at room temperature or elevated (60 °C) temperatures in the presence of the nickel catalyst.

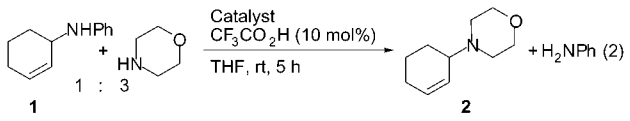
Dienes other than cyclohexadiene also formed 1:1 adducts. Reaction of 1,3-cyclopentadiene with *N*-benzylmethylamine, as well as reaction of 1,3-cycloheptadiene with *N*-benzylmethylamine and morpholine (entries 12−14), occurred in good yield. However, reaction of 1,3-cyclooctadiene gave a mixture of three regioisomers in 38% yield after 84 h at 60 °C (entry 15). Reaction of butadiene, which usually generates telomerization products, gave 83% yield (entry 16) of the simple 1:1 adduct under the standard conditions. The major product resulted from 1,2-addition of the amine. Only about 5% of the other two regioisomers was observed. However, when this reaction was conducted for long time periods, the terminal allylic amine product was formed. As revealed by studies described below, this time-dependent selectivity results from isomerization and exchange reactions between the product allylic amines and the amine reagent. Reactions of 2- and 2,3-substituted acyclic 1,3-dienes were slow, even at higher catalyst loadings and temperatures.

Reactions containing lower catalyst loadings occurred under modified procedures involving neat or highly concentrated substrate. Reaction of *N*-benzylmethylamine with 1,3-cyclohexadiene in the presence of 1.0 mol % catalyst and no solvent gave 99% isolated yield of allylic amine at 65 °C after only 4 h. Under these conditions, reaction of morpholine with cyclohexadiene occurred in 92% yield after 36 h in the presence of only 0.2 mol % catalyst. Reaction between a *n*-butylamine (2 M) and 1,3-cyclohexadiene (4 M) occurred after 15 h in the presence of 1 mol % catalyst to give the allylic amine in 91% yield.

Exchanges of Allylic Amines with Primary and Secondary Amines. The catalysts for diene hydroamination also catalyzed

(20) Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Chemistry*, 2nd ed.; Wiley: New York, 1991; Chapter 7.

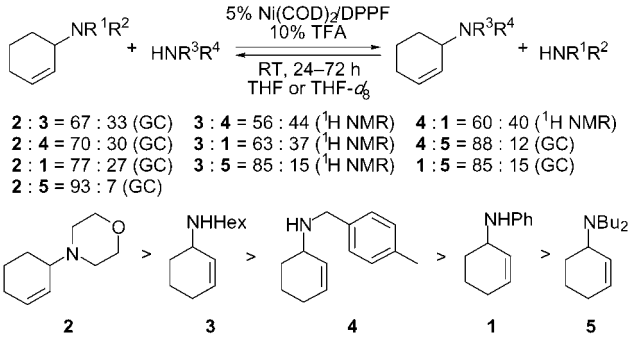
Table 2. Nickel- and Palladium-Catalyzed Exchange of Amines with Allylic Amines



entry	catalyst (5 mol %)	conv. of **1** (%)[a]	yield of **2** (%)[a]
1	$Ni(COD)_2$/DPPF	77 ± 4[b]	81 ± 4[b]
2	$Ni(COD)_2$/2 PPh_3	0	4
3[c]	$Ni(COD)_2$/DPPF	43	42
4	1/2 [(π-allyl)PdCl]$_2$/DPPF	96	100
5	1/2 [(π-allyl)PdCl]$_2$/2 PPh_3	0	0
6	1/2 [(π-allyl)PdCl)]$_2$/DPPF	54	60

[a] Determined by GC. [b] Similar errors of 4−5% were estimated for the other reactions. [c] Without trifluoroacetic acid.

Scheme 1



the reaction of allylic amines with primary or secondary alkyl- or arylamines to generate mixtures of allylic amines (Scheme 1). This reaction provided the opportunity to determine the thermodynamic stability of various allylamines. We evaluated different catalysts and reaction conditions for the exchange process, and determined the relative stability of the various allylic amines.

Table 2 reveals the activity of various nickel and palladium complexes as catalysts for the exchange of *N*-(2-cyclohexen-1-yl)aniline with morpholine (eq 2) in the presence and absence of acid cocatalyst. Both nickel and palladium complexes of DPPF were active catalysts for this exchange process in the presence of acid cocatalyst (entries 1 and 4). Analogous complexes ligated by the monodentate ligand PPh_3 were inactive (entries 2 and 5). Exchange also occurred in the presence of $Ni(COD)_2$ and DPPF, but in the absence of acid. However the exchange was slower than it was in the presence of acid (entries 3 and 6).

Scheme 1 presents data on the thermodynamic stability of allylic amines. The exchange processes that uncovered these thermodynamics were catalyzed by 5 mol % of $Ni(COD)_2$/DPPF and 10 mol % of trifluoroacetic acid in THF or THF-d_8. The reactions were initiated with the combination of materials on the left side of the equation and with those on the right side to confirm that an equilibrium was established. The ratio of the amines at equilibrium was determined by GC or ^{1}H NMR spectroscopy. One can see that the allylic amines from cyclic secondary amines are more stable than those from acyclic secondary amines, when compared to the stability of the free secondary amine. This preference is presumably steric in origin. However, electronic effects were also observed. The product from addition of aniline was less stable than the product from

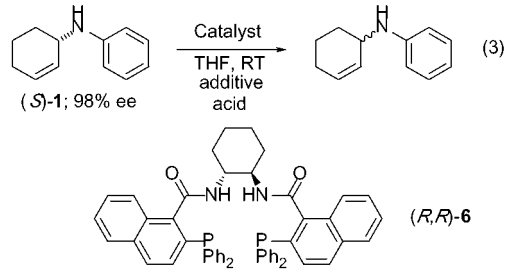
Table 3. Racemization of (*S*)-*N*-(2-Cyclohexen-1-yl)aniline

entry	catalyst	acid (10 mol %)	additive (1 mol)	time (h)	ee (%)[a]
1	Ni(COD)2/DPPF (5 mol %)	CF_3CO_2H	none	72	98
2	Ni(COD)2/DPPF (5 mol %)	none	aniline	72	97
3	Ni(COD)2/DPPF (5 mol %)	CF_3CO_2H	aniline	72	66
4	1/2 ((π-allyl)$PdCl)_2$ (10 mol %)/ (*R*,*R*)-**6** (11 mol %)	none	none	20	98
5	1/2 ((π-allyl)$PdCl)_2$ (10 mol %)/ (*R*,*R*)-**6** (11 mol %)	none	aniline	20	72
6	1/2 ((π-allyl)$PdCl)_2$ (10 mol %)/ (*R*,*R*)-**6** (11 mol %)	CF_3CO_2H		20	8
7	1/2 ((π-allyl)$PdCl)_2$ (10 mol %)/ (*R*,*R*)-**6** (11 mol %)	CF_3CO_2H	aniline	5	5

[a] Determined by HPLC.

addition of both more and less hindered alkylamines. Factors that control the difference in X−H versus X−C bond strengths have been studied, and more electronegative heteroatoms, such as that in the arylamine, have a larger preference for the X−H bond than do less electronegative heteroatoms such as the nitrogen in the alkylamines.[21]

Effect of the Exchange Process on Allylic Amine Stereochemistry. The exchange reaction of optically active allylic amines with free amines should lead to racemization. To determine the qualitative rate of racemization of an allylic amine and whether this racemization occurs in the presence or in the absence of acid or both, we treated enantioenriched (*S*)-*N*-(2-cyclohexen-1-yl)aniline with a series of palladium and nickel complexes in the presence and absence of acid and in the presence and absence of aniline (eq 3).



The results from experiments on the racemization of allylic amines are shown in Table 3. In the presence of catalysts derived from $Ni(COD)_2$ and DPPF, racemization of the amine occurred only in the presence of both acid and additional aniline (entries 1−3). In the presence of catalysts derived from $[Pd(allyl)Cl]_2$, the ligand (*R*,*R*)-**6**, and added acid (entries 6 and 7), the optically active allylic amine became nearly racemic. This catalyst precursor and ligand were shown previously to catalyze enantioselective hydroamination of 1,3-dienes with arylamines in the absence of the added acid. Indeed, racemization of the amine was slow or did not occur at all in the absence of acid (entries 4 and 5). These disparate results on the racemization of allylic amines in the presence and absence of acid explain why the enantioselectivity from reactions catalyzed by this complex in the presence of acid was much lower than it was when the reactions were conducted in the absence of acid.

The stereochemistry for a single turnover was determined by evaluating the diastereoselectivity for exchanges of amines with allylic amines. We prepared 3-amino-5-methylcyclohexene that was comprised of 93% trans and 7% cis isomers. We allowed this amine to react with morpholine in the presence of the nickel catalyst and TFA cocatalyst. The exchange product 3-moropholino-5-methylcyclohexene could be formed as either a nearly pure diastereomer or as a mixture of diastereomers. In the event, the reaction formed in 75% isolated yield *trans*-3-moropholino-5-methylcyclohexene that was found to be greater than 95% of the trans diastereomer, as determined by ^1H NMR spectroscopic and GC analysis. The relative stereochemistry was determined by a series of 2D NOESY, COSY, and ^1H and ^{13}C correlation spectral experiments. An nOe observed between the protons α to the nitrogen of morpholine and the proton geminal to the methyl group was one strong indicator of the trans stereochemistry. Although we have not determined the fate of the small amount of cis isomer in the starting allylic amine, the reaction clearly occurs with a high degree of retention of configuration.[22] This reaction stereochemistry is consistent with inversion of configuration to form the nickel allyl and inversion of configuration to form the exchange product.[23,24]

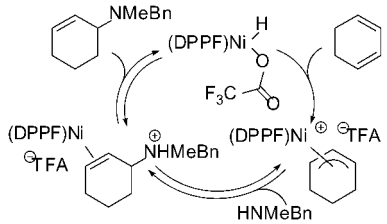
Mechanistic Studies. Many mechanisms for olefin hydroamination have been proposed or discussed,[25−33] and additional pathways are available for the hydroamination of dienes. Diene hydroamination could involve an initial uncatalyzed reaction of the acid cocatalyst with diene to give an allylic trifluoroacetate, followed by the well-known metal-catalyzed or an uncatalyzed amination of the allylic trifluoroacetate.[1] Although trifluoroacetic acid adds to 1,3-cyclohexadiene in the absence of amine, it does not react in the presence of amine because of the leveling effect.[6]

Other mechanisms would involve initial activation of one or the other substrate by reaction with the metal catalyst. A previous mechanistic proposal included attack of amine on a diene that is coordinated in an η^2 fashion to Ni(0).[34] Proposed mechanisms for telomerization have involved initial, metal-mediated dimerization of the diene and subsequent attack of amine on the resulting allyl complex.[34] Some proposals for hydroamination of olefins have involved initial N−H activation, followed by insertion and reductive elimination.[33] Yet, simple oxidative addition to late metals of the N−H bonds in the aliphatic amines we used is unknown, and mechanisms involving this step need not be invoked to account for the data presented below.

A third class of mechanism for the diene hydroamination is shown in Scheme 2. This mechanism involves the generation

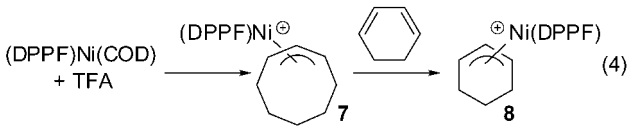
(21) Bensen, S. W.; Francis, J. T.; Tsotsis, T. T. *J. Phys. Chem.* **1988**, *92*, 4515.
(22) We did not prepare the *cis*-allylic amine reactant for the parallel study on this species. It seems unlikely that the trans product is thermodynamically favored because 1,3-diequatorial conformers are generally most stable. Allinger, N. L.; Miller, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 2145−2149.
(23) Åkermark, B.; Backvall, J.-E.; Lowenborg, A.; Zetterberg, K. *J. Organomet. Chem.* **1978**, *166*, C33−C36.
(24) Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215−3216.
(25) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275−294.
(26) Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Müller, T. E.; Zapf, A. *J. Organomet. Chem.* **1998**, *566*, 277−285.
(27) Pohlki, F.; Doye, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2305−2308.
(28) Muller, T. E.; Berger, M.; Grosche, M.; Herdtweck, E.; Schmidtchen, F. P. *Organometallics* **2001**, *20*, 4384−4393.
(29) Ovchinnikov, M. V.; LeBlanc, E.; Guzei, I. A.; Angelici, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 11494−11495.
(30) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708−1719.
(31) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753−2767.
(32) Senn, H.; Blochl, P.; Togni, A. *J. Am. Chem. Soc.* **2000**, *122*, 4098−4108.
(33) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738−6744.
(34) Jolly, P. W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 283−295.

Scheme 2

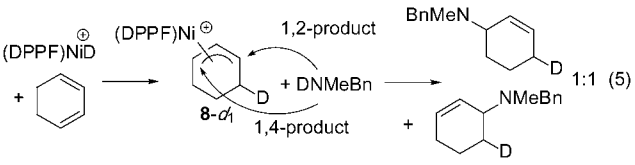


of a nickel hydride, insertion of the diene to give a nickel allyl,[35] and external attack of the amine on the coordinated allyl.[7] Our mechanistic data is consistent with this pathway, but we show that reaction with amine is thermodynamically favorable only in the presence of additional diene.

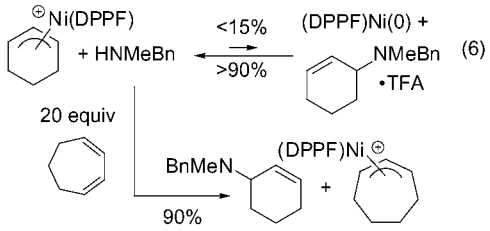
To obtain mechanistic information, we conducted studies to generate potential reaction intermediates and to investigate their reactivity with various components of the catalytic reaction solutions. We initially attempted to generate a DPPF-ligated nickel hydride[36] using reagents involved in the catalytic system. To do so, we treated Ni(COD)DPPF[37] with TFA. This reaction generated the DPPF-ligated nickel(η^3-cyclooctenyl) complex **7** (eq 4) and, not surprisingly, no stable nickel hydride. This cationic cyclooctenyl complex was fully characterized by spectroscopic means, and its structure was confirmed by X-ray diffraction.[38] Cyclooctenyl **7** reacted with 1,3-cyclohexadiene to form cyclohexenyl complex **8** (eq 4) after heating at 50 °C for 12 h. This complex was generated independently and was isolated in 81% yield by reaction of $Ni(COD)_2$, DPPF, and 1,3-cyclohexadiene in the presence of TFA. The structure of **8** was confirmed by X-ray diffraction.



Allyl complex **8** was particularly relevant to the catalytic reactions. Monitoring by ^{31}P NMR spectroscopy of the catalytic reaction between cyclohexadiene and *N*-benzylmethylamine showed that cyclohexenyl **8** was the catalyst resting state. Moreover, reactions of 1,3-cyclohexadiene and *N*-benzylmethylamine containing isolated **7** or **8** as catalyst occurred at rates that were qualitatively indistinguishable from those observed for reactions catalyzed by a species generated in situ from $Ni(COD)_2$, DPPF, and TFA.



Deuterium labeling studies on the catalytic process further supported the intermediacy of the observed allyl species and the formation of product by addition of amine to this allyl intermediate. We allowed cyclohexadiene to react with *N*-deuterio, *N*-benzylmethylamine in the presence of TFA-d_1 and catalytic amounts of $Ni(COD)_2$ and DPPF. As shown in eq 5, insertion of 1,3-cycohexadiene into a nickel deuteride would form a cyclohexenyl complex **8**-d_1, which is symmetric except for the presence of deuterium in the position α to the allyl unit. Thus, formation of product by nucleophilic attack on the allylic intermediate would generate a 1:1 mixture of the 1,2- and 1,4-addition products. ^2H NMR spectroscopy showed that this addition of deuterated amine gave the equal mixture of 1,2- and 1,4-addition products that are predicted for reaction by the pathway in eq 5.



Although these data allowed one to outline the individual steps in the catalytic cycle and supported the intermediacy of the observed allyl intermediate, the mechanism for this process was not as straightforward as these results imply. To demonstrate that attack of amine on the nickel allyl **8** forms the organic product and closes the catalytic cycle, we treated cyclohexenyl complex **8** with *N*-benzylmethylamine. This stoichiometric reaction did not form allylic amine in yields comparable to those of the catalytic reaction. Reaction between isolated **8** and 1 equiv of *N*-benzylmethylamine gave only 15% yield or less of the allylic amine product (eq 6). Reaction of **8** with an excess of amine formed $Ni(DPPF)_2$[39] and presumably some amine-ligated nickel complexes, but the yield of allylic amine was as low as it was from the reaction of **8** with 1 equiv of amine.

To account for the low yield of allylic amine from addition of amine to the nickel allyl, we hypothesized that the formation of product from cyclohexenyl complex **8** would be thermodynamically favorable if the reaction formed a nickel(II) allyl complex instead of a Ni(0) species. To test this hypothesis we evaluated additions of *N*-benzylmethylamine to **8** in the presence of dienes other than cyclohexadiene. By doing so, we could determine if trapping of the nickel product with a diene improved the yield for formation of the 2-aminocyclohexen-1-ylamine product. In control experiments, we observed that **8** did not react with cycloheptadiene; no exchange to form a cycloheptadienyl complex was observed. Thus, we allowed cyclohexenyl **8** to react with amine in the presence of cycloheptadiene.

Indeed, reaction of *N*-benzylmethylamine with **8** in the presence of an excess of cycloheptadiene provided the 2-cyclohexen-1-ylamine in 90% yield, along with the same set of nickel species that are present in the catalytic reaction of cycloheptadiene with *N*-benzylmethylamine. This clean formation of the 2-cyclohexen-1-ylamine product in the presence, but not in the absence, of added diene is consistent with our proposal that attack of the amine on **8** is endothermic.

Reaction of the allyl complex is apparently even more endoergic when a less nucleophilic amine is used. For example,

(35) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 6785−6790.
(36) Tolman has studied this process extensively with $Ni[P(OEt)_3]_4$ and strong acids: Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 4217−4222.
(37) Formed by stoichiometric reaction of $Ni(COD)_2$ with DPPF, ^{31}P NMR, δ 35.6 ppm.
(38) See the Supporting Information for the full details of these studies.
(39) Lee, M. T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 539−547.

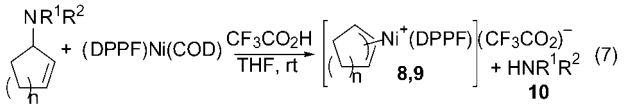
Table 4. Oxidative Addition of Allylic Amines to (DPPF)Ni(COD)[a]

entry	n	$-NR^1R^2$	time (h)	yield (%) 8–9[b]	yield (%) 10[c]
1	2	−NMeBn	3	73	72
2	2	−NHBn	4	53	nd[d]
3	2	−NHPh	5	90	73
4	2	−(1-Morpholine)	3	76	nd
5	1	−NMeBn	1	84	81
6	3	−NMeBn	1	*e*	85

[a] Reactions conducted with a 5:1:1 ratio of allylic amine to nickel to acid. [b] Determined by ^{31}P NMR spectroscopy. [c] Determined by GC. [d] Not determined. [e] Identity of the nickel products not determined (see text).

reaction of aniline with cyclohexenyl **8** in the presence or absence of cyclooctadiene formed the *N*-aryl allylic amine slowly and in low yield. Reaction between aniline and **8** in the presence of cyclooctadiene required 5 d at room temperature for completion and gave less than 10% yield of *N*-aryl allylic amine. No phosphine-ligated nickel complexes were generated from this reaction; only free DPPF was observed. These results explain the absence of a catalytic reaction between aniline and cyclohexadiene in the presence of the DPPF-ligated nickel.

Oxidative Addition of Amine C−N Bonds. The unfavorable thermodynamics for addition of amine to the nickel allyl leads one to predict that the opposite reaction, oxidative addition of allylic amine C−N bonds, should occur to DPPF-ligated Ni(0) in the presence of added acid. To evaluate this proposal, equal amounts of $Ni(COD)_2$, DPPF, TFA, and the allylic amine product were combined in C_6D_6. Indeed, formation of the cyclohexenyl complex **8** and free *N*-benzylmethylamine occurred within 12 h at room temperature.



(7)

To avoid any complications that could be created by generating the nickel complex in situ, we investigated in detail the reaction of allylic amines with isolated [(DPPF)Ni(COD)][40] in the presence of added TFA (eq 7). Yields of the oxidative addition products were higher when the reactions were conducted with the isolated complex than they were when conducted with the complex generated in situ.

The yields for oxidative addition of a variety of allylic amines are provided in Table 4. Various secondary and tertiary *N*-alkyl or *N*-aryl-2-cyclohexen-1-ylamines reacted with (DPPF)Ni(COD) to form the cyclohexenyl nickel complex **8** and free amine in good-to-excellent yield (entries 1−4). Allylic amines containing five-membered rings also gave the corresponding nickel complexes in good yield (entry 5). In most cases, yields of free amine were parallel to those of the nickel complexes. Cleavage of 2-cyclohepten-1-ylamine systems occurred to form the free amine in yields that were as high as those observed from cleavage of cyclohexenyl- and cyclopentenylamines. However, the identity of the nickel product was not determined in this case. The product was not simply the cycloheptenyl complex **11** analogous to cyclohexenyl **8** and cyclopentenyl **9** and was unstable in the reaction solution over long times. This exothermic cleavage of allylic amines to form free amine and dienyl complexes creates the reversible additions of amines to dienes discussed above. The oxidative addition of ammonium salts by Pd(0) complexes in catalysis and the oxidative addition of protonated amines by Ni(0) has been observed only rarely.[12,41−43]

Effects of Allylic Amine C−N Bond Cleavage. This oxidative addition of allylamine C−N bonds by Ni(0) complexes explains several current and previous observations about the reactions of amines with dienes and with metal allyl complexes. First, attack of the less nucleophilic aromatic amines appears to be too endoergic to allow turnover in the nickel system. Reaction of the isolated allyl complex with aniline produced the allylic amine in low yield, even in the presence of added cycloheptadiene. Second, reversible attack by amine could allow for telomerization with related catalysts and less hindered dienes.

Third, the exchange of amino groups in allylamines affects enantioselective aminations. Of course, racemic product is always the thermodynamically stable mixture of enantiomers from a catalytic reaction that forms chiral material. Thus, a reversible reaction that is run for extended times will generate a racemic mixture, even if the catalyst is highly enantioselective or the reagent is enantiopure. Thus, the exchange of amino groups in allylic amines that occurs by C−N oxidative addition can generate racemic product from the amination of dienes or allyl electrophiles, even when the kinetic selectivity of the catalyst highly favors one enantiomer.

For example, we observed previously that one of Trost's ligands provided high enantioselectivity for the addition of anilines to dienes in the absence of acid but provided low enantioselectivity in the presence of acid. We considered that two discrete reaction pathways could account for these results. However, the results in this work show that a combination of $[Pd(allyl)Cl]_2$ and Trost's ligand catalyzes the exchange of allylic amines with anilines rapidly in the presence of acid but slowly in the absence of acid. In the presence of acid and this catalyst, the product exchanges with free amine as fast as it is formed, and therefore, it loses its optical activity. Thus, the kinetic selectivity of the catalyst containing Trost's ligand may be the same in the presence of acid as it is in the absence of acid; the exchange process leads to an apparent reduction in selectivity. These results underscore that an enantioselective addition process, whether it be to a diene or an allylic acetate, must be faster than any parallel exchange process.

Summary

These studies have shown that a simple colorimetric assay can be used to obtain lead results on a project that uncovers not only catalysts for a new process but fundamental information about the reactivity and stability of transition-metal complexes. In this case, we have uncovered and initiated an understanding of catalysts for the formation of 1:1 adducts of a variety of amines with dienes. For the first time, the reaction scope has been broad enough to encompass both primary and secondary alkylamines, including amines containing common protective groups.

This nickel-catalyzed hydroamination occurs by generation of a nickel allyl complex, endothermic attack of amine on the

(40) van Soolingen, J.; Brandsma, L.; Kruse, C. G. Eur. Pat. Appl. EP 613719 A1 19940907, 1994.

(41) Aresta, M.; Dibenedetto, A.; Quaranta, E.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **2000**, *19*, 4199−4207.

(42) Aresta, M.; Quaranta, E.; Dibenedetto, A.; Giannoccaro, P.; Tommasi, I.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1997**, *16*, 834−841.

(43) Hirao, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *J. Organomet. Chem.* **1982**, *236*, 409−414.

coordinated diene, and displacement of the allylic amine by diene to form Ni(0). The resulting combination of Ni(0), coordinated diene, and acid regenerates the nickel allyl by a process that presumably involves insertion of the diene into a cationic nickel hydride formed by proton transfer from the ammonium salt of the allylic amine. A portion of this cycle occurs reversibly. Allylic amines are cleaved by Ni(0) and acid, and this cleavage leads to the exchange of amino groups in allylic amines with free amines. This reactivity also allows for the rare direct observation of oxidative addition of amine C−N bonds.

The highly active catalysts we have uncovered for the addition of aliphatic amines to dienes exactly complement the palladium catalysts we reported recently for the addition of aromatic amines.[6] In the future, we will compare the mechanistic results here with more detailed studies on Pd-catalyzed diene hydroamination to understand the different kinetic and thermodynamic factors that control this complementary reactivity.

Experimental Procedures.

General. Unless otherwise specified, all chemicals were used as received from commercial suppliers. All reactions were assembled in an inert atmosphere drybox using screw-cap sealed reaction vessels or NMR tubes. Trifluoroacetic acid (TFA) and acetic acid (AcOH) were added outside the drybox by microsyringe. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were obtained on a Brucker AM400 Fourier transform spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded relative to residual protiated solvent; a positive value of the chemical shift denotes a resonance downfield from TMS. ^{31}P{^{1}H} NMR spectra were recorded relative to 85% H_3PO_4; a positive value of the chemical shift denotes a resonance downfield from H_3PO_4. Mass spectrometric analyses were performed by the Mass Spectrometry Facility at the University of Illinois at Urbana-Champaign. Analytical data were obtained from either Robertson Microlit Laboratories, Inc. or Atlantic Microlab Inc. GC analyses were conducted on a Hewlett-Packard 5890 instrument connected to a 3395 integrator. Benzene, toluene, THF, and ether were distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from calcium hydride.

High Throughput Analysis of the Addition of Morpholine to 1,3-Cyclohexadiene. A stock solution of metal complexes (16.0 or 32.0 μL, 0.0040 mmol), ligands (16.0 or 32.0 μL, 0.0040 mmol), benzoic acid (10.0 μL, 0.040 mmol), morpholine (17.0 μL, 0.20 mmol), and 1,3-cyclohexadiene (19 μL, 0.80 mmol) were loaded into a glass 96-well plate using a multichannel pipet. The 96-well plate was covered with a Teflon sheet and a glass slide, which was clamped to the plate. The plate was then shaken using a rotary shaker for 24 h at room temperature. Aliquots of the reaction mixture (15 μL) were transferred to another glass 96-well plate using a multichannel pipet. Acetaldehyde (15 μL, 0.270 mmol) and 20% $Na_2Fe(CN)_5NO{\cdot}2H_2O$ in saturated aqueous $NaHCO_3$ were added to visualize the presence or absence of unreacted morpholine. A representative experiment is shown in Figure 1.

Effect of Ligand/Precatalyst Ratio. A reaction vial was charged with DPPF (0.025 to 0.20 equiv vs amine), $Ni(COD)_2$ (5.5 mg, 0.020 mmol, 0.050 equiv vs amine), *N*-benzylmethylamine (48 mg, 0.40 mmol, 1.0 equiv), 1,3-cyclohexadiene (64 mg, 0.80 mmol, 2.0 equiv), *n*-dodecane (internal standard, 9.0 μL, 0.040 mmol, 0.10 equiv), and 1.0 mL of toluene under a N_2 atmosphere in a drybox. The reaction vessel was sealed using a PTFE septum and removed from the drybox. TFA (6.2 μL, 0.080mol, 0.20 equiv) was added by syringe, and the mixture was stirred at room temperature. Aliquots (10.0 μL) were taken at 4, 8, 16, 27, and 63 h, diluted to 0.5 mL with ether, and injected onto the gas chromatogram. Yields were calculated by comparing the areas of peaks corresponding to *n*-dodecane and *N*-benzyl(2-cyclohexen-1-yl)methylamine in the gas chromatogram, using the response factors obtained from independent runs involving known quantities of isolated material.

Effect of Acid Concentration, Acid Counterion, and Solvent. A reaction vial was charged with DPPF (16.6 mg, 0.030 mmol, 0.075 equiv vs amine), $Ni(COD)_2$ (5.5 mg, 0.020 mmol, 0.050 equiv vs amine) *N*-benzylmethylamine (48 mg, 0.40 mmol, 1.0 equiv), 1,3-cyclohexadiene (64 mg, 0.80 mmol, 2.0 equiv), *n*-dodecane (internal standard, 9.0 μL, 0.040 mmol, 0.10 equiv), and 1.0 mL of solvent (toluene, benzene, Et_2O, THF, CH_2Cl_2, or CH_3CN) under a N_2 atmosphere in a drybox. The reaction was capped using a PTFE septum. Acid (0.000−0.20 equiv vs amine) was then added by syringe, and the mixture was stirred at room temperature. When the acid added was TFA, TFA-d_1, or AcOH, the acid was added after removing the reaction from the drybox. When the acid was $PhCO_2H$ or $C_6F_5CO_2H$, the acid was added in the box before sealing. Aliquots (10.0 μL) of the reaction were taken at 2, 5.25, 9, 18, 27, and 120 h, diluted to 0.5 mL with ether, and injected onto the gas chromatogram. Yields were calculated by comparing the areas of peaks corresponding to *n*-dodecane and *N*-benzyl(2-cyclohexen-1-yl)methylamine in the gas chromatogram, using the response factors obtained from independent runs involving known quantities of isolated material.

General Procedure for Preparative Scale Reactions. (2-Cyclohexen-1-yl)diethylamine (Entry 1).[44] A reaction vial was charged with DPPF (55.4 mg, 0.100 mmol, 0.0500 equiv), $Ni(COD)_2$ (27.5 mg, 0.100 mmol, 0.0500 equiv), 1,3-cyclohexadiene (320 mg, 4.00 mmol, 2.00 equiv), diethylamine (146 mg, 2.00 mmol, 1.00 equiv), and 2 mL of toluene under a N_2 atmosphere in a drybox. The reaction vessel was sealed with a PTFE septum and removed from the drybox. TFA (30.8 μL, 0.400 mmol, 0.200 equiv) was added by syringe, and the mixture was stirred at room temperature for 20 h. The mixture was then filtered through a pad of silica gel and concentrated in vacuo, and the product was isolated by Kügelrohr distillation (50 mT, 65 °C) to give 239 mg (79% yield) of the purified product as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 5.61 (d, J = 10.4 Hz, 1H) 5.49 (d, J = 10.4 Hz, 1H), 3.29 (m, 1H), 2.45 (m, 2H), 2.28 (m, 2H), 1.82 (s, 2H), 1.72−1.56 (m, 2H), 1.38 (m, 1H), 1.25 (m, 1H), 0.89 (t, J = 7.4 Hz, 6 H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 130.93, 129.21, 56.43, 44.00, 25.25, 23.51, 21.88, 14.39.

(2-Cyclohexen-1-yl)piperidine (Entry 2).[8] The product from reaction by the general procedure on a 2 mmol scale was isolated by Kügelrohr distillation (60 mT, 70 °C) to give 272 mg (82% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 5.79 (d, J = 11.2 Hz, 1H), 5.70 (d, J = 11.2 Hz, 1H), 3.22 (m, 1H), 2.56 (br q, J = 4.9 Hz, 2H), 2.48 (br q, 5.7 Hz, 2H), 1.98 (s, 2H), 1.78 (m, 2H), 1.56 (m, 6H), 1.43 (m, 2H), 1.26 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 130.42, 129.70, 61.20, 49.99, 26.78, 25.53, 25.05, 22.90, 22.02.

(2-Cyclohexen-1-yl)morpholine (Entry 3).[8] The product from reaction by the general procedure on a 2 mmol scale was isolated by Kügelrohr distillation (50 mT, 65 °C) to give 269 mg (80% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 5.89 (d, J = 10.4 Hz, 1H), 5.60 (d, J = 10.4 Hz, 1H), 3.72−3.65 (m, 4H), 3.12 (m, 1H), 2.53−2.47 (m, 4H), 1.94 (m, 2H), 1.76 (m, 2H), 1.50 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 130.43, 128.96, 67.62, 60.49, 49.35, 25.39, 23.13, 21.54.

***N*-Benzyl-(2-cyclohexen-1-yl)methylamine (Entry 4).** The product from reaction by the general procedure on a 2 mmol scale was isolated by Kügelrohr distillation (60 mT, 95 °C) to give 356 mg (80% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.36−7.18 (m, 5H), 5.94 (d, J = 10.4 Hz, 1H), 5.82 (d, J = 10.4 Hz, 1H), 3.65 (d, J = 13.3 Hz, 1H), 3.44 (d, J = 13.3 Hz, 1H), 3.30 (m, 1H), 2.23 (s, 3H), 1.98 (m, 2H), 1.84 (m, 2H), 1.55 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 140.30, 130.40, 129.85, 128.71, 128.15, 126.68, 59.37, 57.30, 37.80, 25.33, 22.72, 21.70. Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.33; H, 9.62; N, 7.07.

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***N*-Butyl-(2-cyclohexen-1-yl)amine (Entry 5).** Using the general procedure and a 7 h reaction time, the product from reaction on a 2 mmol scale was isolated by Kügelrohr distillation (40 mT, 35 °C) to give 273 mg (89% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 5.76−5.58 (m, 2H), 3.10 (m, 1H), 2.59 (m, 2H), 1.95 (m, 2H), 1.82 (m, 1H), 1.68 (m, 1H), 1.50 (m, 1H), 1.41 (m, 3H), 1.32 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 130.25, 128.68, 53.16, 46.78, 32.79, 29.68, 25.41, 20.66, 20.39, 14.10. GC/MS(EI); *m*/*z* 153. Anal. Calcd for $C_{10}H_{19}N$: C, 78.37; H, 12.50; N, 9.14. Found: C, 78.28; H, 12.59; N, 9.16.

***N*-Benzyl-(2-cyclohexen-1-yl)amine (Entry 6).**[45] Product from reaction for 6 h on a 2 mmol scale using the general procedure was isolated by Kügelrohr distillation (35 mT, 95 °C) to give 348 mg (93% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.36−7.20 (m, 5H), 5.78−5.65 (m, 2H), 3.87 (d, J = 13.0 Hz, 1H), 3.83 (d, J = 13.0 Hz, 1H), 3.22 (m, 1H), 1.99 (m, 2H), 1.89 (m, 1H), 1.72 (m, 1H), 1.48 (m, 2H), 1.31 (br s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 140.87, 130.03, 129.03, 128.46, 128.24, 126.92, 52.48, 51.10, 29.59, 25.45, 20.33.

(2-Cyclohexen-1-yl)cyclohexylamine (Entry 7).[46] Product from reaction for 37 h on a 2 mmol scale using the general procedure was isolated by Kügelrohr distillation (50 mT, 140 °C) to give 292 mg (82% yield) of clear oil. ^{1}H NMR ($CDCl_3$) δ 5.78−5.65 (m, 2H), 3.22 (m, 1H), 2.55 (m, 1H), 1.93 (m, 2H), 1.80 (m, 3H), 1.67 (m, 3H), 1.45−1.60 (m, 2H), 1.32 (m, 1H), 1.30−1.00 (m, 5H), 0.81 (br m, 1H). ^{13}C-{^{1}H} NMR ($CDCl_3$) δ 130.83, 128.46, 53.49, 49.31, 34.41, 33.94, 30.27, 26.27, 25.43, 25.33, 25.28, 20.39.

(2-Cyclohexen-1-yl)-4-methoxybenzylamine (Entry 8).[47] Product from reaction for 30 h on a 2 mmol scale using the general procedure was isolated by chromatography using 10 g silica gel and 1/3 EtOAc−hexanes as the eluent to give 378 mg (87% yield) of the purified product as a thick oil. ^{1}H NMR ($CDCl_3$) δ 7.28 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.80−5.68 (m, 2H), 3.81 (d, J = 10.5 Hz, 1H), 3.77 (s, 3H), 3.70 (overlapped d, J = 10.5 Hz, 1H), 3.18 (m, 1H), 1.98 (m, 2H), 1.88 (m, 1H), 1.72 (m, 1H), 1.48 (m, 2H), 1.22 (br s, 1H). ^{13}C-{^{1}H} NMR ($CDCl_3$) δ 158.71, 133.07, 130.13, 129.51, 129.11, 113.94, 55.47, 52.49, 50.59, 29.69, 25.54, 20.45. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.57; H, 8.74; N, 6.38.

(2-Cyclohexen-1-yl)diphenylmethylamine (Entry 9).[48] Product from reaction for 60 h on a 2 mmol scale using the general procedure was isolated by Kügelrohr distillation (0.01 mmHg, 175 °C) to give 448 mg (85% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.45−7.10 (m, 10H), 5.85−5.68 (m, 2H), 5.05 (s, 1H), 3.05 (m, 1H), 1.96 (m, 2H), 1.88 (m, 1H), 1.69 (m, 1H), 1.50 (m, 2H), 1.42 (br s, 1H). ^{13}C-{^{1}H} NMR ($CDCl_3$) δ 144.79, 144.47, 130.46, 128.85, 128.65, 128.62, 127.64, 127.60, 127.12, 127.10, 64.21, 50.37, 29.82, 25.55, 20.36. Anal. Calcd for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.89; H,8.16; N, 5.33.

(2-Cyclohexen-1-yl)dibenzylamine (Entries 10 and 11).[49] Using the general procedure, allowing the reagents to react for 113 h at room temperature, the product from reaction on a 2 mmol scale was isolated by Kügelrohr distillation (60 mT, 116 °C) to give 310 mg (56% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.40−7.10 (m, 10H) 5.82−5.65 (m, 2H), 3.68 (d, J = 14.1 Hz, 2H), 3.50 (d, J = 14.1 Hz, 2H), 3.31 (m, 1H), 1.93 (m, 3H), 1.76 (m, 1H), 1.53 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 141.10, 131.08, 130.26, 128.69, 128.32, 126.81, 54.72, 54.05, 25.58, 23.40, 22.07. Using the general procedure, but allowing the reagents to react at 60 °C for 72 h, the product from reaction on a 2 mmol scale was isolated by Kügelrohr distillation (60 mT, 116 °C) to give 392 mg (71% yield) of colorless oil.

***N*-Benzyl-(2-cyclopenten-1-yl)methylamine (Entry 12).** Product from reaction for 43 h on a 2 mmol scale using the general procedure and freshly cracked cyclopentadiene was isolated by Kügelrohr distillation (40 mT, 62 °C) to give 341 mg (91% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 7.40−7.11 (m, 5H), 5.92−5.72 (m, 2H), 3.90 (m, 1H), 3.56 (d, J = 12.9 Hz, 1H), 3.39 (d, J = 12.9 Hz, 1H), 2.45−2.20 (m, 2H), 2.10 (s, 3H), 2.02−1.75 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 139.95, 135.56, 131.46, 129.04, 128.26, 126.85, 70.40, 58.37, 38.09, 31.91, 23.70. HRMS Calcd for $C_{13}H_{17}N^+$ 187.1361; Found 187.1360.

***N*-Benzyl-(2-cyclohepten-1-yl)methylamine (Entry 13).** Product from reaction for 60 h on a 2 mmol scale using the general procedure was isolated by Kügelrohr distillation (50 mT, 85 °C) to give 404 mg (94% yield) of colorless oil. ^{1}H NMR (C_6D_6) δ 7.47 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.7 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 6.08−6.02 (m, 1H), 5.92−5.82 (m, 1H), 3.62 (d, J = 13.5 Hz, 1H), 3.55 (d, J = 13.5 Hz, 1H), 3.39 (d, J = 10.1 Hz, 1H), 2.25 (s, 3H), 2.10 (m, 1H), 2.00−1.84 (m, 3H) 1.61 (m, 1H), 1.52−1.25 (m, 3H). ^{13}C{^{1}H} NMR (C_6D_6) δ 141.22, 136.43, 131.28, 129.26, 128.86, 127.41, 64.53, 58.59, 37.95, 29.45, 29.27, 29.18, 27.53. Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.53; H, 9.90; N, 6.50.

(2-Cyclohepten-1-yl)morpholine (Entry 14).[50] Product from reaction for 60 h on a 2 mmol scale using the general procedure was isolated by Kügelrohr distillation (50 mT, 85 °C) to give 404 mg (94% yield) of colorless oil. ^{1}H NMR ($CDCl_3$) δ 5.92−5.75 (m, 2H), 3.72−3.65 (m, 4H), 3.20 (d, J = 11.5 Hz, 1H), 2.65−2.50 (m, 4H), 2.16 (m, 1H), 2.01 (m, 2H), 1.84 (m, 1H), 1.66 (m, 1H), 1.43 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 134.39, 131.64, 67.66, 65.09, 49.23, 29.01, 28.98, 28.51, 26.72. Anal. Calcd for $C_{11}H_{19}N$: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.42; H, 10.61; N, 7.72.

***N*-Benzyl-(2-cycloocten-1-yl)methylamine (Entry 15).** Product from reaction for 84 h on a 2 mmol scale at 60 °C using the general procedure was isolated by Kügelrohr distillation (50 mT, 78 °C) to give 176 mg (38% yield) of colorless oil as a mixture of three cyclooctenyl regioisomers that were not separated. ^{1}H NMR ($CDCl_3$) δ 7.30−7.10 (m, 7.9 H), 5.80−5.48 (m, 3.3 H), 3.70 (d, J = 20.4 Hz, 1.0 H), 3.60−3.40 (m, 3.2 H), 2.70−2.20 (m, 2.2 H), 2.20 (s, 3.0 H), 2.17 (s, 1.3 H), 2.11 (s, 1.1 H), 2.15−2.00 (m, 2.8 H), 1.90−1.25 (m, 12.4 H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 140.36, 139.78, 130.91, 130.22, 130.13, 129.94, 129.76, 129.00, 128.71, 128.63, 128.47, 128.14, 128.10, 126.69, 126.65, 126.64, 64.45, 63.01, 60.17, 59.15, 58.04, 57.31, 38.48, 38.13, 37.71, 33.42, 30.56, 29.69, 29.52, 29.36, 28.14, 27.86, 26.90, 26.85, 26.77, 25.68, 25.03, 24.84, 23.91, 23.66. GC/MS 10.71 min (50.1%) *m*/*z* 229, 10.76 min (16.4%) *m*/*z* 229, 10.97 min (30.2%) *m*/*z* 229. Anal. Calcd for $C_{15}H_{23}N$: C, 83.79; H, 10.11; N, 6.11. Found: C, 83.74; H, 10.16; N, 6.08.

***N*-Benzyl-(1-buten-3-yl)methylamine (Entry 16).**[51] Under a nitrogen atmosphere, butadiene (216 mg, 4 mmol, 2 equiv) was condensed into a preweighed, flame-dried Schlenk flask at −78 °C. The flask was then allowed to warm to room temperature, the exact weight of the diene was determined, and the excess of diene was removed. The flask was then cooled to −78 °C, and a solution of DPPF (55.4 mg, 0.100 mmol, 0.0500 equiv), $Ni(COD)_2$ (27.5 mg, 0.100 mmol, 0.0500 equiv), *N*-benzylmethylamine (242 mg, 2.00 mmol, 1.00 equiv), and TFA (30.8 μL, 0.400 mmol, 0.200 equiv) in 2 mL of toluene was added by syringe. The reaction was allowed to warm to room temperature, and after 0.5 h it was filtered through a pad of silica gel and concentrated in vacuo. The product was isolated by Kügelrohr distillation (40 mT, 30 °C) to give 291 mg (83% yield) of colorless oil as a mixture of three butenyl regioisomers in a 10:1:1 ratio. ^{1}H NMR ($CDCl_3$) δ 7.40−7.15 (m, 6.1H), 6.00−5.83 (m, 1.0 H), 5.62−5.50 (m, 0.4H), 5.15−5.00 (m, 2.0H), 3.55 (d, J = 13.3 Hz, 1.1H), 3.40 (d, J = 13.3 Hz, 1.1 H), 3.32−3.15 (m, 1.0H), 3.08 (d, J = 6.4 Hz, 0.2H), 2.95 (d, J = 5.7 Hz, 0.2H), 2.15

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(s, 3.6H), 1.70 (d, $J = 4.9$ Hz, 0.3H), 1.61 (d, $J = 6.2$ H, 0.3H), 1.18 (d, $J = 6.7$ Hz, 3.1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 140.38, 140.16, 139.36, 139.32, 129.21, 129.18, 128.92, 128.78, 128.66, 128.30, 127.03, 126.99, 126.86, 115.57, 61.97, 61.79, 60.89, 59.87, 58.16, 53.75, 42.30, 42.13, 37.83, 28.18, 17.97, 16.25, 13.27. GC/MS 7.85 min (86.3%) *m*/*z* 175, 8.05 min (6.7%) *m*/*z* 175, 8.17 min (6.6%) *m*/*z* 175.

Ni-Catalyzed 1,3-Diene Hydroaminations at Low Catalyst Loadings. Representative Procedure. (2-Cyclohexen-1-yl)morpholine. A reaction vial was charged with DPPF (13.9 mg, 0.0250 mmol, 0.0020 equiv), $Ni(COD)_2$ (6.9 mg, 0.025 mmol, 0.0020 equiv), 1,3-cyclohexadiene (1.00 g, 12.50 mmol, 1.000 equiv), pentafluorobenzoic acid (5.3 mg, 0.025 mmol, 0.0020 equiv), and morpholine (1.09 mg, 12.50 mmol, 1.000 equiv) under a N_2 atmosphere in a drybox. The reaction vessel was sealed with a PTFE septum and removed from the drybox, and the mixture was stirred at 65 °C for 36 h. The product was isolated by Kügelrohr distillation (15 mT, 60 °C) to give 1.918 g (92% yield) of colorless oil that was identical to the material described above.

Screening of Catalysts for Exchange Reaction. A reaction vial was charged with metal complex [$Ni(COD)_2$ (2.8 mg, 0.010 mmol, 0.050 equiv), [(π-allyl)PdCl]$_2$, (1.8 mg, 0.0050 mmol, 0.025 equiv)], ligand [DPPF (5.5 mg, 0.010 mmol, 0.050 equiv), PPh_3 (5.2 mg, 0.020 mmol, 0.100 equiv)], (2-cyclohexen-1-yl)aniline (35 mg, 0.20 mmol, 1.0 equiv), morpholine (52 mg, 0.60 mmol, 3.0 equiv), *n*-dodecane (internal standard, 17 mg, 0.10 mmol, 0.50 equiv), and 0.50 mL of THF under a N_2 atmosphere in a drybox. The reaction vessel was sealed using a PTFE septum and removed from the drybox. TFA (1.6 μL, 0.020 mmol, 0.10 equiv) was added by syringe, and the mixture was stirred at room temperature. Aliquots (10.0 μL) were taken at 5 and 20 h, diluted to 0.5 mL with ether, and injected onto the gas chromatogram. Yields were calculated by comparing the areas of peaks corresponding to *n*-dodecane and (2-cyclohexen-1-yl)morpholine in the gas chromatogram, using the response factors obtained from independent runs involving known quantities of isolated material.

Determination of Thermodynamic Stability of Allylic Amines: Preparation of Substrates. Allylic amines **3**, **4**, and **5** were synthesized by the method described above on a 4 mmol reaction scale. (2-Cyclohexen-1-yl)aniline (**1**) was synthesized by the method reported before.[6] Data for allylic amines **3**, **4**, and **5** are shown below.

(2-Cyclohexen-1-yl)hexylamine (3): ^1H NMR ($CDCl_3$) δ 5.76−5.63 (m, 2H), 3.16−3.08 (m, 1H), 2.68−2.56 (m, 2H), 2.05−1.82 (m, 3H), 1.76−1.65 (m, 1H), 1.59−1.21 (m, 11H), 0.87 (t, $J = 6.8$ Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 130.11, 128.62, 53.04, 47.01, 31.78, 30.51, 29.55, 27.13, 25.29, 22.60, 20.28, 14.03. Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79; N, 7.72. Found: C, 79.23; H, 12.54; N, 7.66.

(2-Cyclohexen-1-yl)-4-benzylmethylamine (4): ^1H NMR ($CDCl_3$) δ 7.23 (d, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 2H), 5.81−5.69 (m, 1H), 3.83 (d, $J = 12.8$ Hz, 1H), 3.78 (d, $J = 12.8$ Hz, 1H), 3.25−3.18 (m, 1H), 2.33 (s, 3H), 2.08−1.85 (m, 3H), 1.80−1.70 (m, 1H), 1.62−1.41 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 137.63, 136.36, 129.90, 129.03, 128.89, 128.08, 52.27, 50.66, 29.46, 25.31, 21.06, 20.22. Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.23; H, 9.37; N, 6.91.

(2-Cyclohexen-1-yl)dibutylamine (5): ^1H NMR ($CDCl_3$) δ 5.79−5.72 (m, 1H), 5.60 (d, $J = 10.0$ Hz, 1H), 3.40−3.31 (m, 1H), 2.51−2.29 (m, 4H), 2.05−1.87 (m, 2H), 1.83−1.74 (m, 2H), 1.57−1.22 (m, 10H), 0.89 (t, $J = 7.0$ Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 131.24, 129.23, 56.89, 50.63, 31.56, 25.36, 23.68, 22.01, 20.70, 14.13. Anal. Calcd for $C_{14}H_{27}N$: C, 80.31; H, 13.00; N, 6.69. Found: C, 80.13; H, 12.85; N, 6.68.

Determination of Thermodynamic Stability of Allylic Amines by GC Analysis. A reaction vial was charged with $Ni(COD)_2$ (2.8 mg, 0.010 mmol, 0.050 equiv), DPPF (5.5 mg, 0.010 mmol, 0.050 equiv), allylic amine (0.20 mmol, 1.0 equiv), free amine (0.20 mmol, 1.0 equiv), *n*-tetradecane (internal standard, 20 mg, 0.10 mmol, 0.50 equiv), and 0.50 mL of THF under a N_2 atmosphere in a drybox. The reaction vessel was sealed using a PTFE septum and removed from the drybox. TFA (1.6 μL, 0.020mol, 0.10 equiv) was added by syringe, and the mixture was stirred at room temperature. Aliquots (10.0 μL) were taken at 1, 3, 9, 24, 48, and 72 h and diluted to 0.5 mL with ether, and injected onto the gas chromatogram. Yields of two allylic amines were calculated by comparing the areas of peaks corresponding to *n*-tetradecane and allylic amines in the gas chromatogram, using the response factors obtained from independent runs involving known quantities of isolated material. The ratio of two allylic amines at the equilibrium was determined from yields.

Determination of Thermodynamic Stability of Allylic Amines by ^1H NMR Analysis. An NMR sample tube equipped with a screw cap containing a Teflon-lined septum was charged with $Ni(COD)_2$ (2.2 mg, 0.0080 mmol, 0.050 equiv), DPPF (4.4 mg, 0.0080 mmol, 0.050 equiv), allylic amine (0.16 mmol, 1.0 equiv), free amine (0.16 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (internal standard, 9.0 mg, 0.053 mmol, 0.33 equiv), and 0.40 mL of THF-d_8 under an N_2 atmosphere in a drybox. The tube was removed from the drybox. TFA (1.2 μL, 0.016mol, 0.10 equiv) was added by syringe, and the tube was shaken at room temperature. ^1H NMR spectra were obtained at 1, 8, 24, 48, and 72 h. Yields of two allylic amines were calculated by comparing the areas of peaks corresponding to 1,3,5-trimethoxybenzene and allylic amines in the ^1H NMR spectra. The ratio of two allylic amines at the equilibrium was determined from these yields.

Determination of the Stereochemistry of the Exchange Reaction: Synthesis of Substrate. Diisopropyl azodicarboxylate (1.4 g, 6.9 mmol, 1.3 equiv) was added dropwise in the dark to a solution of 5-methyl-2-cyclohexen-1-ol (590 mg, 5.3 mmol, 1.0 equiv),[52] phthalimide (1.0 g, 6.9 mmol, 1.3 equiv), and triphenylphosphine (1.8 g, 6.9 mmol, 1.3 equiv) in 50 mL of THF, and the resulting mixture was stirred at room temperature for 22 h. The mixture was poured into a separating funnel containing 200 mL of water, and the aqueous layer was extracted with *n*-hexane (150 mL × 3). The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane:EtOAc = 9:1 to 4:1) to give 697 mg (55% yield) of *trans*-*N*-(5-methyl-2-cyclohexen-1-yl)phthalimide as a white solid. ^1H NMR ($CDCl_3$) δ 7.87−7.78 (m, 2H), 7.76−7.66 (m, 2H), 6.04−5.97 (m, 1H), 5.59 (dq, $J = 10.1$, 2.4 Hz, 1H), 4.99−4.86 (m, 1H), 2.46−2.33 (m, 1H), 2.31−2.18 (m, 1H), 2.16−2.05 (m, 1H), 1.86−1.60 (m, 2H), 1.04 (d, $J = 6.4$ Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 168.38, 133.78, 132.00, 129.93, 124.22, 123.00, 44.97, 34.69, 31.93, 25.46, 20.02. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.40; H, 6.13; N, 5.80. *trans*-*N*-(5-Methyl-2-cyclohexen-1-yl)phthalimide (697 mg, 2.89 mmol) was then dissolved in 2.5 mL of hydrazine monohydrate and 50 mL of methanol, and the resulting mixture was refluxed overnight. Methanol was removed by distillation to give about 15 mL of solution containing a white precipitate. To this mixture was added 5 mL of concentrated HCl, and the resulting mixture was refluxed for a further 1 h. After cooling to room temperature, the white solid that appeared was removed by filtration through a pad of Celite, and the filtrate was concentrated. The residual white solid was dissolved in ethanol and then filtered through a pad of Celite. The filtrate was concentrated, and the residue was treated with 50 mL of a saturated aqueous KOH solution. The aqueous layer was extracted with ether (3 × 20 mL), and the combined organic layers were washed with 50 mL of brine. After drying over Na_2CO_3, careful evaporation of the solvent gave 217 mg (68% yield) of *trans*-5-methyl-2-cyclohexen-1-ylamine containing about 7% of the cis isomer as a pale yellow oil, which was used without further purification. ^1H NMR ($CDCl_3$) δ 5.73 (d, $J = 10.0$ Hz, 1H), 5.69 (d, $J = 10.0$ Hz, 1H), 3.36 (t, $J = 3.8$ Hz, 1H), 2.14−2.03 (m, 1H), 1.90−1.77 (m, 1H), 1.66−1.28 (m, 5H), 0.97 (d, $J = 6.8$ Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 130.71, 127.90, 45.46,

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40.59, 33.57, 23.60, 21.48. HRMS(EI) Calcd for $C_7H_{13}N^+$: 111.0970; found: 111.0966.

Determination of the Stereochemistry of the Exchange Reaction; Exchange of 5-*trans*-Methyl-2-cyclohexen-1-ylamine with Morpholine Catalyzed by Ni-DPPF and Trifluoroacetic Acid. A reaction vial was charged with $Ni(COD)_2$ (6.9 mg, 0.025 mmol, 0.050 equiv), DPPF (13.9 mg, 0.025 mmol, 0.050 equiv), *trans*-5-methyl-2-cyclohexen-1-ylamine (56 mg, 0.50 mmol, 1.0 equiv), morpholine (131 mg, 1.50 mmol, 3.0 equiv), and 1.0 mL of THF under an N_2 atmosphere in a drybox. The reaction vessel was sealed using a PTFE septum and removed from the drybox. TFA (4.0 μL, 0.050 mmol, 0.10 equiv) was added by syringe, and the mixture was stirred at room temperature for 34 h. The mixture was filtered through a pad of silica gel and concentrated. The residue was purified by Kügelrohr distillation (25 mT, 100 °C) to give 68 mg (75% yield) of *trans*-(5-methyl-2-cyclohexen-1-yl)morpholine as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 5.90−5.77 (m, 1H), 5.71−5.62 (m, 1H), 3.77−3.62 (m, 4H), 3.08−3.01 (m, 1H), 2.67−2.57 (m, 4H), 2.20−2.09 (m, 1H), 1.95−1.78 (m, 2H), 1.65−1.54 (m, 1H), 1.36−1.25 (m, 1H), 0.96 (d, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 130.09, 127.29, 67.26, 57.86, 49.99, 33.09, 31.16, 25.59, 20.90. HRMS(EI) Calcd for $C_{11}H_{19}NO^+$: 181.1467; found: 181.1466.

Racemization of Chiral Allylic Amines under the Condition of the Amine Exchange Reaction in the presence of Ni−DPPF. A reaction vial was charged with $Ni(COD)_2$ (1.4 mg, 0.0050 mmol, 0.050 equiv), DPPF (2.8 mg, 0.0050 mmol, 0.0050 equiv), (*S*)-*N*-(2-cyclohexen-1-yl)aniline (17 mg, 0.10 mmol, 1.0 equiv), aniline (9.3 mg, 0.10 mmol or none), and 0.25 mL of THF under an N_2 atmosphere in a drybox. The reaction vessel was sealed using a PTFE septum and removed from the drybox. TFA (0.8 μL, 0.010 mmol, 0.10 equiv or none) was added by syringe, and the mixture was stirred at room temperature. Aliquots (10.0 μL) were taken after 5, 24, and 72 h and diluted to 0.5 mL with ether. The enantiomeric excess at these times were determined by chiral stationary phase HPLC using a Daicel Chiralcel OJ column (flow 0.5 mL/min with hexanes as eluent).

Racemization of Chiral Allylic Amine under the Conditions of the Amine Exchange Reaction in the presence of Pd−(*R*,*R*)-Np-Trost Ligand. A reaction vial was charged with [(π-allyl)PdCl]$_2$ (1.8 mg, 0.0050 mmol, 0.050 equiv), (*R*,*R*)-naphthyl-Trost ligand **6** (8.7 mg, 0.011 mmol, 0.11 equiv), (*S*)-*N*-(2-cyclohexen-1-yl)aniline (17 mg, 0.10 mmol, 1.0 equiv), aniline (9.3 mg, 0.10 mmol or none), and 0.10 mL of THF under an N_2 atmosphere in a drybox. The reaction vessel was sealed using a PTFE septum and removed from the drybox. TFA (0.8 μL, 0.010 mmol, 0.10 equiv or none) was added by syringe, and the mixture was stirred at room temperature. Aliquots (10.0 μL) were taken after 5, 20, and 50 h and diluted to 0.5 mL with ether. The enantiomeric excesses were determined as described above.

[Bis(diphenylphosphino)ferrocene]nickel(II)(cyclooctenyl) Trifluoroacetate (7). A reaction vial was charged with DPPF (554 mg, 1.00 mmol, 1.00 equiv), $Ni(COD)_2$ (275 mg, 1.00 mmol, 1.00 equiv), and 10 mL of benzene under an N_2 atmosphere in a drybox. The resulting orange slurry was stirred for 1 h at which time TFA (77 μL, 1.00 mmol, 1.00 equiv) was added via syringe. The reaction was stirred at room temperature for 1 h, and at that stage the ^{31}P{^{1}H} NMR spectrum exhibited a single resonance at 25.52 ppm (C_6D_6). The benzene solvent was evaporated in vacuo in the drybox, and the resulting yellow/orange solid was dissolved in 5 mL of THF, filtered through a pad of Celite, layered with 10 mL of pentane, and placed in a freezer at −30 °C. Orange crystals formed the next day. These crystals were filtered, washed with pentane (2 × 15 mL), and dried in vacuo to give 610 mg (73%) of **7** as orange crystals. ^{1}H NMR (CD_2Cl_2, −20 °C) δ 7.73−7.48 (m, 20 H), 5.57 (t, J = 8.2 Hz, 1 H), 4.50 (d, J = 8.7 Hz, 4 H), 4.30 (br s, 4 H), 3.98 (br s, 2 H), 1.46 (m, 1 H), 1.16 (m, 7H), 0.78 (m, 2 H); ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C) δ 134.45 (apparent t, 6.1 Hz), 132.73 (apparent t, J_{CP} = 5.5 Hz), 132.24, 132.07 (t, J_{CP} = 53.3 Hz), 132.02 (t, J_{CP} = 53.0 Hz), 131.42, 129.49 (apparent t, J_{CP} = 5.1 Hz), 129.37 (apparent t, J_{CP} = 4.8 Hz), 84.69 (m), 75.80 (apparent t, J_{CP} = 5.9 Hz), 74.47 (apparent t, J_{CP} = 4.1 Hz), 74.22 (m), 73.90 (m), 30.189 (s), 26.49 (broad s), 21.80 (broad s). at −70 °C, the spectral features of the nickel allyl were less well resolved but the TFA counterion was observed: δ 160.06 (q, J_{CF} = 37 Hz), 115.63 (q, J_{CF} = 290.1 Hz) ^{31}P{^{1}H} NMR (C_6D_6) δ 25.52. IR (KBr, cm^{-1}) 3055, 2926, 2849, 1779, 1737, 1686, 1435, 1387, 1308, 1266, 1198, 1098, 1036, 999; HRMS(FAB) Calcd for $C_{42}H_{41}FeNiP_2^+$: 721.13863; found: 721.1385. A crystal suitable for X-ray crystallography was grown by slow evaporation at −30 °C of a solution of **7** in CH_2Cl_2.

[Bis(diphenylphosphino)ferrocene]nickel(II)(cyclohexenyl) Trifluoroacetate (8). A reaction vial was charged with DPPF (554 mg, 1.00 mmol, 1.00 equiv), $Ni(COD)_2$ (275 mg, 1.00 mmol, 1.00 equiv), and 5 mL of THF under an N_2 atmosphere in a drybox. 1,3-Cyclohexadiene (400 mg, 5.00 mmol, 5.00 equiv) was added dropwise, and the resulting orange slurry was stirred for 1 h. After this time, TFA (92.4 μL, 1.20 mmol, 1.20 equiv) was added by syringe, and the reaction immediately turned a deep red color. The reaction was stirred at 50 °C for 15 min, and at that stage the ^{31}P{^{1}H} NMR spectrum exhibited a single resonance at 26.68 ppm (C_6D_6). The THF was evaporated in vacuo, and the resulting thick, gummy residue was dissolved in 3 mL THF, layered with 10 mL of pentane and placed in a freezer at −30 °C. Orange crystals formed over the course of 2 days. These crystals were filtered, washed with pentane (2 × 15 mL), and dried in vacuo to give 653 mg (81%) of **8** as orange crystals. ^{1}H NMR (−20 °C, CD_2Cl_2) δ 8.25−8.09 (m, 20 H), 5.70 (br s, 1 H), 4.70 (br s, 2 H), 4.55 (br s, 4 H), 4.37 (br s, 2 H), 4.02 (br s, 2 H), 1.50−0.50 (m, 6 H). ^{13}C{^{1}H} NMR (−20 °C, CD_2Cl_2) δ 160.37 (q, J_{CF} = 36.7 Hz), 134.33 (apparent t, J_{CP} = 6.1 Hz), 132.99 (apparent t, J_{CP} = 5.5 Hz), 132.15, 132.08 (t, J_{CP} = 96 Hz), 132.04 (t, J_{CP} = 95 Hz), 131.48 (s), 129.56 (d, J_{CP} = 4.8 Hz), 129.46 (d, J_{CP} = 4.5 Hz), 116.30 (q, J_{CF} = 290.1 Hz), 110.71, 86.04 (m), 75.47 (apparent t, J_{CP} = 5.1 Hz), 75.01 (apparent t, J_{CP} = 5.1 Hz), 74.31 (s), 73.89 (s), 73.29 (d, J_{CP} = 55.1 Hz), 29.39, 18.57; ^{31}P{^{1}H} NMR (C_6D_6) δ 26.68; IR (KBr, cm^{-1}) 3057, 3023, 2931, 1966, 1782, 1741, 1586, 1572, 1480, 1436, 1418, 1387, 1308, 1211, 1096, 1035; HRMS(FAB) calcd for $C_{40}H_{37}FeNiP_2^+$ 693.1073; found 693.1075. Anal. Calcd for $C_{42}H_{37}F_3FeNiO_2P_2$: C, 62.49; H, 4.62; Found: C, 62.11; H, 4.67. A crystal suitable for X-ray crystallography was grown by slow evaporation at room temperature of a solution of **8** in a mixture of benzene and THF.

[Bis(diphenylphosphino)ferrocene]nickel(II)(cyclopentenyl) Trifluoroacetate (9). A reaction vial was charged with (DPPF)Ni(COD) (144 mg, 0.200 mmol, 1.00 equiv), freshly cracked 1,3-cyclopentadiene (66 mg, 1.00 mmol, 5.00 equiv), and 1 mL of THF under a N_2 atmosphere in a drybox. The resulting orange slurry was stirred for 45 min, and then TFA (15.4 μL, 0.20 mmol, 1.00 equiv) was added by syringe. The mixture immediately turned a deep red color. The mixture was stirred at 50 °C for 30 min. THF was evaporated, and the resulting thick, gummy residue was dissolved in 3 mL of THF, layered with 10 mL of pentane and placed in a freezer at −30 °C. Orange crystals formed overnight. These crystals were filtered, washed with pentane (2 × 15 mL), and dried in vacuo to give 119 mg (75% yield) of **7** as orange crystal. ^{1}H NMR (−20 °C, CD_2Cl_2) δ 7.46−7.60 (m, 20 H), 5.89 (br s, 1 H), 4.73 (br s, 2 H), 4.26 (br s, 6 H), 4.01 (br s, 2 H), 1.12−1.93 (m, 4 H). ^{13}C{^{1}H} NMR (−70 °C, CD_2Cl_2) δ 159.40 (q, J_{CF} = 31.8 Hz), 133.64 (apparent t, J_{CP} = 5.7 Hz), 132.49 (apparent t, J_{CP} = 5.1 Hz), 131.79 (d, J_{CP} = 49.7 Hz), 131.46, 131.10, 130.69 (d, J_{CP} = 45.9 Hz), 129.12, 129.08, 117.14 (q, J_{CF} = 298.7 Hz), 112.24, 90.68 (apparent t, J_{CP} = 6.0 Hz), 74.77 (apparent t, J_{CP} = 5.4 Hz), 74.53 (apparent t, J_{CP} = 4.2 Hz), 73.81, 73.37, 72.72 (d, J_{CP} = 53.8 Hz), 27.27. ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 24.91. IR (KBr, cm^{-1}) 3067, 2910, 2869, 1680, 1480, 1435, 1389, 1309, 1296, 1197, 1111, 1040, 998, 814, 798, 750, 700, 632. HRMS(FAB) calcd for $C_{39}H_{35}FeNiP_2^+$ 679.0919, found 679.0920.

[Bis(diphenylphosphino)ferrocene]nickel(II)(cycloheptenyl) Trifluoroacetate (11). A reaction vial was charged with DPPF (111 mg,

0.200 mmol, 1.00 equiv), $Ni(COD)_2$ (55 mg, 0.200 mmol, 1.00 equiv), 1,3-cycloheptadiene (94 mg, 1.00 mmol, 5.00 equiv), and 1 mL of THF under a N_2 atmosphere in a drybox. The resulting orange slurry was stirred for 1 h, and then TFA (15.4 μL, 0.20 mmol, 1.00 equiv) was added by syringe. The mixture immediately turned a deep red color. The mixture was stirred at 50 °C for 1 h. THF was evaporated in vacuo, and the resulting thick, gummy residue was dissolved in 3 mL of THF, layered with 10 mL of pentane, and placed in a freezer at −30 °C. Brown solid formed overnight. These solid were filtered, washed with pentane (2 × 15 mL), and dried in vacuo to give 125 mg (75% yield) of product as a brown solid. ^{1}H NMR (−20 °C, CD_2Cl_2) δ 7.57−7.67 (m, 8 H), 7.45−7.57 (m, 12 H), 5.12 (d, J = 9.6 Hz, 1H) 4.71 (d, J = 4.4 Hz, 2 H), 4.60 (br s, 2 H), 4.56 (br s, 2 H), 4.34 (br s, 2H), 3.95 (br s, 2H), 1.32−0.91 (m, 6H), 0.62−0.42 (m, 2H). ^{13}C{^{1}H} NMR (−70 °C, CD_2Cl_2) δ 159.43 (q, J_{CF} = 31.9 Hz), 134.42 (apparent t, J_{CP} = 5.4 Hz), 132.11 (m), 131.93, 130.81, 129.11 (apparent t, J_{CP} = 4.6 Hz), 128.90, 117.10 (q, J_{CF} = 298.9 Hz), 108.48, 89.21 (d, J_{CP} = 13.7 Hz), 75.76 (apparent t, J_{CP} = 5.5 Hz), 73.77, 73.57, 73.15 (d, J_{CP} = 54.5 Hz), 31.05, 26.44 (two aromatic quaternary carbons could not be observed). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 24.44. IR (KBr, cm^{-1}) 3050, 2918, 2825, 1695, 1480, 1435, 1385, 1306, 1196, 1164, 1112, 1029, 999, 893, 841, 810, 795, 749, 701, 635. HRMS(FAB) calcd for $C_{41}H_{39}FeNiP_2^+$ 707.1230, found 707.1229.

Reaction of Cyclohexadiene with DNMeBn. Deuterated amine was generated by mixing the neat amine with three equal volumes of D_2O, adding ether, drying over $MgSO_4$, and evaporating the ether. This amine contained roughly 85% deuterium. This amine was allowed to react with cyclohexadiene using the standard procedure, except that TFA-d_1 was used as cocatalyst. GC/MS analysis of this reaction showed product that was between 45 and 60% d_1 and 55−40% d_0. No appreciable polydeuterated products were present. ^{2}H NMR spectrometry showed resonances of equal intensity at 1.95 and 1.55 ppm.

Reaction of Cyclohexenyl Complex 8 with Amines in the presence of Cycloheptadiene. Complex **8** (6.5 mg, 7.7 μmol) was dissolved in 0.7 mL of THF. To this solution was added 26 μL (237 μmol) of cycloheptadiene, followed by 26 μL (202 μmol) of *N*-benzylmethylamine or 26 mg of *p*-toluidine, and 4.6 μL (20 μmol) of dodecane as internal standard. The resulting mixture was transferred to a screw-capped NMR sample tube. After 30 min a ^{31}P NMR spectrum showed in the reaction of *N*-benzylmethylamine conversion of **6** to the same set of signals observed in the reaction of cycloheptadiene with *N*-benzylmethylamine catalyzed by $Ni(COD)_2$, DPPF, and TFA co-catalyst. A GC at this time showed formation of *N*-2-cyclohexen-1-yl, *N*-benzylmethylamine in 90% yield. ^{31}P NMR spectra obtained on the reaction of aniline over the course of 5 d showed conversion of the ligated DPPF in the starting complex to free DPPF, and GC showed the formation of *N*-2-cyclohexen-1-yl aniline in 10% yield.

Reaction of $Ni(COD)_2$, DPPF, TFA, and *N*-Benzyl(2-cyclohexen-1-yl)methylamine. Into a vial were placed 5.5 mg (0.02 mmol) of $Ni(COD)_2$ and 11 mg (0.02 mmol) of DPPF. These materials were dissolved in 0.7 mL of C_6D_6. This mixture was added to a second vial containing 4.0 mg (0.02 mmol) of *N*-benzyl(2-cyclohexen-1-yl)-methylamine. This solution was transferred to an NMR sample tube equipped with a screw cap containing a Teflon-lined septum. To this solution was added 0.02 mmol of trifluoroacetic acid. After 14 h, ^{31}P and ^{1}H NMR spectroscopy showed complete conversion to cyclohexenyl complex **8** and free amine. GC/MS confirmed the presence of free amine.

Oxidative Addition of Allylic Amines to (DPPF)Ni(COD). An NMR sample tube equipped with a screw cap containing a Teflon-lined septum was charged with (DPPF)Ni(COD)[40] (14.4 mg, 0.020 mmol, 1.0 equiv), allylic amine (0.10 mmol, 5.0 equiv), *n*-dodecane (internal standard, 1.7 mg, 0.010 mmol, 0.5 equiv), (*o*-tolyl)$_3$P (internal standard, 3.0 mg, 0.010 mmol, 0.33 equiv), and 0.80 mL of THF under a N_2 atmosphere in a drybox. The tube was removed from the drybox. TFA (1.5 μL, 0.020 mol, 1.0 equiv) was added by syringe, and the tube was shaken at room temperature. Aliquots (10.0 μL) were taken at 1, 3, and 5 h, diluted to 0.5 mL with ether, and injected onto the gas chromatogram. ^{31}P NMR spectra were also obtained at the same time intervals. Yields of free *N*-benzylmethylamine and aniline were calculated by comparing the areas of peaks corresponding to *n*-dodecane and amines in the gas chromatogram by using the response factors obtained from independent runs involving known quantities of isolated material. Yields of π-allyl nickel complexes were determined by comparing the areas of peaks corresponding to (*o*-tolyl)$_3$P in ^{31}P NMR spectra.

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Supporting Information Available: X-ray structural analysis of **7** and **8** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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