Regioselectivity in the Palladium/(*S*)-BINAP(S)-Catalyzed Asymmetric Allylic Amination: Reaction Scope, Kinetics, and Stereodynamics

J. W. Faller* and Jeremy C. Wilt

Department of Chemistry, Yale University, New Haven, Connecticut 06520

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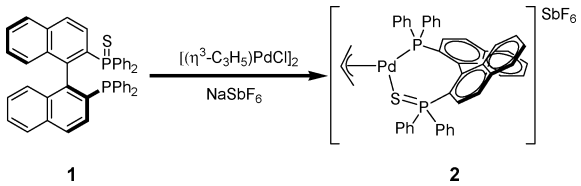
Studies defining the scope of the reaction and understanding the factors controlling the unusual regioselectivity observed in the Pd/{BINAP(S)}-catalyzed allylic amination reaction are presented. Most of the unsymmetrically substituted allylic substrates tested show regioselectivity that is the reverse of that which would normally be expected in Pd-catalyzed systems. Several cationic η^3-allylic complexes containing a Pd{BINAP(S)} fragment have been synthesized in an attempt to correlate this behavior with structural features of the ligand and the solution structure of the allylpalladium complex. Notably, allylic amines with an α-quaternary carbon center may be prepared with high regioselectivity with this system. Spin-saturation transfer studies (SST) were performed on two (κ^2-*P,S*)Pd-π-allyl complexes in order to determine relative rates for Pd-$\eta^3-\eta^1-\eta^3$-allyl interconversions and the hemilabile behavior of the BINAP(S) ligand.

Introduction

The transition-metal-catalyzed allylic substitution reaction has become a powerful synthetic tool in recent years, and the amount of literature on the subject continues to grow.[1,2] Nevertheless, this reaction remains of considerable interest because significant challenges still exist. Impressive progress has been made with Pd in terms of increasing the scope and stereoselectivity with which symmetrically disubstituted allylic substrates undergo this reaction.[3−7] Additionally, Ir-,[8−13] Rh-,[14−16] and Mo[17]-catalyzed allylic substitutions have provided very high regioselectivity for nucleophilic attack at the substituted allylic terminus when the other terminus is unsubstituted. Considerably less attention has been devoted to the Pd-catalyzed reaction of unsymmetrical 1,3-disubstituted allylic compounds.[18−27] These types of substrates present the possibility of producing regioisomeric products depending on which of the allylic termini undergoes substitution. During the course of our studies on various Pd-catalyzed allylic substitution reactions with (*S*)-BINAP(S) **1** (Scheme 1) as a ligand, we have found several instances in which the regiochemical outcome of the reaction was the reverse of that which Pd normally gives rise to.[28−30] We were interested in defining the factors

Scheme 1. Preparation of [(η^3-Allyl)Pd(*S*-BINAP(S))]SbF_6 (2)



1 **2**

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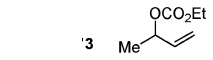
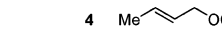
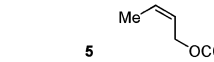
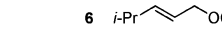
Table 1. Amination of Alkyl-Monosubstituted Allylic Carbonates

3-5, 7: R = Me
6, 8: R = *i*-Pr

	Substrate	%Y	a:b	%ee	Optical Rotation Abs. Cfg.
3		99	93:7	45	(+)-(*S*)
4		99	94:6	44	(+)-(*S*)
5		99	94:6	44	(+)-(*S*)
6		36	9:91	ND	ND

that contribute to these unusual regioselectivities in the context of Pd-catalyzed allylic amination. Substrate scope, ligand architecture, and the solid and solution structure of some of the intermediate Pd-π-allyl complexes were examined. These studies include the measurement of $\eta^3-\eta^1-\eta^3$ and allylic termini interconversion processes by spin-saturation transfer experiments.

Catalysis Results

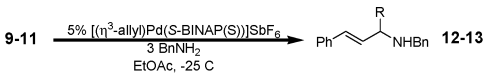
As a starting point, we chose to examine the effects of using different regio- and stereoisomers of butenyl ethyl carbonates **3**−**5** (Table 1). Not unexpectedly, substrates **3**−**5** gave very similar results, which presumably arises from rapid equilibration of the isomeric intermediate Pd-η^3-crotyl species with respect to attack of benzylamine. In the great majority of Pd-catalyzed allylic substitution reactions, nucleophilic attack on the less substituted, more sterically accessible, allylic terminus is preferred. What is unusual about these results when using **2** as catalyst is the extremely high regioselectivity in favor of attack on the more substituted allylic terminus.

Upon increasing the size of R to *i*-Pr, however, the substitution pattern now resembles what one expects from most Pd-catalyzed allylic substitution reactions, heavily favoring the linear achiral product **8b**.

When unsymmetrically substituted allylic substrates **9**−**11** incorporating Ph are employed in this reaction, we also find that amination occurs exclusively at the less substituted terminus (Table 2). These results are in accord with what is observed when substrate **6** is used, i.e., a large R group giving rise to the traditional regioselectivity observed with Pd.

The selectivity we observed for substitution on the more substituted allylic position with small alkyl substituents encouraged us to attempt the preparation of quaternary carbon centers from 3,3-disubstituted allylic starting materials (Table 3). Previously, we reported that amination of a 3,3-dimethyl-substituted allyl, **14**, with **2** produced **17a** and **17b** in a 91:9 ratio. When using the related [(η^3-allyl)Pd{BIPHEP(S)}]SbF_6 complex **20**, based on BIPHEP(S), **21**, as the catalyst (Figure 1), this ratio was further increased to >99:1 in favor of **17a**. Extension of this methodology using **20** as catalyst

Table 2. Amination of Unsymmetrical Phenyl-Substituted Substrates



12: R = H
13: R = Me

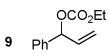
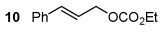
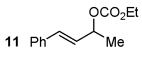
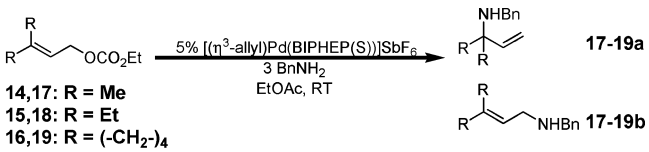
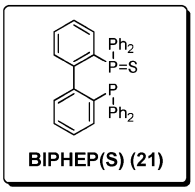
	Substrate	Product	%Y	%ee	Optical Rotation
9		12	99	NA	NA
10		12	99	NA	NA
11		13	99	43	(-)

Table 3. Amination of 3,3-Alkyl Disubstituted Substrates



14,17: R = Me
15,18: R = Et
16,19: R = (-CH_2-)$_4$

Substrate	%Y	a:b
14	99	>99:1
15	90	>99:1
16	72	98:2



with other 3,3-disubstituted starting materials **15** and **16** gave the branched products **18a** and **19a**, respectively, in greater than 98:2 regioisomeric ratios. This methodology could possibly be effective in the creation of chiral quaternary centers with pendant amine and terminal alkene functionality.

Discussion

To investigate the origin of the selectivity in these systems, an evaluation of a number of factors must be

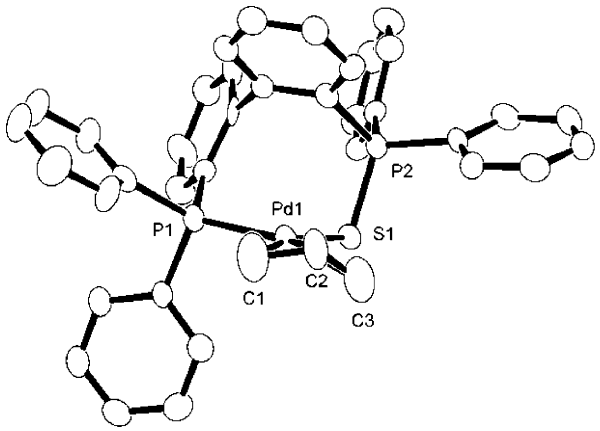


Figure 1. ORTEP diagram of [(η^3-allyl)Pd{BIPHEP(S)}]SbF_6 (**20**). Pd1−C1 = 2.194(9)Å; Pd1−C3 = 2.244(10) Å; Pd−S1−P2 = 100.28(9)°. Major conformation of allyl is shown.

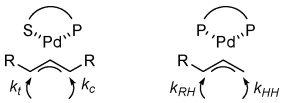


Figure 2. Differing rate constants for cis vs trans and RH vs HH nucleophilic attack.

considered. Assuming that the relevant intermediate is a cationic [(η^3-allyl)Pd(κ^2-*P,S*)] species, we decided to undertake a thorough investigation of several of these types of complexes, in the solid state as well as in solution. Thus, the critical transition states should involve attack on the face of the allyl opposite of the metal. The regiochemistry of the amination product should be controlled by the relative importance of the electronic and steric effects of the substituent on the terminus of the allyl versus the relative reactivity of the allylic termini trans or cis to phosphorus. When the ligand is a *P,X*-heterobidentate, there is a preference for attack trans to the phosphorus for symmetrically substituted allyls. This preference can be restated as a ratio of rate constants for attack trans or cis to phosphorus as k_t:k_c > 20:1 (Figure 2).[31−37]

For a homobidentate *P,P*-ligand there is a preference for attack on the unsubstituted terminus for monosubstituted allyls. That is, the rate constant ratio is k_{HH} > k_{MeH}, which is ∼7:3 for BINAP, but >20:1 for many others; this can be attributed to a steric effect to the approach of the nucleophile (Figure 2).[31,38,39] One should note, however, that for the case of two methyl substituents on the same terminus, the steric effect can be potentially overcome by the modified bonding of that terminus to the metal owing to adjustment of the relative nucleophilicity of the termini yielding k_{MeMe} > k_{HH} (see for example refs 38, 40−43).

To summarize briefly, the regioselectivity of these reactions will be determined by a combination of these factors: the positioning of the R group relative to the donor atoms, the relative rate of attack on termini trans to P and S, and the balance of steric and electronic effects controlling the rates of attack on the two allylic termini.

We expect that, owing to the large/small nature of the *P,S* donor set, the larger R group should prefer to be trans to P owing to less severe steric repulsions that would be present were it cis to P. If we take into account that the attack of the nucleophile in Pd-catalyzed allylic

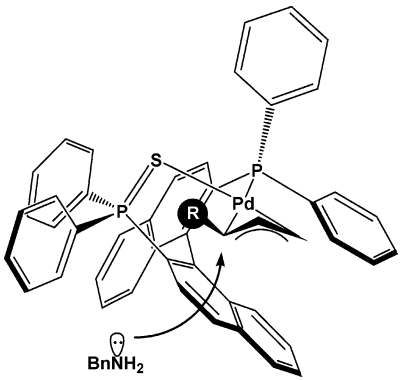
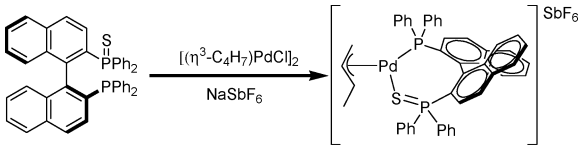


Figure 3. Regio- and stereochemical model for allylic aminations.

Scheme 2. Preparation of [(η^3-Crotyl)Pd(*S*-BINAP(S))]SbF_6 (22)



1 **22**

substitution occurs trans to the highest trans-effect donor, then we have a working model for prediction of the regiochemistry of the products when starting from unsymmetrically substituted allylic starting materials (Figure 3). To test this hypothesis, the crotyl complex **22** was synthesized (Scheme 2) in order to determine the preference for the positioning of the methyl group with respect to the *P,S* donor set. Although X-ray quality crystals of **22** could not be obtained, ^{1}H NMR spectroscopy reveals that it exists as >90% of the diastereomers with the methyl group trans to P, as indicated by the magnitude of ^{1}H−^{31}P couplings. Fortunately, crystallization of the 1,1-dimethylallyl complex **23** occurs readily, and the structure is shown in Figure 4. The ^{1}H NMR spectrum in CD_2Cl_2 solution shows that the doubly substituted allylic terminus is trans to P, consistent with the structure observed in the solid state. Additionally, η^3-cinnamyl complex **24** was synthesized, and in the solid state it exists as a ∼2:1 mixture of

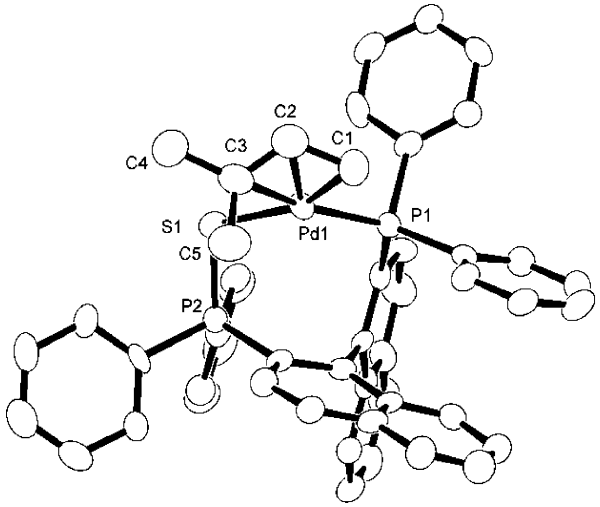


Figure 4. ORTEP diagram of [(η^3-1,1-dimethylallyl)Pd(*S*-BINAP(S))]SbF_6 (**23**). Pd1−C1 = 2.098(6) Å; Pd1−C3 = 2.268(7) Å; Pd−S1−P2 = 106.17(8)°.

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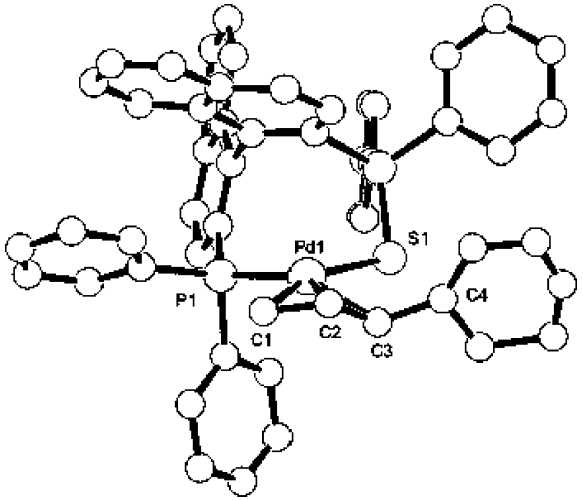


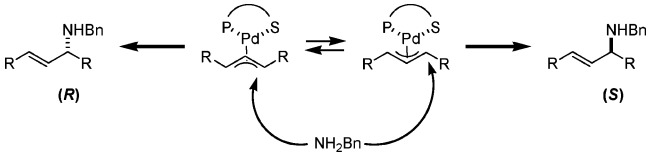
Figure 5. ORTEP diagram of [(η^3-cinnamylallyl)Pd(*S*-BINAP(S))]SbF_6 (**24**). Pd1−C1 = 2.136(5) Å; Pd1−C3 = 2.308(10) Å; Pd−S1−P2 = 104.74(6)°. Major conformation found in crystal is shown.

diastereomers, both of which have the Ph group trans to P (Figure 5). In CD_2Cl_2 solution, complex **24** exists as a 96:4 regioisomeric mixture, with the isomers having Ph trans to P predominating. These complexes clearly demonstrate the role of the relative *steric* effects presented by the *P,S* arrangement in determining the preferred regiochemistry of intermediates of the substituted complexes if we assume that nucleophilic attack occurs trans to P.

However, there is clearly more involved in regiocontrol than simple steric effects; although **3**−**5** and **14**−**16** are preferentially attacked at the more substituted position, *i*-Pr-substituted **6** and phenyl-containing substrates **9**−**11** are attacked at the less substituted position exclusively. This reversal of regioselectivity is most likely due to a change in the relative reactivity of the allylic termini of the intermediate Pd-π-allyl species involved. As the R group gets larger, based on the aforementioned ligand effects, we one would expect that a larger proportion of the Pd-η^3-allyl would have that large R group trans to P, which predisposes the allylic fragment for substitution on the more substituted end. However, as the size of R increases, the steric hindrance toward nucleophilic substitution on that terminus also increases. The relative importance of these factors may impart a greater reactivity for nucleophilic substitution on the minor isomer (unsubstituted terminus). Since these reactions are presumably operating under Curtin−Hammett conditions, even a small percentage of a minor isomer can give rise to a major percentage of the product if that minor isomer is sufficiently more reactive.

The cinnamyl substrate **10** proceeded with addition to the less substituted terminus. This implies that the minor regioisomer of **24** (methylene trans to P) is much more reactive than the major regioisomer (Ph trans to P). However, in order for the reaction to proceed exclusively through the minor regioisomer, it must be occurring under Curtin−Hammett conditions; that is, the regio- and stereoisomers of the allylic moiety must be interconverting at a greater rate than the reaction is occurring. This allows the more reactive isomer to be

Scheme 3. Attack on Enantiotopic π-Allyl Faces



trapped selectively, regardless of its relative concentration under the reaction conditions.

While the selective trapping of a particular regioisomer gives rise to the observed regiochemistry when starting from an unsymmetrically substituted subtrate, the selective addition to one of the enantiotopic allylic faces gives rise to the observed enantioselectivity (Scheme 3). When Curtin−Hammett conditions are met, the rapidly interconverting allylic faces provide the means to transform chiral racemic substrates into enantiopure products. When these conditions are not met, the consequence is a "memory effect". A "memory effect" may be conveniently defined as an incomplete scrambling of regio- and stereochemical information in the allylic starting material.[22,25,44−46] These effects often result from the rate of nucleophilic attack being faster than (or approximately equal to) the rates of Pd-π-allyl interconversions. We have noted "memory effects" in our previous work with catalyst **2**; we therefore desired to quantify the rates of these Pd-π-allyl interconversions in order to obtain a better understanding of our observed regio- and stereochemistry in the allylic amination reaction.

The viability of our allylic amination reactions operating under Curtin−Hammett conditions was examined by performing variable-temperature ^{1}H NMR and spin-saturation studies on some [(η^3-allyl)Pd(*P,S*)]SbF_6 complexes.[47] Generally one expects that Curtin−Hammett conditions will be met owing to rapid $\eta^3-\eta^1-\eta^3$ equilibration and interconverting T-shaped intermediates.[48,49] One should note, however, that the barrier to interconversion and/or preference for a specific T-shaped intermediate may be increased for heterobidentate ligands owing to the general difficulty of placing two high trans effect ligands trans to each other (e.g., η^1-allyl and P). Finally, one must consider the possibility that the heterobidentate ligand may be hemilabile. An interconversion of this kind would proceed through decoordination of the S atom followed by rearrangement of the T-shaped intermediate *without* apparent allyl rotation. This would allow for the equivalent of a π-allyl pseudorotation, which has the effect of switching the allylic termini with respect to their position relative to the *P,S* donor set (Figure 6). The processes that lead to allylic termini interconversion are especially important in understanding the regioselectivity of the Pd-catalyzed allylic aminations presented here.

Complex **2** and its achiral analogue **32** (Scheme 4) were examined with NMR line broadening and SST

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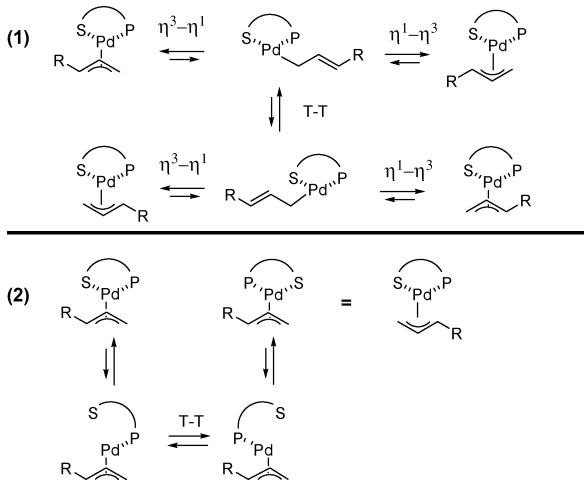
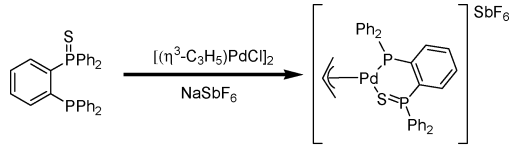


Figure 6. η^3-Allyl pseudorotation (1) vs *P,S*-ligand hemilability (2).

Scheme 4. Preparation of 32



31 **32**

experiments in order to determine both the barriers to $\eta^3-\eta^1-\eta^3$ exchange and allylic termini exchange (π-allyl pseudorotation or ligand hemilability). Several features are noted on heating and irradiation of the allyl resonances of **32** (Figure 7): (1) there are four resonances observed for the terminal protons, and those for the two enantiomeric complexes are equivalent; (2) the anti resonances (A, B) are distinguished by the greater coupling to the central proton and the resonances trans to P by greater coupling to ^{31}P; (3) resonances cis to S (A,D) show greater line broadening than those cis to P; (4) irradiation at C produces no significant saturation transfer to B, but an increase in intensity owing to an NOE; (5) irradiation at A produces a large decrease in the intensity at A and smaller intensity decreases in B and D. This demonstrates that an expected $\eta^3-\eta^1-\eta^3$ interconversion is the fastest process, as it interconverts anti (A) and syn (D) protons cis to P and results in

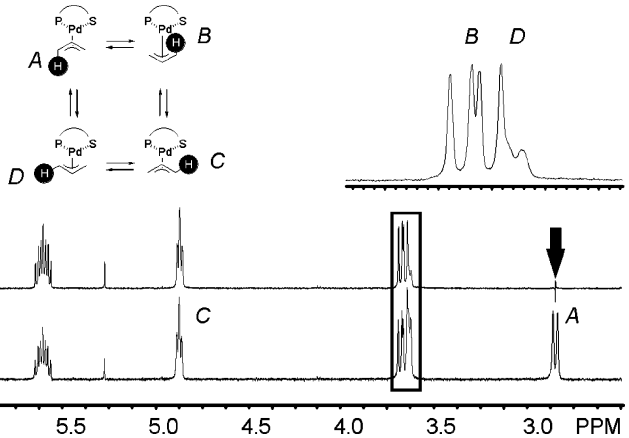


Figure 7. SST study on **32** (72 °C), $k_{\eta^3-\eta^1-\eta^3} = 3.52\ s^{-1}$; $k_{hemi} = 0.14\ s^{-1}$.

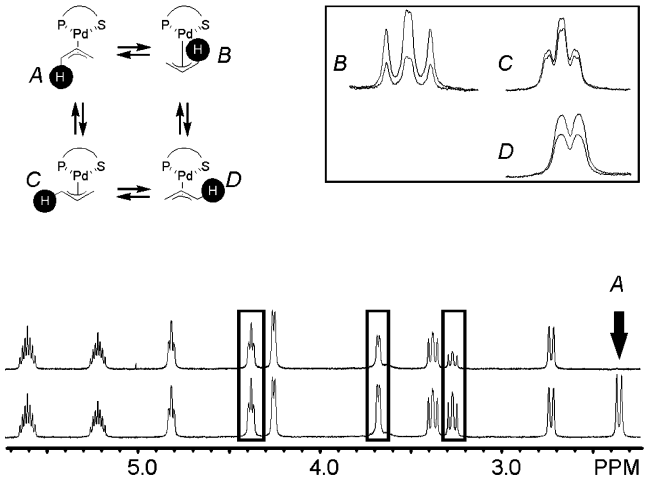


Figure 8. SST study of **2** (62 °C): $k_{\eta^3-\eta^1-\eta^3} = 1.60\ s^{-1}$; $k_{hemi} = 2.19\ s^{-1}$. [Note owing to the proximity of the resonance at 2.7 δ there is some inadvertent saturation of the resonance.]

conversion to the other enantiomer of the complex. This process *would not* cause exchange between sites B and C.

The observation of saturation in B and C must occur via a slower process. This could occur via interconversion of a T-shaped intermediate of either an η^1-allyl or a κ^1-form of the hemilable ligand *P,S*-ligand (Figure 7 shows the exchanges for the hemilabile ligand; an η^1-allyl would provide a direct path from A to C). Direct exchange between B and C could also occur via formation of an η^1-allyl cis to S, but saturation transfer was not observed there. The decrease in intensity at C can be attributed to a high degree of saturation at D and this magnetization then being transferred on to C. Thus, a decrease in B and C upon irradiation at A is consistent with hemilability of the *P,S*-ligand.

Thus, we interpret the results for complex **32** as $\eta^3-\eta^1-\eta^3$ exchange at a rate of $\sim$3.5 s^{-1} and allylic termini interconversion at a rate from *P,S*-ligand hemilability of $\sim$0.1 s^{-1} at 72 °C (Figure 7).

Owing to the chirality of BINAP(S) and the enantiomeric nature of the binding of the allyl moiety to an unsymmetrical chelate, the allyl resonances are rendered diastereotopic in complex **2**. If the exchanges are as outlined for **32**, then there will be two sets of resonances that exchange among themselves. Quite unexpectedly, the BINAP(S) complex **2** showed preferential transfer of saturation from the terminus trans to S to the terminus trans to P. This implies that BINAP(S) is more prone to hemilability than **31**. A saturation transfer experiment shows that allylic termini interconversion occurs $\sim$1.4 times faster than $\eta^3-\eta^1-\eta^3$ exchange at 62 °C (Figure 8). The observation that the allylic termini exchange rate is faster than $\eta^3-\eta^1-\eta^3$ exchange is extremely unusual; the $\eta^3-\eta^1-\eta^3$ exchange is usually the faster process. The result of this rapid exchange is that the regioselectivity of the reaction most likely depends on the relative reactivity of the allylic termini to an approximately equal extent as the steric effects presented by **1**, placing the allylic amination reaction under Curtin–Hammett control. It is likely that these rates of exchange are increased under the reaction conditions owing to the presence of other ligands (amines and counterions).

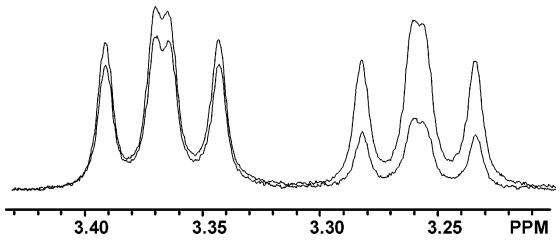


Figure 9. Preferential saturation of diastereomeric anti protons trans to P in complex **2** at δ 2.33.

Additionally, when complex **2** undergoes its allylic termini interconversion, the rate constants of the irradiated anti proton trans to S going to the two diastereomeric anti protons trans to P are different, as evidenced by the differing amounts of signal decrease in the spin-saturation transfer experiment. This observation implies that the allylic termini exchange mechanism occurs mainly by ligand hemilability rather than by a mechanism through an η^1-allyl mechanism.

Because complex **2** exists as a 52:48 ratio of exo/endo diastereomers in solution, it is clear that the energetic difference between the two diastereomeric η^3-allyl positions is negligible. Therefore, if the allylic termini exchange was taking place via an η^1-allyl mechanism, we would expect that the two diastereomeric positions would be saturated equally, since the incipient allyl moiety should have no significant preference for which diastereomer it forms. However, they are saturated in an approximately 2:1 ratio with a preference for the opposite diastereomer (Figure 9). This is strong evidence that the allylic terminus exchange that is observed is due to the hemilability of **1** on Pd. We believe that the origin of this hemilability may lie in the chelate ring size that the BINAP(S) ligand forms on complexation with Pd. As both BINAP(S) and ligand **31** present the same steric and electronic arrangement to Pd (both are bis(triaryl)phosphine monosulfides), the only notable difference lies in the fact that **1** forms a nine-membered chelate ring versus the six-membered chelate ring formed with **31**.

Since ligand **1** is hemilabile on Pd, it is possible that the true catalyst under our reaction conditions may be one in which **1** is monodentate, with an amine, solvent molecule, or cation filling the vacant coordination site.

In conclusion, a variety of factors are responsible for the regioselectivity observed in the Pd/BINAP(S)-catalyzed allylic amination reaction. The steric effects of **1** serve to direct the sterically larger allylic terminus trans to P. Owing to the preference for nucleophilic attack trans to P, this should lead to the more substituted product predominantly. Since under some conditions these reactions may be under Curtin−Hammett control, the ratio of products may be unrelated to the thermodynamic ratio observed for the equilibrating substrates. For example with cinnamyl derivatives, it appears that the more reactive species is that with the less-substituted terminus trans to P and the reaction proceeds exclusively through the minor Pd-η^3-allyl isomer. The dynamic processes that lead to the allylic interconversion processes were examined by spin-saturation transfer techniques, and the hemilability of **1** was confirmed. The rate of allylic termini exchange was found to be faster than the rate of $\eta^3-\eta^1-\eta^3$ exchange in complex **2**, which is highly unusual. These insights into the allylic amination reaction catalyzed by **2** and its congeners will prove useful in understanding future results and potentially in new catalyst design.

Experimental Section

General Procedures. All synthetic manipulations were carried out using standard Schlenk techniques under inert atmosphere. Dichloromethane and thf were distilled over appropriate drying agents prior to use. Ethyl acetate was dried over $MgSO_4$ and degassed with a stream of N_2 before use. Allylpalladium chloride dimer, (η^3-1-phenylallyl)palladium chloride dimer, and (η^3-1,1-dimethylallyl)palladium chloride dimer were prepared according to their literature procedures.[50] *S*-BINAP(S) **1**[28] and catalyst **2**[28] were prepared as previously described. (*Z*)-Crotyl alcohol, 3-methyl-2-buten-1-ol, benzylamine, (η^3-crotyl)palladium chloride dimer, *S*-BINAP, BIPHEP, 1,2-bis(diphenylphosphino)benzene, and $NaSbF_6$ were purchased and used as received. All spectra were recorded on either a Bruker 400 or 500 MHz spectrometer. Spectral characterization and optical rotation data of product amines **7a**,[18] **12**,[51] **13**,[52] **17a**,[53] **28**,[54] **29**,[7] and **30**[7] were consistent with their respective literature data. Enantiomeric excesses were determined by ^{1}H NMR chiral shift experiments using (−)-MTPA as previously described.[30] Optical rotations were measured on a Perkin-Elmer model 341 polarimeter at 589 nm and 25 °C, using a 1 dm path length. Spin-saturation transfer experiments were performed using standard techniques.[55−57]

Preparation of Allylic Carbonates. To a stirred solution of the appropriate alcohol (10 mmol), pyridine (3.2 mL, 40 mmol), and DMAP (10 mg) in thf (60 mL) at 0 °C was added ethyl chloroformate (2.6 mL, 27 mmol) dropwise. The resulting cloudy mixture was stirred for 12 h at RT. Brine (60 mL) and Et_2O (20 mL) were added, and the organic layers were separated, washed successively with 10% HCl and brine, dried over $MgSO_4$, and concentrated to leave the crude product. Column chromatography over silica gel (10% EtOAc/90% hexanes) provided the pure allylic carbonates as clear, colorless to pale yellow oils. Yields were generally 75−95%.

(*Z*)-2-Buten-1-yl ethyl carbonate (5): from (*Z*)-2-buten-1-ol. ^{1}H NMR (400 MHz, C_6D_6): δ 5.54 (1H, dt, J = 6.8, 11.0 Hz); 5.41 (1H, dq, J = 7.0, 11.0 Hz); 4.57 (2H, d, J = 6.8 Hz); 3.90 (2H, q, J = 7.0 Hz); 1.35 (3H, d, J = 7.0 Hz); 0.90 (3H, t, J = 7.0 Hz). ^{13}C NMR (125 MHz, C_6D_6): δ 156.3, 130.4, 125.2, 64.2, 63.6, 14.8, 13.5. Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.25; H, 8.46.

(*E*)-4-Methyl-2-penten-1-yl ethyl carbonate (6): from (*E*)-4-methyl-2-penten-1-ol.[58] ^{1}H NMR (400 MHz, C_6D_6): δ 5.53 (1H, dd, J = 6.2, 15.5 Hz); 5.42 (1H, dt, J = 6.8, 15.5 Hz); 4.47 (2H, d, J = 6.2 Hz); 3.91 (2H, q, J = 7.1 Hz); 2.01 (1H, sept., J = 6.8 Hz); 0.91 (3H, t, J = 7.1 Hz); 0.79 (6H, d, J = 6.8 Hz). ^{13}C NMR (100 MHz, C_6D_6): δ 156.2, 143.8, 121.9, 68.9, 64.2, 31.6, 22.6, 14.8. Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.63; H, 9.56.

3-Methyl-2-buten-1-yl ethyl carbonate (14): from 3-methyl-2-buten-1-ol. ^{1}H NMR (400 MHz, C_6D_6): δ 5.35 (1H, t, J = 7.2 Hz); 4.56 (2H, d, J = 7.2 Hz); 3.92 (2H, q, J = 7.0 Hz);

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1.44 (3H, s); 1.40 (3H, s); 0.91 (3H, t, J = 7.0 Hz). ^{13}C NMR (125 MHz, C_6D_6): δ 156.5, 139.7, 119.8, 64.9, 64.1, 26.2, 18.4, 14.9. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.52; H, 9.01.

3-Ethyl-2-penten-1-yl ethyl carbonate (15): from 3-ethyl-2-penten-1-ol.[59] ^{1}H NMR (500 MHz, C_6D_6): δ 5.35 (1H, t, J = 7.2 Hz); 4.65 (2H, d, J = 7.2 Hz); 3.92 (2H, q, J = 7.0 Hz); 1.89 (2H, q, J = 7.6 Hz); 1.81 (2H, q, J = 7.4 Hz); 0.91 (3H, t, J = 7.0 Hz); 0.82 (3H, t, J = 7.4 Hz); 0.80 (3H, t, J = 7.6 Hz). ^{13}C NMR (125 MHz, C_6D_6): δ 156.5, 150.5, 117.7, 64.7, 64.1, 29.9, 24.5, 14.9, 14.1, 13.0. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.37; H, 9.79.

2-Cyclohexyliden-1-yl ethyl carbonate (16): from 2-cyclohexylidene ethanol.[60] ^{1}H NMR (500 MHz, C_6D_6): δ 5.35 (1H, t, J = 7.2 Hz); 4.62 (2H, d, J = 7.2 Hz); 3.92 (2H, q, J = 7.0 Hz); 1.99 (2H, m); 1.89 (2H, m); 1.32 (6H, m); 0.91 (3H, t, J = 7.0 Hz). ^{13}C NMR (125 MHz, C_6D_6): δ 156.5, 147.5, 116.5, 64.2, 64.1, 37.8, 29.7, 29.1, 28.5, 27.4, 14.9. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.53; H, 9.30.

Product Amine Characterization Data. Benzyl-4-methyl-2-pentenylamine (8b): ^{1}H NMR (400 MHz, C_6D_6): δ 7.29 (2H, d, J = 7.4 Hz); 7.18 (2H, t, J = 7.4 Hz); 7.09 (1H, t, J = 7.4 Hz); 5.55 (2H, m); 3.60 (2H, s); 3.08 (2H, d, J = 4.0 Hz); 2.17 (1H, m); 0.93 (6H, d, J = 6.8 Hz). ^{13}C NMR (125 MHz, C_6D_6): δ 142.0, 139.7, 129.1, 129.0, 127.6, 126.9, 54.2, 52.1, 31.8, 23.3.

Benzyl-3-ethyl-2-pentenylamine (18a): ^{1}H NMR (400 MHz, C_6D_6): δ 7.37 (2H, d, J = 7.4 Hz); 7.20 (2H, t, J = 7.4 Hz); 7.11 (1H, t, J = 7.4 Hz); 5.51 (1H, dd, J = 11.0, 17.7 Hz); 5.08 (1H, d, J = 11.0 Hz); 5.03 (1H, d, J = 17.7 Hz); 3.47 (2H, s); 1.33 (4H, q, J = 7.4 Hz); 0.76 (6H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, C_6D_6): δ 145.7, 142.7, 129.2, 129.1, 127.6, 114.4, 60.2, 47.1, 28.8, 8.2.

Benzyl-1-vinylcyclohexylamine (19a): ^{1}H NMR (400 MHz, C_6D_6): δ 7.38 (2H, d, J = 7.4 Hz); 7.20 (2H, t, J = 7.4 Hz); 7.11 (1H, t, J = 7.4 Hz); 5.55 (1H, dd, J = 10.9, 17.7 Hz); 5.07 (1H, d, J = 10.9 Hz); 4.98 (1H, d, J = 17.7 Hz); 3.51 (2H, s); 1.62−1.14 (10H, m). ^{13}C NMR (125 MHz, C_6D_6): δ 146.5, 142.9, 129.2, 129.1, 127.5, 113.2, 56.7, 47.2, 36.1, 27.1, 22.7. Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.34; H, 9.83; N, 6.37.

General Procedure for Syntheses of (η^3-allyl)Pd(Ligand)SbF_6 Complexes 20, 22, 23, 24, 31, and 33. To a flame-dried Schlenk flask were added the appropriate allylpalladium chloride dimer (1 equiv), the appropriate ligand (2 equiv), and $NaSbF_6$ (2.5 equiv). The contents were placed under inert atmosphere, and CH_2Cl_2 was added. The resulting cloudy solution was stirred for 16 h at RT. The solution was then filtered through a pad of Celite, evaporated to dryness, and triturated with Et_2O to leave the desired compound as a yellow powder. Yields and crystallization details (where appropriate) are given below with the individual complexes.

[(η^3-Allyl)Pd(BIPHEP(S))]SbF_6 (20): yield 86%. X-ray quality crystals were grown from CH_2Cl_2/Et_2O. In solution, complex **10** exists as a 1:1 ratio of diastereomers. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.26−6.29 (28H, aryl region); 5.51 (central, 1H, dddd, J = 7.0, 7.6, 12.6, 14.0 Hz); 5.18 (central, 1H, dddd, J = 7.0, 7.6, 12.6, 14.0 Hz); 4.93 (syn to central, trans to P, 1H, dd, J_{PH} = 7.0 Hz, J_{HH} = 7.6 Hz); 4.58 (syn to central, trans to P, 1H, dd, J = J_{PH} = 7.0 Hz, J_{HH} = 7.6 Hz); 4.00 (syn to central, trans to S, 1H, d, J = 7.0 Hz); 3.91 (syn to central, trans to S, 1H, d, J = 7.0 Hz); 3.65 (anti to central, trans to P, 1H, dd, J_{PH} = 10.2 Hz, J_{HH} = 14.0 Hz); 2.92 (anti to central, trans to P, 1H, dd, J_{PH} = 10.2 Hz, J_{HH} = 14.0 Hz); 2.72 (anti to central, trans to S, 1H, d, J = 12.6 Hz); 2.35 (anti to central, trans to S, 1H, d, J = 12.6 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 41.3 (s, P=S), 41.2 (s, P=S), 26.4 (s, P), 24.0 (s, P). ^{13}C NMR (125 MHz, CD_2Cl_2, allylic region only): δ 120.2 (central, d, J_{PC} = 6.5 Hz); 119.4 (central, d, J_{PC} = 6.5 Hz); 80.3 (trans to P, d, J_{PC} = 32.1 Hz); 78.7 (trans to P, d, J_{PC} = 32.1 Hz); 66.3 (trans to S, d, J_{PC} = 3.0 Hz); 64.9 (trans to S, d, J_{PC} = 3.0 Hz). Anal. Calcd for $C_{39}H_{33}F_6P_2PdSSb$: C, 49.95; H, 3.55. Found: C, 49.69; H, 3.81.

BIPHEP(S) (21). To a solution of BIPHEP (678 mg, 1.3 mmol) in thf (20 mL) was added sulfur (29 mg, 0.91 mmol), and the resulting cloudy solution was stirred until clear. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography over silica gel (3:1 CH_2Cl_2/hexanes) to provide the pure product in 27% yield based on sulfur (136 mg). Compound **11** can be recrystallized from CH_2Cl_2/hexanes. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.73−7.64 (4H, m); 7.46 (1H, t, J = 7.2 Hz); 7.36 (3H, m); 7.32−7.17 (12H, m); 7.12 (2H, t, J = 7.8 Hz); 7.05 (1H, t, J = 7.7 Hz); 7.05 (1H, t, J = 7.7 Hz); 6.93 (1H, dd, J = 7.8, 11.6 Hz); 6.72 (1H, t, J = 7.8 Hz); 6.51 (1H, m); 6.40 (1H, m). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 42.0 (P=S); −14.7 (P). Anal. Calcd for $C_{36}H_{28}P_2S$: C, 77.96; H, 5.09. Found: C, 77.49; H, 4.90.

[(η^3-Crotyl)Pd(*S*-BINAP(S))]SbF_6 (22): yield 77%. Complex **8** exists predominantly as a 55:45 ratio of exo/endo diastereomers with Me trans to P. Major diastereomer: (400 MHz, CD_2Cl_2): δ 8.34−6.02 (32 H, aryl region); 5.12 (central H, ddd, J = 6.4, 6.9, 12.8 Hz); 4.05 (1H, anti to central, trans to P, ddq, J_{HH} = 6.4, 12.8 Hz, J_{PH} = 10.2 Hz); 3.43 (1H, syn to central, trans to S, d, J = 6.9 Hz); 2.32 (1H, anti to central, trans to S, d, J = 12.0 Hz); 1.81 (3H, dd, J_{HH} = 6.4 Hz, J_{PH} = 9.8 Hz). Minor diastereomer: (400 MHz, CD_2Cl_2): δ 8.34−6.02 (32 H, aryl region); 5.12 (central H, ddd, J = 6.4, 6.9, 12.8 Hz); 4.34 (1H, anti to central, trans to P, ddq, J_{HH} = 6.4, 12.8 Hz, J_{PH} = 10.2 Hz); 3.76 (1H, syn to central, trans to S, d, J = 6.9 Hz); 2.17 (1H, anti to central, trans to S, d, J = 12.0 Hz); 1.65 (3H, dd, J_{HH} = 6.4 Hz, J_{PH} = 9.8 Hz). ^{31}P NMR (both major diastereomers, 162 MHz, CD_2Cl_2): δ 45.5 (P=S, d, J_{PP} = 4 Hz); 44.6 (P=S, d, J_{PP} = 4 Hz); 25.5 (P, d, J_{PP} = 4 Hz); 23.9 (P, d, J_{PP} = 4 Hz). ^{13}C NMR (both major diastereomers, 125 MHz, $CDCl_3$, allylic region only): δ 118.3 (central C, d, J_{PC} = 4.7 Hz); 116.9 (central C, d, J_{PC} = 4.7 Hz); 102.1 (trans to P, d, J_{PC} = 28.0 Hz); 98.2 (trans to P, d, J_{PC} = 28.0 Hz); 61.3 (trans to S, d, J_{PC} = 2.8 Hz); 58.2 (trans to S, d, J_{PC} = 2.8 Hz); 17.9 (Me, d, J_{PC} = 4.2 Hz); 17.8 (Me, d, J_{PC} = 4.2 Hz). Anal. Calcd for $C_{48}H_{39}F_6P_2PdSSb$: C, 54.80; H, 3.74. Found: C, 54.85; H, 3.72.

[(η^3-1,1-Dimethylallyl)Pd(*S*-BINAP(S))]SbF_6 (23): yield 90%. X-ray quality yellow crystals were grown from slow evaporation of a CH_2Cl_2/Et_2O solution. Major diastereomer: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.20−6.46 (31 H, aryl region); 6.04 (1H, aryl, d, J = 8.6 Hz); 4.88 (1H, central allylic H, dd, J = 7.5, 13.0 Hz); 3.57 (1H, syn to central, trans to S, d, J = 7.5 Hz); 2.24 (1H, anti to central, trans to S, d, J = 13.0 Hz); 1.72 (3H, syn to central, d, J_{PH} = 9.8 Hz); 1.19 (3H, anti to central, d, J_{PH} = 6.3 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 45.3 (P=S, d, J_{PP} = 4 Hz); 26.6 (P, d, J_{PP} = 4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, allylic region only): δ 117.4 (quat. C, d, J_{PC} = 25.5 Hz); 112.0 (central C, d, J_{PC} = 4.7 Hz); 57.6 ($-CH_2$, d, J_{PC} = 2 Hz); 27.4 (Me, d, J_{PC} = 4.8 Hz); 22.3 (Me, d, J_{PC} = 5.8 Hz). Minor diastereomer: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.20−6.46 (31 H, aryl region); 5.81 (1H, aryl, d, J = 8.6 Hz); 4.72 (1H, central allylic H, dd, J = 7.5, 13.0 Hz); 3.00 (1H, syn to central, trans to S, d, J = 7.5 Hz); 2.84 (1H, anti to central, trans to S, d, J = 13.0 Hz); 1.93 (3H, syn to central, d, J_{PH} = 10.0 Hz); 1.19 (3H, anti to central, d, J_{PH} = 6.6 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 47.3 (P=S, d, J_{PP} = 6 Hz); 24.5 (P, d, J_{PP} = 6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, allylic region only): δ 116.3 (quat. C, d, J_{PC} = 25.5 Hz); 110.1 (central C, d, J_{PC} = 4.7 Hz); 56.8 ($-CH_2$, d, J_{PC} = 2 Hz); 27.5 (3H, d, J_{PC} = 4.8 Hz); 21.8 (3H, d, J_{PC} = 5.8 Hz). Anal. Calcd for $C_{49}H_{41}F_6P_2PdSSb$: C, 55.21; H, 3.88. Found: C, 55.13; H, 3.85.

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[(η^3-1-Phenylallyl)Pd(*S*-BINAP(S))]SbF_6 (24): yield 82%. X-ray quality yellow crystals were grown from a CH_2Cl_2/Et_2O solution. Complex **24** exists as a 52:44:4 ratio of diastereomers in solution. ^{1}H NMR (52% isomer, 400 MHz, CD_2Cl_2): δ 8.24−6.50 (aryl region, 36 H); 5.85 (aryl, 1H, d, J = 8.6 Hz); 5.84 (central, 1H, ddd, J = 6.8, 12.8, 13.0 Hz); 5.06 (trans to P, 1H, dd, J = 10.7, 13.0 Hz); 3.97 (syn to central, trans to S, 1H, d, J = 6.8 Hz); 2.41 (anti to central, trans to S, 1H, d, J = 12.8 Hz). ^{1}H NMR (44% isomer, 400 MHz, CD_2Cl_2): δ 8.24−6.50 (aryl region, 36 H); 6.06 (aryl, 1H, d, J = 8.6 Hz); 5.67 (central, 1H, ddd, J = 6.8, 12.8, 13.0 Hz); 4.78 (trans to P, 1H, dd, J = 10.7, 13.0 Hz); 3.55 (syn to central, trans to S, 1H, d, J = 6.8 Hz); 2.52 (anti to central, trans to S, 1H, d, J = 12.8 Hz). ^{31}P NMR (both major isomers, 162 MHz, CD_2Cl_2): δ 45.5 (P═S, d, J = 4.0 Hz); 43.7 (P═S, d, J = 4.0 Hz); 25.3 (P, d, J = 4.0 Hz); 25.1 (P, d, J = 4.0 Hz). ^{13}C NMR (both major isomers, allyl region only, 125 MHz, CD_2Cl_2): δ 111.6 (central, d, J_{PC} = 6.9 Hz); 111.5 (central, d, J_{PC} = 6.9 Hz); 103.3 (trans to P, d, J_{PC} = 27.5 Hz); 96.5 (trans to P, d, J_{PC} = 27.5 Hz); 63.3 (trans to S, d, J_{PC} = 2.8 Hz); 59.0 (trans to S, d, J_{PC} = 2.8 Hz). Anal. Calcd for $C_{53}H_{41}F_6P_2PdSSb$: C, 57.14; H, 3.71. Found: C, 57.18; H, 3.68.

1,2-Bis(diphenylphosphino)benzene monosulfide (31): prepared in an identical manner to BIPHEP(S) (**21**); yield 65% with respect to S; recrystallized from CH_2Cl_2/Et_2O. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81−7.73 (aryl, 4H); 7.42−7.26 (aryl, 8H); 7.23−7.06 (aryl, 8H); 7.04−6.97 (aryl, 4H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 45.0 (P═S, d, J_{PP} = 31.7 Hz); −16.5 (P, d, J_{PP} = 31.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8−128.4 (aryl, 30 C). Anal. Calcd for $C_{30}H_{24}P_2S$: C, 75.23; H, 5.06. Found: C, 74.87; H, 4.80.

[(η^3-Allyl)Pd(1,2-bis(diphenylphosphino)benzene monosulfide)]SbF_6 (32): yield 93%. X-ray quality yellow crystals were grown from a CH_2Cl_2/hexanes solution. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (aryl, 1H, app. t, J = 7.6 Hz); 7.62 (aryl, 1H, app. t, J = 7.6 Hz); 7.57−7.21 (aryl, 18H); 7.11 (aryl, 1H, d, J = 7.7 Hz); 7.09 (aryl, 1H, d, J = 8.2 Hz); 6.99 (aryl, 1H, d, J = 7.7 Hz); 6.97 (aryl, 1H, d, J = 8.2 Hz); 5.64 (dddd, J = 7.0, 7.3, 12.7, 13.8 Hz); 4.92 (syn to central, trans to P, 1H, dd, J = 7.3, 10.0 Hz); 3.71 (anti to central, trans to P, 1H, dd, J = 10.0, 13.8 Hz); 3.64 (syn to central, trans to P, 1H, d, J = 7.0 Hz); 2.85 (anti to central, trans to S, 1H, d, J = 12.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.4 (P═S, d, J_{PP} = 47.4 Hz); 15.1 (P, d, J_{PP} = 47.4 Hz). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 120.2 (central, J_{PC} = 4.8 Hz); 78.0 (trans to P, J_{PC} = 28.4 Hz); 70.3 (trans to S, J_{PC} = 2.8 Hz). Anal. Calcd for $C_{33}H_{29}F_6P_2PdSSb$: C, 45.99; H, 3.39. Found: C, 45.94; H, 3.33.

General Procedure for Catalytic Allylic Amination. These reactions (Tables 1−3) were performed as previously reported[30] at the indicated temperatures.

Stability of Amine Products under Reaction Conditions. Since amination at more substituted termini of allyls has the potential of rearranging to linear products,[61−63] we tested for potential conversion to thermodynamic products. This is particularly relevant to the formation of linear product from cinnamyl reactions. It was found that, upon subjecting amine product **7a** to our standard reaction conditions, no isomerization or racemization was observed. However, upon subjecting branched *N*-(1-phenyl-2-propenyl)benzylamine[8] to our standard reaction conditions, we observed partial isomerization (50%) to the linear product **12** over a 24 h period. This rearrangement could reflect the greater thermodynamic stability of the linear product with respect to the conjugation of the double bond into the aromatic ring. The rate of isomerization would suggest that isomerization of a kinetic branched isomer could account for only part of the linear isomer. This control experiment, however, does not have an excess of ethyl carbonate, which could accelerate the process.

Structure Determination and Refinement. Crystals were obtained by slow diffusion of diethyl into methylene chloride solution of complexes **20**, **23**, and **24**. Data were collected on a Nonius KappaCCD (Mo Kα radiation) diffractometer at −100 °C and were not specifically corrected for absorption other than the inherent corrections provided by Scalepack.[64] The structures were solved by direct methods (SIR92)[65] and refined on F for all reflections.[66] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 1.

Structure Determination of 20. This structure determination was straightforward, and the compound had crystallized in a triclinic cell with Z = 2, indicating a space group of $P\bar{1}$. There was a disorder with two orientations of the allyl in a ratio of 54:46. The major conformer is shown in Figure 1. Note that the Pd to terminal carbon atom distances are the average of the two conformers.

Structure Determination of 23. The data showed an orthorhombic cell with absences consistent with $P2_1$. There were no disorder problems with this structure, as shown in Figure 4.

Structure Determination of Orthorhombic 24. The data showed an orthorhombic cell with absences consistent with $P2_12_12_1$. An endo:exo disorder of the cinnamyl ligand was found with both conformers having the phenyl group trans to P, but the geometry superimposed the phenyl groups to some extent. The phenyl group was modeled with a single rigid group and partial occupancies (67:33) for two of the allyl carbons. This approximation will lead to some significant error in the Pd−C distances. Neverthless, the overall trend of longer distances trans to P are evident. This structure was included to demonstrate that, although some metrical data may be suspect, the geometrical preference for the substituted terminus being trans to P is retained.

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Supporting Information Available: Crystallographic data, ^{13}C NMR data, and rate constant calculations for SST experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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