Synthesis and Characterization of Palladium(II) π-Allyl Complexes with Chiral Phosphinocarbene Ligands. Kinetics and Mechanism of Allylic Amination

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New palladium π-allyl complexes with chelating phosphinocarbene ligands (P−C) have been prepared and fully characterized. The adopted synthetic strategy is based on the reaction between the appropriate silver precursors and the labile [Pd(η^3-allyl)$OCOCF_3$]$_2$. These complexes react with amines in the presence of dimethyl fumarate, yielding the new palladium(0) complexes [Pd(η^2-dmfu)(P−C)] and allylamine. Under pseudo-first-order conditions, the amination rates obey the simple law $k_{obs} = k_2[NHR_2]$, and this observation seems to rule out the possibility of a simultaneous amine attack at the central atom with displacement of the bidentate ancillary ligand (or of one of its donor groups). The k_2 values increase with increasing basicity of the amine, with decreasing steric hindrance at the allyl fragment, and with increasing bulkiness of the P−C heterocyclic nitrogen substituent. Moreover a remarkable decrease of the amination rate is observed for the phosphinocarbene complexes as compared to the "isostructural" phoshinopyrazole (P−N) derivatives, in agreement with the strong σ-donating and weak π-accepting character of the carbene ligands. The new posphinocarbene ligands are tested in the palladium-catalyzed amination of 1,3-diphenylallylethyl carbonate, and the resulting low enantioselectivity may support the view of the comparable trans influence of carbene and phosphine ligands, which renders the corresponding trans allyl carbons electronically equivalent.

Introduction

The discovery of stable N-heterocyclic carbenes by Arduengo and co-workers[1] led to a rapid development of the chemistry of these compounds. In particular, increasing attention has been focused on using them as ancillary ligands for a number of transition metal-mediated catalytic reactions.[2] The reasons for this success are the high stability of metal−heterocyclic-carbene complexes against heat, moisture, and oxygen,[3] the strong coordination to the metal, which reduces dissociation so that no excess of ligand is required in catalytic processes, and finally the low toxicity.

In all these aspects they are not only competitive but often superior to usual phosphines.[2a,4] Additionally, the N-heterocyclic carbene moiety easily permits a fine-tuning of the ligand structure, through the introduction of appropriate substituents at the nitrogen atoms or at the five-membered-ring carbon atoms. In this respect considerable attention has been given to the incorporation of the carbene functionality into ligand systems containing other "classical" donor groups; in this way it is possible to obtain an electronic tuning of the metal coordination sphere.[5] Therefore, the syntheses of several chelating N-functionalized NHCs with various substituted pyridines,[6] imines,[7] ethers,[8] arylphosphines,[8a,9] and arylsulfides[9] and of their complexes with platinum-group metals, mainly Pd, Ru, Ir, and Rh, have been recently reported.

The electronic asymmetry of the chelating ligands renders the corresponding trans sites electronically inequivalent, due to the large difference of the chelating ends. In this work we were interested in the effect of this dissymmetry on the palladium-catalyzed allylic amination; it has been shown that in the absence

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Scheme 1

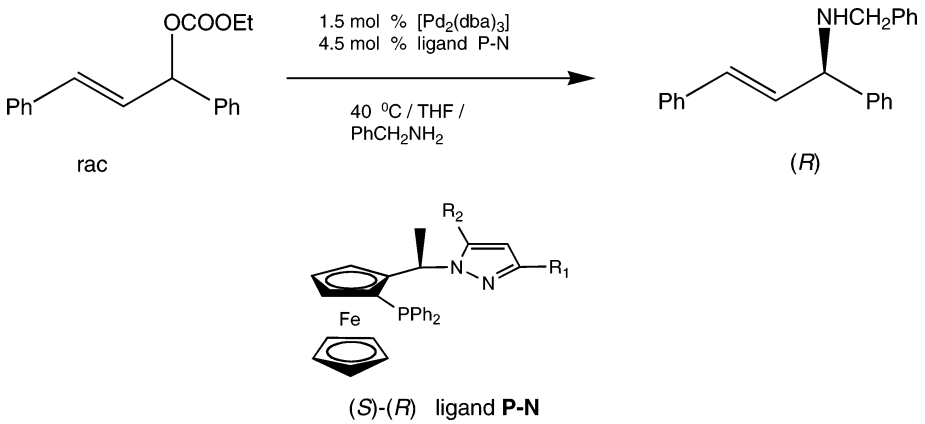

Chart 1

P-N ligands **P-C** ligands

of overriding steric factors addition of amine to allyl complexes is regioselective, occurring at the terminal carbon trans to the ligand with the strongest trans influence.[10] In a previous paper a very high enantioselectivity (99% ee) was obtained for the reaction of 1,3-diphenylallylethyl carbonate and benzylamine using pyrazole-containing ferrocenyl phosphines (P−N ligands),[11] and it was possible to prove that the site of nucleophilic attack was the carbon trans to phosphorus, which is more electrophilic than its companions trans to nitrogen. Moreover the shape of the P−N ligand made this reaction path much more favorable.We now present a study describing the synthesis and reactivity of new allyl-palladium complexes with the corresponding N-heterocyclic carbene ferrocenyl phosphine (P−C ligands) as ancillary ligands; in fact we exchange the position of a nitrogen and a carbon atom in the pyrazole ring (Chart 1), obtaining a chelating ligand with the same steric encumberance, but with completely different electronic character of one of the donor atoms. NHCs are considered strong σ-donating but weak π-accepting ligands; this characteristic increases the electron density at the metal center and seems to induce a higher trans effect/influence.[12]

This system provides the opportunity to test this property through a simple comparison of the enantioselectivity of palladium-catalyzed asymmetric allylic aminations using P−C or P−N ligands.

Results and Discussion

N-Functionalized Imidazolium Salts. Phosphinoimidazolium salts are the appropriate precursors of the phosphinocarbene ligands. These species can be prepared by quaternization of the susbstituted alkyl imidazole.

As in a recent report,[13] the ferrocene scaffold was introduced using (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine (**1**) as starting material;[14] its diasteroselective ortho fuctionalization with $ClPPh_2$ has allowed the preparation of (*R*),(*S*)-PPFA, **2**. After conversion to the corresponding acetate **3** (with retention of configuration at the stereogenic center), we had the suitable substrate for the alkylation of the appropriate imidazole. This reaction proceeded smoothly in a 2:1 mixture of acetonitrile and water to give the desired product.[15] Finally, ion-exchange with NaBr in methanol afforded the phosphinoimidazolium salts **4a** and **4b** in good yield, eventually after purification over silica gel. The stable orange-yellow solids obtained were characterized by analytical and spectroscopic methods. The general synthetic protocol is summarized in Scheme 2.

Silver Complexes. The most obvious method for the introduction of a NHC ligand into a palladium center is the "free carbene route" involving the abstraction of the acidic imidazolium proton (with NaO^tBu or other strong bases in nonprotic solvent) and trapping of the free carbene, after isolation or *in situ*, with a suitable metal precursor. In our case, despite several attempts, it was impossible to isolate the free carbene. On the other hand, the strongly basic conditions for its generation *in situ* are not compatible with every palladium-allyl substrate; indeed for these systems there are several precedents for nucleophilic attack by an alkoxide either at the allyl fragment[16] or at the palladium center.[17] Sometimes this reactivity was used to generate the catalytically active (NHC)-Pd^0 species in some cross-coupling reactions.[18]

After all, the most convenient approach to the problem seems to be the silver-mediated transfer of functionalized carbene ligands to the palladium-allyl precursor. In this alternative procedure, previously adopted by other authors with different

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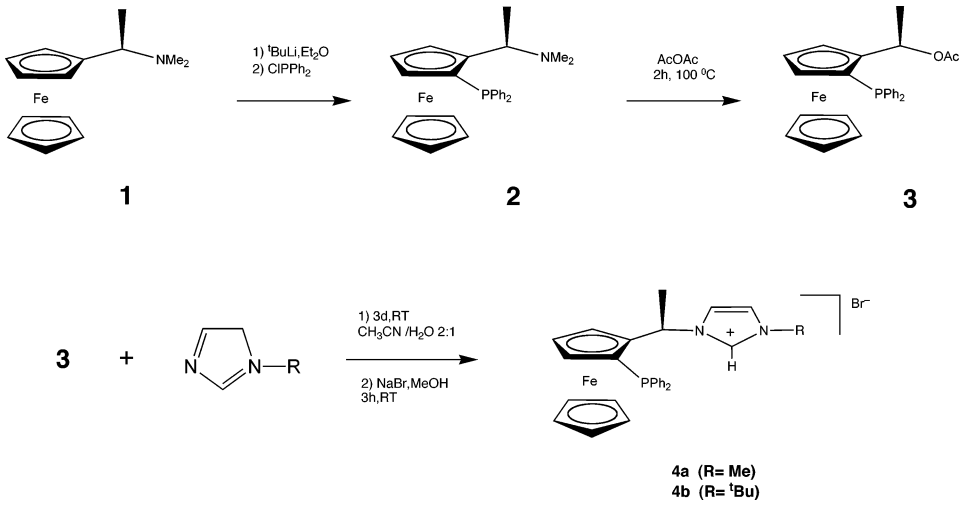
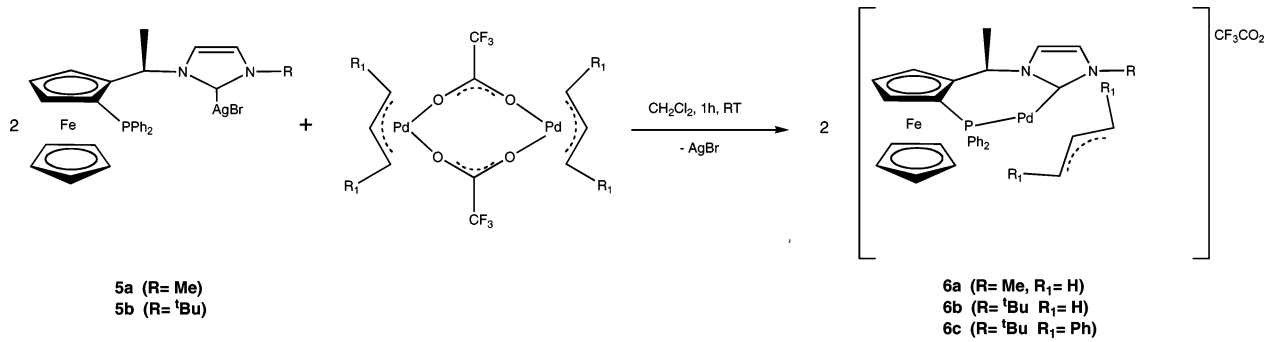
Scheme 2



Scheme 3



palladium systems,[3c,6a,c,7b,19] the free carbene is probably never involved, since silver complex formation is thought to occur by a base-mediated proton abstraction and the silver complex may be considered as a protected carbene.

The silver(I) carbene complexes were conveniently prepared by treatment of imidazolium salts with 0.5 equiv of silver oxide in CH_2Cl_2.[20] The experiment was easily followed since Ag_2O is insoluble in dichloromethane and slowly disappeared in the course of the reaction. The time required to quantitatively afford the product was 6 h for the silver complex **5a** and 24 h for the more encumbered complex **5b**. The compounds thus obtained are air-stable orange solids, soluble in most common organic solvents, except for diethyl ether and aromatic and nonaromatic hydrocarbons.

The elemental analyses for both complexes were in good agreement with a $[Ag(carbene)Br]_n$ composition. However, it is far from trivial to establish the solution structure of these species. In addition to the usual structural diversity exhibited by silver(I) heterocyclic carbenes (including monomeric, dimeric, and polymeric solid-state structures[6a,21]), we have to consider the possible interaction of metal centers with the phosphine side arm. A further complication is the high fluxionality of the system, which is clearly shown by a single broad signal in the $^{31}P\{^1H\}$ NMR spectra of both complexes, at room temperature.[22] The ^1H NMR spectra are similar to those of the parent imidazolium salts, except for the expected absence of the signals attributed to the NC(H)N proton and a broadening of some signals.

In any case, although the exact structure remains uncertain, this has no apparent effect on further reactions of these compounds. In particular, their behavior in the transmetalation process is the same as the usual well-characterized silver(I) carbene complexes (*vide infra*).

Synthesis and Characterization of Palladium-Allyl Complexes. The synthesis of these palladium complexes is shown in Scheme 3. The driving force for the transfer of the fuctionalized NHC, from silver to other metals, is the silver halide precipitation. This process is favored by the presence of weakly coordinated ligands in the accepting metals[19] (e.g., CH_3CN, COD, bridging ligands[23]). For this reason we chose $[Pd(\eta^3\text{-allyl})OCOCF_3]_2$ as starting material for the preparation of palladium-allyl complexes, since it can more easily free the two coordination sites necessary for the entering bidentate

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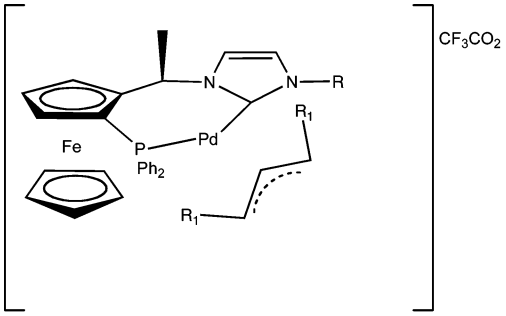
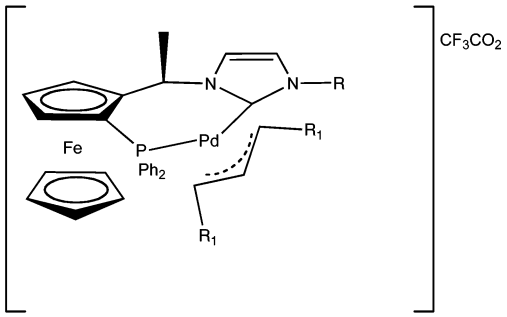
Chart 2



***exo* isomer**



***endo* isomer**

phosphinocarbene ligand. It is preferable to use the more common precursor $[Pd(\eta^3\text{-allyl})Cl]_2$, because in this case, after cleavage of the bridge, chloride could remain competitive for a coordination site;[23] indeed, the higher coordination ability of the chloride as compared to the trifluoroacetate anion is well known, especially in the chlorinated solvents generally used in transmetalations.

The reaction of **5a** or **5b** with $[Pd(\eta^3\text{-allyl})OCOCF_3]_2$ proceeded rapidly and smoothly in CH_2Cl_2 at room temperature. Precipitation of AgBr was observed almost immediately. After filtration and subsequent workup of the solution the complexes **6a** and **6b** were obtained as yellow solids in good yield (80−85%). These compounds are stable and can be handled in air with no noticeable degradation; only a slight decomposition was observed for **6a** after several days in chlorinated solvents. While some examples of Pd-allyl complexes with monodentate NHC ligands[18a,24] were already reported, to the best of our knowledge **6a** and **6b** are the first ones with bidentate ligands containing a carbene donor group.[25] Their elemental analyses were in accordance with the expected compositions.

The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of both complexes show two sets of signals, denoting the presence in solution of a mixture of two configurational isomers. The major isomer displays an *exo* configuration (*exo* refers to the relative orientation of the central allylic C−H vector pointing away from the ferrocene core, see Chart 2). The assignment of this structure for the complex **6b** is based on an NOE between the central allyl proton and the protons of the ^{t}Bu group, and it is extended for analogy to complex **6a**.

In the case of **6b** the ratio (∼82:18) between *exo* and *endo* isomers is virtually the same observed for the corresponding complex with a pyrazole-phoshine ligand,[26] confirming that the two systems appear to be comparable from a steric point of view.

One of the most important features used to identify the formation of palladium complexes was (a) a weak doublet[27] ($J_{CP} \approx 23$ Hz) at 171.4 for **6a** and at 167.8 ppm for **6b** in the $^{13}C\{^1H\}$ NMR spectra assigned to the carbene carbon. This assignment was confirmed by a 2D HMBC experiment, in which the couplings of the two olefinic protons of the imidazole unit[13] and of C(*H*)CH_3 with the carbene carbon were detectable. Furthermore, the coupling with the phosphorus confirmed the bidentate coordination of the ligand on the palladium center. The other important feature was (b) the magnetic inequivalence of terminal allylic protons and carbons; in particular, the allylic proton and carbon signals trans to phosphine were easily distinguished by the characteristic couplings J_{HP} (respectively ∼9.5 Hz and ∼8 Hz for *anti* and *syn*) and J_{CP} (∼30 Hz).[28] Moreover, an interesting coupling between the carbenic carbon and the *anti* proton in trans position was found in the 2D HMBC spectrum.

The complex **6c** was prepared in the same manner starting from $[Pd(\eta^3\text{-}1,3\text{-diphenylallyl})OCOCF_3]_2$. The ^1H and $^{31}P\{^1H\}$ NMR spectra indicated the presence of four isomers. The more abundant species (76%) was identified as the *exo*−*syn*−*syn* isomer on the basis of the 2D 1H NOESY spectrum. Indeed, the diagnostic NOE between the terminal *anti*-allyl protons evidenced the *syn*−*syn* configuration (confirmed by the absence of NOEs between the central and terminal allyl protons and by the typical allylic ^1H-H coupling constants), while the NOE between the central allyl proton and the protons of the ^{t}Bu group is in agreement with the *exo* form of the isomer. Also in this case the doublet ($J_{CP} = 29.6$ Hz) due to to the carbene carbon coordinated to palladium is visible in the $^{13}C\{^1H\}$ NMR spectrum at 169.7 ppm.

Kinetic Studies. The nucleophilic attack of an amine at the allyl fragment of palladium(II) complexes is considered the key step in the palladium-catalyzed amination of allylic substrates.[29] Therefore, we decided to extend our previous kinetic studies[30] to these new compounds in order to investigate the influence on the reaction rates of the simultaneous presence in the ancillary ligands of a carbene and a phosphine donor (P−C ligand). In this context the comparison with isostructural complexes of the phosphine-pyrazole ligand (P−N) becomes particularly interesting.

The η^3-propenyl complexes reacted smoothly with an excess of secondary amines (piperidine, benzylamine) in $CHCl_3$ at 25 °C, in the presence of dimethyl fumarate (dmfu), to give the zerovalent complexes $[Pd(\eta^2\text{-dmfu})(P-C)]$ or $[Pd(\eta^2\text{-dmfu})(P-N)]$ and the corresponding allylamine. The use of an electron-

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(27) This signal is visible only for the major *exo* isomer.

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Scheme 4

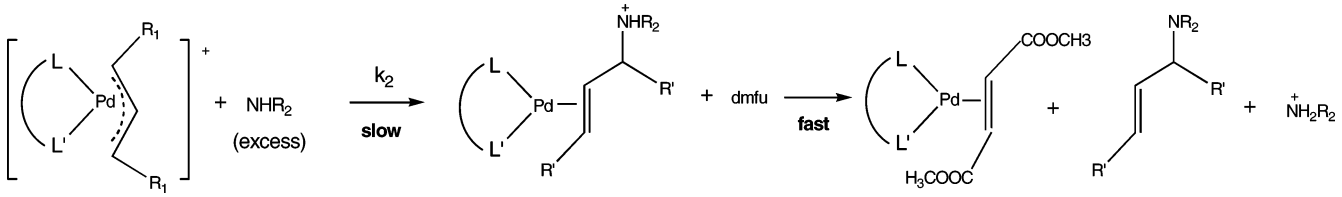
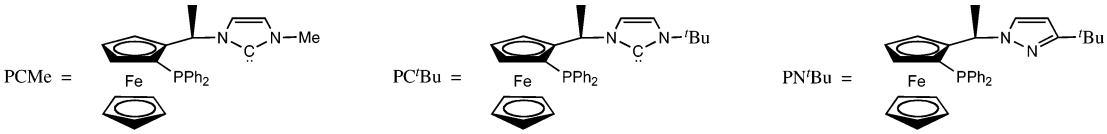


Table 1. Second-Order Rate Constants (k_2, mol^{-1} dm^3 s^{-1}) for Reactions of Allyl Complexes with Amines at 25 °C in $CHCl_3$



entry	complex	amine	k_2
1	[Pd(η^3-allyl)(PCMe)]CF_3CO_2, **6a**	piperidine	$(2.70 \pm 0.06) \times 10^{-3}$
2	[Pd(η^3-allyl)(PC^{t}Bu)]CF_3CO_2, **6b**	piperidine	$(2.26 \pm 0.07) \times 10^{-2}$
3	[Pd(η^3-allyl)(PC^{t}Bu)]CF_3CO_2, **6b**	benzylamine	$(3.4 \pm 0.1) \times 10^{-4}$
4	[Pd(η^3-allyl)(PN^{t}Bu)]CF_3CO_2, **6d**	piperidine	33.5 ± 0.9
5	[Pd(η^3-allyl)(PN^{t}Bu)]CF_3CO_2, **6d**	benzylamine	0.687 ± 0.009
6	[Pd(η^3-1,3-Ph_2-allyl)(PC^{t}Bu)]CF_3CO_2, **6c**	piperidine	$\sim 5 \times 10^{-5}$ [a]
7	[Pd(η^3-1,3-Ph_2-allyl)(PN^{t}Bu)]PF_6, **6e**	piperidine	$(1.41 \pm 0.02) \times 10^{-2}$

[a] Approximate value obtained from a ^{31}P NMR experiment ([complex] = 1.5×10^{-2} mol dm^{-3}; [piperidine]= 0.2 mol dm^{-3}, in $CDCl_3$) since with the usual concentrations of the UV−vis studies the reaction is too slow and the complex partially decomposes.

withdrawing olefin ensured the stabilization of the Pd(0) fragment, thus reducing the possibility of its decomposition and of secondary reactions.

The reaction was monitored by NMR spectroscopy, and its course was confirmed by the appearance of the typical signals of the allylamine and of the Pd(0) complex in the ^{1}H NMR spectra. A simplified view of the process could be obtained by ^{31}P{^{1}H} NMR spectra, observing in this case only the signals of palladium species. In this respect it is interesting to emphasize that the isomer ratio of the initial complexes (*exo* and *endo*) remained constant throughout the reaction, revealing that nucleophilic attack by the amine may take place at the allyl carbons of both isomers at rates lower than that of interconversion (Curtin−Hammett regime).[31]

However, we preferred to gather the data for the kinetic analysis following the progress of the reaction by UV−vis spectral changes in the wavelength range 300−500 nm of $CHCl_3$ solutions of Pd-allyl complexes (ca. 1×10^{-4} mol dm^{-3}) in the presence of dimethylfumarate (dmfu) ($(2-8) \times 10^{-4}$ mol dm^{-3}), upon addition of variable aliquots of excess amine (1×10^{-3} to 6×10^{-2} mol dm^{-3}). Under such pseudo-first-order conditions the reactions went smoothly to completion, as indicated by comparison of solution spectra after 7−8 half-lives with those of the independently prepared final products. The conversion to the zerovalent palladium complexes appears to obey the customary monoexponential absorbance (A) versus time (t) relationship $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obs}t)$. The pseudo-first-order constants were determined by nonlinear regression of the absorbance A_t data to time. No dependence of the rates on the dimethylfumarate concentration could be detected in the range investigated. The values of k_{obs} fit the second-order rate law:

$$k_{obs} = k_2[NHR_2]$$

In light of all these data we propose the mechanistic picture of Scheme 4, where the cationic substrate undergoes rate-determining nuclephilic attack by amine (k_2 step) to give a labile Pd(0) intermediate bearing an η^2-bound allylammonium fragment, which is rapidly and quantitatively displaced by the more π-accepting dimethylfumarate ligand to produce the final derivative [Pd(η^2-dmfu)(P−C)] or [Pd(η^2-dmfu)(P−N)]. The values of rate constants k_2 are listed in Table 1.

The simple linear dependence of k_{obs} on amine concentration seems to exclude the possibility of a displacement of the bidentate ligand (or of one of its donor groups), for a simultaneous amine attack at the metal center, previously observed in similar systems with N−N, N−S, and P−N ancillary ligands and described by a fast pre-equilibrium.[28,30] This observation is consistent with the predicted high coordination ability of these P−C ligands, due to the strong metal−carbene and metal−phosphine bonds. In addition, the steric protection provided by the ^{t}Bu substituent adjacent to the coordinating atom in the heterocyclic ring (see Chart 1) could play an important role in stabilizing the complexes; this applies also to the phosphine-pyrazole ligand (PN).

From Table 1 it is apparent that (a) the k_2 constants increase with increasing basicity of the amine[32] (see entries 2, 3 and 4, 5), in agreement with our previous kinetic studies.[28,30] (b) A marked decrease is observed on going from η^3-propenyl complexes to the corresponding η^3-1,3-diphenylallyl derivatives (see entries 3/6 and 4/7), as a result of increased steric hindrance, which cannot be compensated by the electrophilic character of the allyl fragment bearing phenyl substituents. (c) For the P−C ligands, a marked influence on k_2 is also exerted by the nature of the substituent on the heterocyclic nitrogen atom. Surprisingly, with the bulkier $C(CH_3)_3$ group a higher k_2 value is observed than with the Me substituent (entries 1, 2). This finding can be rationalized by invoking a destabilizing distortion of the

(31) (a) Auburn, P. R.; Mackenzie, P. B.; Bosnich, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 2046. (b) Mackenzie, P. B.; Whelan, J.; Bosnich, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 2046. For a general treatment of the Curtin−Hammett principle, see: (c) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

(32) At 25 °C the pK_a values for piperidine and benzylamine are 11.12 and 9.34, respectively (Albert, A.; Serjeant, E. P. In *The Determination of Ionization Constant*; Chapman and Hall: London, 1984; p 151.

η^3-allyl fragment in the more crowded substrate **6b**, which increases its reactivity. An analogous sterically activating effect has already been observed with iminophosphine[28] and pyridyl thioether[30c,d] ligands. (d) Finally, a striking decrease in reactivity (nearly 3 orders of magnitude) was recorded on going from pyrazole P−N to carbene P−C complexes. This trend is maintained for both amines and allyl groups under scrutiny (see entries 4/2, 5/3, and 7/6, in Table 1). It is evident that the powerful σ-donating and weak π-accepting character of the carbene ligand[7a,12e,33a,b] increases the electron density at the metal center and consequently at the allyl group, with a detrimental effect on its reactivity with respect to the nucleophilic attack by the amine. This behavior is not unexpected; Sato and coworkers have already observed that amines do not react with allyl acetate in the Pd−NHC system,[33c]and other purely electron-donating ligands have shown an analogous negative influence.[33d] However, this detrimental effect was quantified here for the first time from a kinetic point of view.

These conclusions are valid also if we take into account that, in the case of the complexes with P−C ligands, the nucleophilic attack may occur at both terminal allyl carbons (i.e., trans to P and trans to C, *vide infra*), and therefore the k_2 values in Table 1 should be considered as the sum of four contributions (two for each diasteroisomer).

Synthesis and Characterization of a New Palladium(0) Olefin Complex. The complexes [Pd(η^2-dmfu)(P−C)] can be synthesized by making use of the amination reaction described above. After all, it constitutes an alternative to the method proposed by Cavell et al.[34] for the preparation of analogous compounds, starting from [Pd(η^2-alkene)(COD)] and free carbene ligands. Therefore, we reproduced the reaction between complex **6b** and piperidine (entry 2, Table 1) on a preparative scale with the aim of isolating and characterizing the corresponding Pd(0) compound **7b**. After separation of organic products, the complex was obtained as a yellow solid. It was soluble in most common organic solvents, except for aromatic and nonaromatic hydrocarbons, and stable in solution and in the solid state when exposed to air.

Its elemental analysis was in good agreement with the expected compositions. The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra revealed the presence of two diastereoisomers, deriving from the coordination of the olefin via its *re* or *si* enantioface. The relative isomer population is 85:15.

As a consequence of the olefin binding mode, upfields shifts of 2.6−3.1 ppm for the alkene protons and of 85.2−91.5 ppm for the corresponding carbons were observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra, respectively, as compared to the signals of free dmfu at 6.86 (^{1}H) and 133.9 (^{13}C). This may be attributed to the strong shielding afforded by the extensive π-back-bonding from the Pd center, which somewhat lessens the double-bond character of the dmfu ligand.[35] Moreover, the asymmetric structure of the P−C ligand makes the two olefinic termini different; the proton and the carbon trans to phosphorus could be identified by the large values of J_{HP} (10 Hz) and J_{CP} (∼28.5 Hz).

The small difference between the resonances of the olefinic carbon trans to the carbene (42.4 ppm) and trans to phosphorus (48.7 ppm) is noteworthy and attests the similar electronic character of these two donors.

For the more abundant isomer the signal of the carbene carbon bound to the metal was detected as a weak doublet (J_{CP} = 15.9 Hz) at 187.0 ppm. Again, this assignment was confirmed by a 2D HMBC experiment, in which the couplings of the carbene carbon with the two alkene protons of the imidazole unit with the C(*H*)CH$_3$ proton and with the dimethyl fumarate olefinic proton trans to carbene were observable.

Asymmetric Allylic Amination Catalysis. The new complex **6b** has been tested in Pd-catalyzed reactions of racemic 1,3-diphenylallylethyl carbonate with benzylamine and piperidine. The reaction was carried out in THF at 40 °C in the presence of 3 mol % of complex as catalyst. After 72 h, the amination products were isolated after chromatographic purification.

Only a partial conversion of the starting allylic carbonate occurred (32% and 58% for benzylamine and piperidine, respectively), and the allyl amination products are virtually racemic (5% ee of *S* enantiomer) in both cases.

The same reactions involving the complex with the corresponding pyrazole ligand **6d** as catalyst gave completely different results, affording a quantitative conversion to the allylic amine products with a high stereoselectivity (97.7% ee for benzylamine and 97.2 for piperidine), after only 20 h, as previously reported for a very similar system.[11] We have verified here that the trifluoroacetate ion, thanks to its coordinating properties, favors the selectivity of the process, being an efficient anion in ensuring Curtin−Hammett conditions, which is considered an essential requisite in order to obtain high ee's.[36]

The lower yield observed with **6b** as compared to **6d** as catalyst may be easily correlated to the remarkable difference of the k_2 values for amine nucleophilic attack onto allyl intermediates (see Table 1), confirming that this step is rate-determining in the catalytic process. The better result attained with piperidine is, in turn, a consequence of its higher reactivity in this step.

The dramatic loss of stereoselectivity observed with the carbene complex **6b** appears much more intricate. It has been verified that no kinetic resolution of the starting racemic allylic carbonate takes place under the reaction conditions,[37] and consequently its oxidative addition to the catalyst, proceeding with inversion of configuration, produces equal amounts of diastereomeric η^3-allyl complexes, with opposite configurations at the allylic termini. At this point a rapid equilibrium between the diasteroisomers permits a thermodynamic redistribution of the species (Curtin−Hammett regime), in agreement with the isomeric composition obtained in the synthesis of **6c**. Since the observed enantiomeric composition of the allylamine product is likely to reflect the regioselectivity of the nucleophilic attack on the major *exo-syn*−*syn* isomer (76% in **6c**), we may conclude that this attack is virtually nonselective, as shown by the almost racemic product obtained.[38] It is apparent that this effect is not due to steric reasons since the "isostructural" P−N ligand leads to an exclusive attack trans to phosphorus, as proven by the high stereoselectivity obtaned with complex **6d**. The more plausible explanation is the comparable trans influence of

(33) (a) Douthwaite, R. E.; Hodgson, R. *J. Organomet. Chem.* **2005**, *690*, 5822. (b) Lee, M.-T.; Hu, C.-H *Organometallics* **2004**, *23*, 976. (c) Sato, Y.; Mori, T. *J. Organomet. Chem.* **2005**, *690*, 5753. (d) For example [Pd-(η^3-allyl)(NHR$_2$)$_2$]$^+$ are pratically inert toward nucleophilic attack (see ref 30a).

(34) McGuiness, D. S; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596.

(35) Antonaroli, S.; Crociani, B. *J. Organomet. Chem.* **1998**, *560*, 137.

(36) Burckhardt, U.; Baumann, M.; Togni, A. *Tetrahedron: Asymmetry* **1997**, *8*, 155.

(37) The unreacted 1,3-diphenylallylethyl carbonate was still racemic.

(38) It seems improbable that the minor isomers may display such different rates for the nucleophilic attack to compensate for a possible preferential attack at one allylic terminus in the major isomer. Indeed, the case of a pyrazole-phosphine complex with an isomeric distribution very similar to **6f** was reported, for which a preferential attack at the carbon trans to phosphorus led to high ee's (see ref 11a).

carbene and phosphine ligands, which renders the corresponding trans allyl carbons electronically equivalent. In fact, the difference between the chemical shifts of the terminal allyl carbons (an indirect probe of their different electrophilcity) is much less marked in the P−C complex than in the corresponding P−N complexes (8.1 against 28 ppm, respectively, for the simple allyl complexes **6b** and **6d**, and 20.7 and 41 ppm, respectively, for the diphenyl derivatives **6c** and **6e**). Therefore, the electronic factor is predominant in determining stereoselectivity, compensating also for the more drastic rearrangement required in the transition state when the nucleophilic attack takes place trans to carbene rather than trans to phosphine.[13]

Conclusion

In this contribution new palladium π-allyl complexes with chelating phosphinocarbene ligands have been prepared and fully characterized. The synthetic procedure involves a silver-mediated transfer of the carbene ligand to a labile palladium π-allyl precursor. Their reaction with benzylamine and piperidine in the presence of an activated olefin (dimethylfumarate) has been studied. It involves a slow nucleophilic attack at the allyl moiety, producing the new zerovalent complexes [Pd(η^2-dmfu)(P−C)] and the corresponding allylamine. A detailed kinetic study has shown a remarkable decrease in the amination rate for the phosphinocarbene complexes as compared to the "isostructural" phosphinopyrazole derivatives. This fact may be attributed mainly to the powerful σ-donating and weak π-accepting character of the carbene ligand, which increases the electron density at the metal center and consequently at the allyl group, thereby drastically retarding the nucleophilic attack of the amine. The comparable trans effect/influence of phosphine and carbene donor groups seems to be the basis of the loss of enantioselectivity when the new P−C ligands were tested in the palladium-catalyzed amination of 1,3-diphenylallylethyl carbonate.

Experimental Section

Materials. Unless otherwise stated, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were purified by standard procedures and distilled under argon immediately prior to use. 1D- and 2D-NMR spectra were recorded using a Bruker DPX300 or Bruker DPX500 spectrometer. Chemical shifts (ppm) are given relative to TMS (^{1}H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR).

Peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). The proton and carbon assignment was performed by ^{1}H-2D COSY, ^{1}H-2D NOESY, ^{1}H−^{13}C HMQC, and HMBC experiments.

UV−vis spectra were taken on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Perkin-Elmer PTP6 (Peltier temperature programmer) apparatus.

A general procedure for the catalysis experiments and the details for the determination of the enantiomeric purity of the products have been reported previously.[13a] Enantiomeric excesses were determined by HPLC using Daicel Chiralcel OJ and OD-H columns and eluting with a hexane/^{i}PrOH mixture (99.5/0.5 v/v, 0.45 mL/min for the benzylamine-derived product; 96/4 v/v, 0.35 mL/min for the corresponding piperidine derivative; T = 25 °C; detection at 254.8, 230.4, 210.8).

(*R*)-*N*,*N*-Dimethyl-1-((*S*)-2-diphenylphosphinoferrocenyl)ethylamine (**2**),[13] (*R*)-1-((*S*)-2-diphenylphosphinoferrocenyl)ethyl acetate (**3**),[13] 1-*tert*-butylimidazole,[39] and the complexes [Pd(μ-CF_3CO_2)(η^3-C_3H_5)]$_2$,[40] [Pd(μ-CF_3CO_2)(η^3-PhCHCHCHPh)]$_2$,[40] [Pd(η^3-C_3H_5)(1-[(*R*)-1-((*S*)-2-diphenylphosphinoferrocenyl)ethyl]-3-*tert*-buyl-1*H*-pyrazole)]CF_3CO_2 (**6c**), and [Pd(η^3-PhCHCHCHPh)(1-[(*R*)-1-((*S*)-2-diphenylphosphinoferrocenyl)ethyl]3-*tert*-buyl-1*H*-pyrazole)]PF_6 (**6d**)[26] were prepared following literature procedures. All other chemicals were commercial grade and were used without further purification.

1-[(*R*)-1-((*S*)-2-Diphenylphosphinoferrocenyl)ethyl]3-methylimidazolium Bromide (4a). A suspension of **3** (0.82 g, 1.8 mmol) and 1-methylimidazole (0.18 g, 2.2 mmol) in a mixture of acetonitrile (8 mL) and water (4 mL) was stirred at room temperature for 3 days to give a clear orange solution. After evaporation of the solvent under vacuum, the residue was dissolved in 9 mL of methanol with NaBr (0.55 g, 5.3 mmol) and stirred for 3 h. After removal of the solvent, dichloromethane was added to the residue and the white undissolved solid (excess NaOAc and NaBr) was separated by filtration. The orange solution was evaporated to dryness, affording the product as a yellow solid, which was washed first with benzene and then *n*-pentane and finally dried under vacuum. Yield: 0.90 g (89.6%), orange-yellow solid. ^{1}H NMR ($CDCl_3$, 298 K): δ 2.07 (d, J_{CHMe} = 7.1 Hz, 3H, CH*Me*), 3.65 (s, 3H, NCH_3), 3.92 (m, 1H, Cp), 4.14 (s, 5H, Cp′), 4.54 (t, J_{CHCH} = 2.6 Hz, 1H, Cp) 4.99 (m, 1H, Cp), 5.98 (qd, J_{CHMe} = 7.1 Hz, J_{PH} = 3.4 Hz 1H, C*H*Me) 6.53 (m, 1H, CH═CH Im), 6.79 (m, 1H, CH═CH Im), 6.92 (m, 2H, PPh_2), 7.18 (m, 3H, PPh_2), 7.43 (m, 5H, PPh_2), 9.84 (s, 1H, $^+$CH Im). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 21.6 (CH_3 CH*Me*), 36.5 (CH_3, N*Me*), 56.3 (d, J_{CP} = 10.1 Hz, CH, *C*HMe), 70.2 (d, J_{CP} = 3.1 Hz, CH, Cp), 70.4 (CH, Cp′), 71.0 (CH, Cp), 73.0 (d, J_{CP} = 3.7 Hz, CH, Cp), 75.7 (C, Cp), 87.7 (d, J_{CP} = 24.4 Hz, C, Cp), 119.2 (CH, HC═CH Im), 122.1 (CH, HC═CH Im), 128.1, 128.2, 128.4, 128.5, 128.6, 129.8 (CH, P*Ph*$_2$), 132.3 (d, J_{CP} = 18.8 Hz, CH, P*Ph*$_2$), 134.5 (C, P*Ph*$_2$), 134.7 (d, J_{CP} = 20.4 Hz, CH, P*Ph*$_2$), 136.8 (CH, $^+$*C*H Im), 137.8 (C, P*Ph*$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ −27.3. Anal. Calcd for $C_{28}H_{28}BrFeN_2P$: C, 60.13; H, 5.05; N, 5.01. Found: C, 59.82; H, 5.22; N, 5.16.

1-[(*R*)-1-((*S*)-2-Diphenylphosphinoferrocenyl)ethyl]3-*tert*-buylimidazolium Bromide (4b). A suspension of **3** (1.12 g, 2.45 mmoli) and 1-*tert*-butylimidazole (0.37 g, 2.94 mmol) in a mixture of acetonirile (12 mL) and water (6 mL) was stirred for 3 days to give a clear orange solution. After evaporating the solvent under vacuum, the residue was dissolved in 13 mL of methanol with NaBr (0.76 g, 7.36 mmol) and stirred for 3 h. After removal of the solvent, dichloromethane was added to the residue and the white undissolved solid (exces NaOAc and NaBr) was separated by filtration. The crude product obtained after evaporation of the solvent was chromatographed (silica gel, CH_2Cl_2 + CH_3OH 4%). Yield: 1.21 g (82.3%), orange-yellow solid. ^{1}H NMR ($CDCl_3$, 298 K): δ 1.41 (s, 9H, ^{t}Bu), 2.18 (d, J_{CHMe} = 6.9 Hz, 3H, CH*Me*), 3.96 (m, 1H, Cp), 4.06 (s, 5H, Cp′), 4.52 (t, J_{CHCH} = 2.6 Hz, 1H, Cp) 5.07 (m, 1H, Cp), 6.16 (qd, J_{CHMe} = 6.9 Hz, J_{PH} = 3.3 Hz 1H, C*H*Me) 6.77 (m, 2H, PPh_2), 6.85 (m, 1H, CH═CH Im), 7.01 (m, 1H, CH═CH Im), 7.09 (m, 3H, PPh_2), 7.38 (m, 3H, PPh_2), 7.48 (m, 2H, PPh_2), 9.79 (s, 1H, $^+$CH Im). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 21.4 (CH_3 CH*Me*), 29.6 (CH_3, C*Me*$_3$), 56.3 (d, J_{CP} = 10.4 Hz, CH, *C*HMe), 60.1 (C, *C*Me$_3$), 70.2 (CH, Cp′), 70.2 (CH, Cp), 70.9 (CH, Cp), 72.6 (d, J_{CP} = 4.4 Hz, CH, Cp), 75.7 (d, J_{CP} = 9.5 Hz, C, Cp), 90.4 (d, J_{CP} = 25.8 Hz, C, Cp), 118.2 (CH, HC═CH Im), 118.3 (CH, HC═CH Im), 127.8, 127.9, 128.0, 128.2, 128.3,129.6 (CH, P*Ph*$_2$), 131.4 (d, J_{CP} = 18.1 Hz, CH, P*Ph*$_2$), 134.2 (CH, $^+$*C*H Im), 135.0 (d, J_{CP} = 20.4 Hz, CH, P*Ph*$_2$), 135.9 (d, J_{CP} = 6.6 Hz, C, P*Ph*$_2$), 139.4 (d, J_{CP} = 9.3 Hz, C, P*Ph*$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ −26.7. Anal. Calcd for $C_{31}H_{34}BrFeN_2P$: C, 61.92; H, 5.70; N, 4.66. Found: C, 61.12; H, 5.94; N, 4.56.

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1-[(*R*)-1-((*S*)-2-Diphenylphosphinoferrocenyl)ethyl]3-methylimidazol-2-ylidenebromosilver(I) (5a). The imidazolium bromide **4a** (0.320 g, 0.570 mmol) was dissolved in 13 mL of dichloromethane, and Ag_2O (0.080 g, 0.345 mmol) was added. The mixture was stirred for 6 h at room temperature to produce a clear orange solution with only a trace of black solid. This slight excess of Ag_2O was removed by filtration through Celite, and the solution was concentrated *in vacuo*. The product was precipitated by addition of diethyl ether, filtered off, and washed with diethyl ether and *n*-pentane. Yield: 0.360 g, 94.4%, orange solid. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.87 (d, J_{CHMe} = 6.9 Hz, 3H, CH*Me*), 3.48 (br s, 3H, NCH_3), 3.95 (br s, 1H, Cp), 4.37 (s, 5H, Cp′), 4.57 (t, J_{CHCH} = 2.5 Hz, 1H, Cp) 4.84 (br s, 1H, Cp), 6.14 (br s, 1H, C*H*Me) 6.36 (br s, 1H, CH═CH Im), 7.16 (br s, 1H, CH═CH Im), 7.36 (m, 8H, PPh_2), 7.69 (br s, 2H, PPh_2). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ br s −12.31. Anal. Calcd for $C_{28}H_{27}BrFeN_2PAg$: C, 50.49; H, 4.09; N, 4.21. Found: C, 50.21; H, 4.16; N, 4.29.

1-[(*R*)-1-((*S*)-2-Diphenylphosphinoferrocenyl)ethyl]3-*tert*-butylimidazol-2-ylidenebromosilver(I) (5b). The synthesis of the title complex is analogous to that of **5a**, starting from the appropriate imidazolium bromide **4b** (0.200 g, 0.33 mmol) and Ag_2O (0.046 g, 2 mmol) in 6 mL of dichloromethane with a reaction time of 18 h. Yield: 0.223 g (94.4%), orange solid. ^{1}H NMR (CD_2Cl_2, 298 K): δ 1.43 (s, 9H, ^{t}Bu), 1,93 (d, J_{CHMe} = 6.9 Hz, 3H, CH*Me*), 4,00 (br s, 1H, Cp), 4.17 (br s, 5H, Cp′), 4.57 (bt, 1H, Cp) 4.86 (br s, 1H, Cp), 6.66 (m, 2H, PPh_2), 6.77 (br s, 1H, C*H*Me) 7,03 (br s, 2H, CH═CH Im), 7.07 (m, 1H, CH═CH Im), 7.18 (m, 3H, PPh_2), 7.48 (m, 3H, PPh_2), 7.75 (br s, 2H, PPh_2). ^{31}P{^{1}H}NMR (CD_2Cl_2, 298 K): σ −21.0. Anal. Calcd for $C_{31}H_{33}BrFeN_2PAg$: C, 52.57; H, 4.70; N, 3.96. Found: C, 52.22; H, 4.88; N, 3.84.

[1-[(*R*)-1-((*S*)-2-Diphenylphosphinoferrocenyl)ethyl]3-methylimidazol-2-ylidene Palladium(η^3-allyl)]trifluoroacetate (6a). To a solution of [Pd(μ-CF_3CO_2)(η^3-C_3H_5)]$_2$ (0.060 g 0.115 mmol) in dichloromethane (7 mL) was slowly added dropwise a solution of silver complex **5a** (0.153 g 0.230 mmol, dissolved in 7 mL of CH_2Cl_2). The solution, which suddenly became cloudy, was stirred for 1 h at room temperature and then filtered through Celite to remove the silver salt. The clear yellow solution was concentred under vacuum, and the product, precipitated by addition of diethyl ether, was washed several times with diethyl ether and *n*-pentane. Yield: 0.145 g (85.3%), yellow solid. ^{1}H NMR ($CDCl_3$, 298 K): *exo*-isomer (65%) δ 2.01 (d, J_{CHMe} = 7.0 Hz, 3H, CH*Me*), 2.67 (s, 3H, NCH_3), 3.31 (dd, J_{CH2CH} = 13.7 Hz, J_{PH} = 11.2 Hz, 1H, allyl H_{anti} trans-P), 3.67 (d, 13.6 Hz, 1H, allyl H_{anti} trans-C), 3.91 (m, 1H, Cp), 4.01 (s, 5H, Cp′), 4.41 (d, J_{CH2CH} = 7.0 Hz, allyl H_{syn} trans-C) 4.51 (dd, J_{CH2CH} = 7.6 Hz, J_{PH} = 6.2 Hz, 1H, allyl H_{syn} trans-P), 4.52 (m, 1H, Cp), 4.87 (m, 1H, Cp), 5.56 (m, 1H, allyl H_{center}), 6.14 (m, 1H, C*H*Me), 6.50 (m, 2H, PPh_2), 6.90 (m, 1H, CH═CH Im), 7.23 (m, 1H, CH═CH Im), 7.25 (m, 3H, PPh_2), 7.60 (m, 3H, PPh_2), 7.78 (m, 2H, PPh_2); *endo*-isomer (35%) δ 1.95 (d, J_{CHMe} = 7.3 Hz, 3H, CH*Me*), 2.81 (s, 3H, NCH_3), 3.12 (m, 2H, allyl H_{anti} trans-C allyl and H_{anti} trans-P), 3.89 (m, 1H, Cp), 3.96 (s, 5H, Cp′), 4.48 (m, 1H, Cp), 4.49 (partially obscured, allyl H_{syn} trans-P) 4.76 (d, J_{CH2CH} = 7.6 1H, allyl H_{syn} trans-C), 4.82 (m, 1H, Cp), 5.82 (m, 1H, allyl H_{center}), 5.83 (m, 1H, C*H*Me), 6.60 (m, 2H, PPh_2), 6.93 (m, 1H, CH═CH Im), 7.21 (m, 1H, CH═CH Im), 7.25 (m, 3H, PPh_2), 7.58 (m, 3H, PPh_2), 7.75 (m, 2H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): *exo*-isomer δ 16.5 (CH_3 CH*Me*), 36.6 (CH_3, NCH_3), 55.3 (CH, *C*HMe), 64.3 (CH_2 allyl trans-C), 66.1 (d J_{CP} = 31.8 Hz, CH_2, allyl trans-P), 69.9 (d, J_{CP} = 7.1 Hz CH, Cp), 70.0 (C, Cp), 70.6 (CH, Cp′), 71.1 (br s, CH, Cp), 73.6 (CH, Cp), 92.8 (d, J_{CP} = 14.8 Hz, C, Cp), 120.5 (d, J_{CP} = 5.5 Hz, CH, allyl central), 124.5 (CH, HC═CH Im), 128.5 (CH, HC═CH Im), 171.4 (d, J = 23.2 Hz, C−Pd, Im); *endo*-isomer δ 16.6 (CH_3 CH*Me*), 36.8 (CH_3, NCH_3), 55.0 (CH, *C*HMe), 65.9 (d J_{CP} = 30.0 Hz, CH_2, allyl trans-P), 66.8 (CH_2 allyl trans-C), 69.7 (d, J_{CP} = 7.7 Hz CH, Cp), 69.7 (C, Cp), 70.6 (CH, Cp′), 71.1 (br s, CH, Cp), 73.6 (CH, Cp), 92.7 (d, J_{CP} = 15.9 Hz, C, Cp), 120.5 (d, J_{CP} = 5.5 Hz, CH, allyl central), 124.5 (CH, HC═CH Im), 128.5 (CH, HC═CH Im), 170.8 (d, J = 23.9 Hz, C−Pd, Im). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): *exo*-isomer δ 13.0 (PPh_2); *endo*-isomer 13.8 (PPh_2). Anal. Calcd for $C_{33}H_{32}F_3FeN_2PO_2Pd$: C, 53.64; H, 4.37; N, 3.79. Found: C, 53.41; H, 4.23; N, 3.69.

[1-[(*R*)-1-((*S*)-2-Diphenylphosphinoferrocenyl)ethyl]3-*tert*-buylimidazol-2-ylidene Palladium(η^3-allyl)]trifluoroacetate (6b). The synthesis of the title complex is analogous to that of **6a**, starting from [Pd(μ-CF_3CO_2)(η^3-C_3H_5)]$_2$ (0.060 g 0.115 mmoli) and silver complex **5b** (0.163 g, 0.230 mmol). Yield: 0.152 g (84.4%), yellow solid. ^{1}H NMR ($CDCl_3$, 298 K): *exo*-isomer (82%) δ 0.95 (s, 9H, ^{t}Bu), 2.07 (d, J_{CHMe} = 7.0 Hz, 3H, CH*Me*), 3.64 (dd, J_{CH2CH} = 13.7 Hz, J_{PH} = 9.5 Hz, 1H, allyl H_{anti} trans-P), 3.78 (d, 12.8 Hz, 1H, allyl H_{anti} trans-C), 3.93 (m, 1H, Cp), 3.96 (s, 5H, Cp′), 4.44 (d, J_{CH2CH} = 7.7 Hz, allyl H_{syn} trans-C) 4.48 (dd, J_{CH2CH} = J_{PH} = 8.4 Hz, 1H, allyl H_{syn} trans-P), 4.52 (t, J_{CHCH} = 2.6 Hz, 1H, Cp), 4.90 (m, 1H, Cp), 5.43 (m, 1H, allyl H_{center}), 6.27 (m, 1H, C*H*Me), 6.54 (m, 2H, PPh_2), 7.16 (m, 1H, CH═CH Im), 7.23 (m, 3H, PPh_2), 7.45 (m, 1H, CH═CH Im), 7.61 (m, 3H, PPh_2), 7.80 (m, 2H, PPh_2); *endo*-isomer (18%) δ 1.06 (s, 9H, ^{t}Bu), 2.00 (d, J_{CHMe} = 7.0 Hz, 3H, CH*Me*), 2.94 (dd, J_{CH2CH} = 13.7 Hz, J_{PH} = 9.4 Hz, 1H, allyl H_{anti} trans-P), 3.23 (d, 13.9 Hz, 1H, allyl H_{anti} trans-C), 3.89 (s, 5H, Cp′), 4.86 (signal partially obscured, allyl H_{syn} trans-C) 4.53 (signal partially obscured, allyl H_{syn} trans-P), 6.02 (m, 1H, allyl H_{center}), 5.93 (m, 1H, C*H*Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): *exo*-isomer δ 17.1 (CH_3 CH*Me*), 30.5 (CH_3, C*Me*$_3$), 56.7 (CH, *C*HMe), 57.6 (C, *C*Me$_3$), 61.8 (CH_2 allyl trans-C), 69.4 (d, J_{CP} = 6.6 Hz CH, Cp), 69.9 (d J_{CP} = 30.2 Hz, CH_2, allyl trans-P), 70.6 (CH, Cp′), 71.3 (d, J_{CP} = 6.0 Hz, CH, Cp), 72.0 (C, Cp), 73.1 (CH, Cp), 93.1 (d, J_{CP} = 15.6 Hz, C, Cp), 118.0 (CH, HC═CH Im), 119.2 (d, J_{CP} = 4.9 Hz, CH, allyl central) 122.2 (CH, HC═CH Im), 167.6 (d, J = 23.1 Hz, C−Pd, Im). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): *exo*-isomer δ 12.3 (PPh_2); *endo*-isomer δ 13.2 (PPh_2). Anal. Calcd for $C_{36}H_{38}F_3FeN_2PO_2Pd$: C, 55.37; H, 4.90; N, 3.59. Found: C, 55.12; H, 4.74; N, 3.50.

[1-[(*R*)-1-((*S*)-2-Diphenylphosphinoferrocenyl)ethyl]3-*tert*-buylimidazol-2-ylidene Palladium(η^3-PhCHCHCHPh)]trifluoroacetate (6c). The synthesis of the title complex is analogous to that of **6a**, starting from [Pd(μ-CF_3CO_2[Pd(η^3-PhCHCHCHPh)]$_2$ (0.012 g 0.015 mmol) and silver complex **5b** (0.021 g 0.03 mmol). Yield: 0.025 g (90.0%), orange solid. ^{1}H NMR ($CDCl_3$, 298 K): *exo*−*syn*−*syn*-isomer (76%) δ 0.58 (s, 9H, ^{t}Bu), 2.24 (d, J_{CHMe} = 7.0 Hz, 3H, CH*Me*), 3.93 (m, 1H, Cp), 3.96 (s, 5H, Cp′), 4.46 (t, J_{CHCH} = 2.3 Hz, 1H, Cp), 4.90 (m, 1H, Cp), 5.36 (d, 10.3 Hz, 1H, allyl H_{anti} trans-C), 6.23 (m, 1H, allyl H_{center}), 6.26 (dd, J_{CH2CH} = 11.7; J_{PH} = 9.4 Hz, 1H, allyl H_{syn} trans-P), 6.68 (m, 1H, C*H*Me), 7.16 (m, 1H, CH═CH Im), 7.44 (m, 1H, CH═CH Im). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): *exo*−*syn*−*syn*-isomer δ 17.4 (CH_3 CH*Me*), 29.3 (CH_3, C*Me*$_3$), 56.7 (CH, *C*HMe), 57.1 (C, *C*Me$_3$), 68.4 (d, J_{CP} = 6.7 Hz CH, Cp), 70.7 (d, J_{CP} = 6.6 Hz CH, Cp), 70.9 (CH, Cp′), 71.1 (C, Cp), 73.6 (CH, Cp), 72.8 (CH_2 allyl trans-C), 93.5 (d J_{CP} = 29.6 Hz, CH_2, allyl trans-P), 93.6 (d, J_{CP} = 15.9 Hz, C, Cp), 113.4 (d, J_{CP} = 5.0 Hz, CH, allyl central), 118.0 (CH, HC═CH Im), 122.5 (CH, HC═CH Im), 169.7 (d, J = 29.6 Hz, C−Pd, Im). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): *exo*−*syn*−*syn*-isomer δ 10.7 (76% PPh_2); other isomers δ 10.8 (16%, PPh_2), 10.3 (4%, PPh_2), 10.2 (4%, PPh_2). Anal. Calcd for $C_{48}H_{46}F_3FeN_2PO_2Pd$: C, 61.78; H, 4.97; N, 3.00. Found: C, 61.53; H, 4.84; N, 2.92.

[1-[(*R*)-1-((*S*)-2-Diphenylphosphinoferrocenyl)ethyl]3-*tert*-buylimidazol-2-ylidene Palladium(0)(η^2-dimethyl fumarate)] (7b). An excess of piperidine (0.020 g, 0.230 mmol) was added to 3.5 mL of a solution of complex **6b** (0.036 g, 23 μL, 0.046 mmol) and dimethylfumarate (0.093 g, 0.645 mmol). The mixture was vigorously stirred at room temperature for 7 h, and then the solvent was evaporated to dryness. The residual solid was repeatedly washed with water, dried under vacuum, and redissolved in

dichloromethane. Upon treatment with activated charcoal and filtration through Celite, the volume of the resulting solution was reduced to 4 mL and washed with 10 mL of a 0.1 M aqueous solution of Na_2CO_3 and then 10 mL of water to remove the residual trace of ammonium salts. After drying over Na_2SO_4, the CH_2Cl_2 solution was evaporated to dryness and the residue was washed several times with *n*-hexane. Yield: 0.028 g (78.8%), orange solid. ^{1}H NMR ($CDCl_3$, 298 K): *major* isomer (15%) δ 0.98 (s, 9H, ^{t}-Bu), 1.81 (d, J_{CHMe} = 7.0 Hz, 3H, CH*Me*), 3.52 (s, 3H, OMe), 3.54 (s, 3H, OMe), 3.79 (dd, 1H, $J_{CH=CH} = J_{PH}$ = 10 Hz, 1H, CH═CH trans-P), 3.92 (s, 5H, Cp′), 3.98 (m, 1H, Cp), 4.27 (dd, 1H, $J_{CH=CH}$ = 10 Hz, J_{PH} = 2.6 Hz, CH═CH trans-C), 4.30 (t, J_{CHCH} = 2.8 Hz, 1H, Cp) 4.59 (m, 1H, Cp), 6.35 (m, 2H, PPh_2), 6.74 (m, 1H, C*H*Me), 6.87 (m, 1H, CH═CH Im), 6.88 (m, 1H, CH═CH Im), 7.03 (m, 3H, PPh_2), 7.53 (m, 3H, PPh_2), 8.07 (m, 2H, PPh_2); *minor* isomer (15%) detectable signals δ 0.90 (s, 9H, ^{t}Bu), 1.88 (d, J_{CHMe} = 7.0 Hz, 3H, CH*Me*), 6.97 (m, 1H, C*H*Me), 8.16 (m, 2H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): *major* isomer δ 17.3 (CH_3, CH*Me*), 30.3 (CH_3, C*Me*$_3$), 42.4 (CH, CH═CH trans-C), 48.7 (d, J_{CP} = 28.5 Hz, CH, CH═CH trans-P), 50.3 (CH_3, OMe), 50.4 (CH_3, OMe), 55.3 (CH, *C*HMe), 57.0 (C, *C*Me$_3$), 68.4 (d, J_{CP} = 5.5 Hz, CH, Cp), 69.6 (d, J_{CP} = 3.3 Hz, CH, Cp),70.3 (CH, Cp′), 72.9 (CH, Cp), 74.8 (d, J_{CP} = 22.0 Hz, C, Cp), 93.3 (d, J_{CP} = 17.0 Hz, C, Cp), 114.1 (CH, HC═CH Im), 118.6 (CH, HC═CH Im), 171.1 (CO, *C*OOMe), 175.1 (CO, *C*OOMe), 187.0 (d, J = 15.9 Hz, C−Pd, Im); *minor* isomer, detectable signals δ 17.1 (CH_3, CH*Me*), 30.0 (CH_3, C*Me*$_3$), 55.2 (CH, *C*HMe), 56.6 (C, *C*Me$_3$), 115.0 (CH, HC═CH Im), 119.0 (CH, HC═CH Im). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): *major*-isomer δ 17.9 (PPh_2); *minor* isomer δ 18.9 (PPh_2). Anal. Calcd for $C_{37}H_{41}FeN_2PO_4Pd$: C, 57.64; H, 5.36; N, 3.63. Found: C, 57.52; H, 5.22; N, 3.51.

Kinetic Measurements. The kinetics of the allylic amination of complexes **6a**, **6b**, **6c**, **6d**, and **6e** were studied by adding known aliquots of the appropriate amine solution to a solution of the respective complex and dimethylfumarate in the thermostated cell compartment of the spectrophotometer. The amounts of reactants were such to ensure constant excess over the metal complex ($[Pd]_0$ ca. 1×10^{-4} mol dm^{-3}). The progress of the reaction was monitored by recording absorbance changes either in the range 600−300 nm or at fixed wavelength with time. Mathematical and statistical data analysis was carried out on a personal computer by means of a locally adapted version of the Marquardt algorithm.

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