Discussion

This successful determination of the structure of an intermediate occurring during asymmetric allylic alkylations allows us to offer some suggestions as to the root cause of the chiral induction. It is generally accepted that chelating diphosphine ligands with an ability to form five-membered chelate rings will adopt a gauche conformation. This is particularly true in the case of first-row transition-metal complexes, in which the metal–phosphorus bond distances are comparatively short. In the case of the chiral *S*,*S*-chiraphos ligand, the asymmetry at the C atoms causes the ring to adopt the δ configuration, in which the two methyl substituents are disposed in the energetically favorable equatorial positions. The phenyl ring substituents upon the P atoms accordingly adopt quasi-axial and quasi-equatorial positions relative to the metal,P,P plane. Nonbonded steric interactions between the rings and the methyl groups result in an alternating face–edge profile presented to the two remaining coordination sites in the square-planar geometry at the metal. Examples are known in which either an attractive[18,19] or repulsive[20] interaction has been postulated between substituents on P atoms in order to account for the observed geometry.

In the present study, the η^3-allyl ligand contains three bulky substituents, one phenyl ring, and two even bulkier 3,5-dimethylphenyl groups. Repulsive steric interactions between the substituents on P(1) and those on C(5) result in the adoption of a staggered arrangement. The earlier studies[2] confirmed that a major source of the discrimination occurs at the anti position of C(5). In the solid-state structure, ring six occupies this position. The phenyl ring on C(7) and the equatorial phenyl ring on P(2) lie parallel in the solid state; there may or may not be an attractive interaction between them. This interaction is not important in chiral discrimination.[2] If the alternative allyl ligand configuration were seen, the steric disposition at C(5) would consist of eclipsed substituents, and a presumably much higher energy species. Thus, as has been observed before, the chiral discrimination can be attributed to steric interactions between the substrate molecule and a chiral complex whose profile is fixed by the energetically favored conformation of the chiraphos chelate ring.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for operating grants and major equipment grants to D.H.F. and N.C.P.

Registry No. $[Pd(\eta^3\text{-}C(Xyl)_2CHCHPh)(S,S\text{-}PPh_2(CHMe)_2PPh_2)]\text{-}BPh_4\cdot CH_3CH_2O_2CCH_3$, 95043-25-7.

Supplementary Material Available: A description of the solvent molecule, anisotropic thermal parameters for Pd, P(1), and P(2), rigid group parameters, hydrogen atom parameters, and structure amplitudes as $10|F_o|$ vs. $10|F_c|$ (21 pages). Ordering information is given on any current masthead page.

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Homogeneous Catalysis. Transition-Metal-Catalyzed Claisen Rearrangements

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Abstract: Palladium(0), palladium(II), rhodium(I), and iridium(I) compexes catalyze the rearrangement of allyl imidates to allyl amides under mild conditions. The palladium(II) catalysis is characterized by exclusive [3,3] regioselectivity and high stereoselectivity whereas the palladium(0), rhodium(I), and iridium(I) catalysts generally give both the [3,3] and [1,3] rearrangement products and although the palladium(0) catalyst can give high stereoselectivity, the rhodium(I) and iridium(I) catalysts are nonstereoselective. After a series of experiments using chiral substrates and substrates with specific deuterium labels, the mechanisms of these catalytic reactions have been elucidated. The palladium(II) catalysis is proposed to proceed via cyclic carbonium ion intermediates, and the mechanism resembles the thermal uncatalyzed Claisen rearrangement path. The palladium(0) catalysis is a form of catalytic allylation involving oxidative addition followed by nucleophilic attack on a π-allyl intermediate. The mechanism of the rhodium(I) and iridium(I) catalysis was not as fully investigated as the others, but it appears to involve carbonium ion intermediates formed by cleavage of the allyl–oxygen bond.

The Cope and Claisen [3,3]sigmatropic thermal rearrangements are of considerable synthetic utility. Mechanistic[1] and theoretical[2] studies show that these intramolecular reactions are subject to strong geometrical constraints governed by the intermediates that result from suprafacial cyclization so that there is nearly complete transfer of chirality from reactant to product. This stereocontrol has been ingeniously exploited in a number of synthetic strategies but generally the rearrangements have been embodied early in the synthesis because of the high temperatures (~200 °C) generally required. Because of this thermal restriction, a number of attempts have been made to accelerate these reactions.[3]

The earliest attempts involved the use of protic (H_2SO_4[4]) or Lewis acids (BF_3,[5] BCl_3,[6] alumina[7]). Although rate enhancements were observed,the yields were poor and the side products were numerous presumably because in all of these cases the reactions proceed via carbonium ions as evidenced by the diversity of products and the loss of stereocontrol. The most impressive rate acceleration of a Claisen rearrangement was reported by Ireland,[8]

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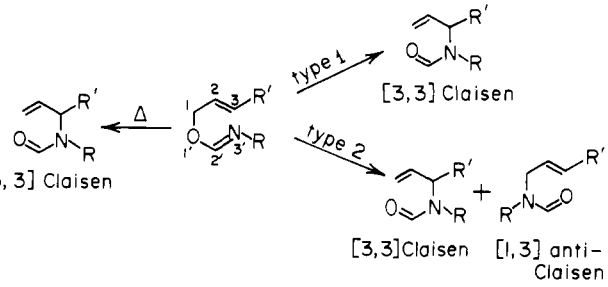


Figure 1. Rearrangements of allyl imidates by the type **1** and type **2** catalysts and the thermal reaction.

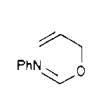
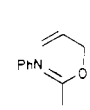
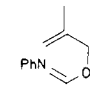
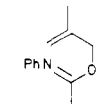
who found that the enolates of allyl esters are rapidly transformed to the corresponding acids at ambient temperatures. Similar rate enhancements were observed in the (anionic) oxy-Cope reaction.[9] These two reactions, however, are restricted to these types of systems and it would be advantageous to develop a series of catalysts which would induce rearrangement for any Cope or Claisen substrate. This possibility is now beginning to emerge with the use of transition-metal catalysts.[3]

The first reports of metal-induced Cope rearrangements were the stoichiometric reactions of $[PdCl_2(PhCN)_2]$ with *cis, trans*-1,5-cyclodecadiene[10] and *cis*-1,2-divinylcyclobutane[11] to produce $[Pd(diolefin)Cl_2]$ complexes of *cis*-1,2-divinylcyclohexane and 1,5-cyclooctadiene, respectively. A similar product was obtained from the reaction of nickel(II) complexes with *cis*-1,2-divinylcyclobutane.[11] Overman[12] was the first to report that $[PdCl_2(PhCN)_2]$ catalyzed the Cope rearrangements of certain acyclic dienes under mild conditions. Rate accelerations of the order of 10^{10} were observed and, moreover, the catalytic reaction was shown to proceed via a chairlike intermediate resembling that established for the thermal uncatalyzed path.[1]

Metal-catalyzed Claisen rearrangements have so far been restricted mainly to allyl imidates, where the thermodynamic driving force[13] (ΔH) is $\sim$14 kcal mol^{-1}. These catalysts can be classified into two groups according to the types of products formed. The first group of catalysts (type **1**) gives a single product which is the same as the thermal product. This class includes the complexes $Hg(CF_3CO_2)_2$,[14] $[PdCl_2(PhCN)_2]$,[15] and $H_2[PtCl_6]$.[16] The second group (type **2**) includes the zero-valent complexes $[Pd(PPh_3)_4]$[15] and $[Pt(PPh_3)_4]$,[17] which can give either the [3,3] product (Claisen) or the [1,3] product (anti-Claisen) or both (Figure 1). Although the thermal allyl imidate reactions typically require hours at $\sim$200 °C for completion, many of these catalysts allow the conversions to occur within minutes at 25 °C, indicating rate accelerations of 10^{10}–10^{12} over the thermal reactions. Little is known about the details of the mechanisms of these catalytic Claisen reactions, however, and it seems opportune to investigate in some detail the way in which these catalysts work.

This paper describes the results of our investigation of the mechanisms of the metal-catalyzed allyl imidate rearrangements. We report on both the type **1** and type **2** catalysts as well as on a brief study of perhaps a third class of catalyst. We begin by surveying the transformations of a number of different allyl imidates with various catalysts.

Table I. Rearrangements of Allyl Imidates to Allyl Amides by Various Catalysts at 25 °C[a]

	substrate			
catalyst				
$[Pd(PPh_3)_4]$	<20 min[c]	d^8-tol. 5 h	d^8-tol. 6 d	d^8-tol. 3 d
$[PdCl_2(PhCN)_2]$	2 h	17 d	NR[b]	NR
$[Rh(NBD)(diphos)]ClO_4$	16 h	48%, 14 d	NR	NR
$[Ir(COD)_2]BF_4$	<20 min	4 d	4 h	NR
$[Ir(COD)Cl]_2$	45 min	3 d	5 d	NR
$[Ir(COD)(CH_3CN)_2]BF_4$	45 min	4 d	2 d	NR
$[Ir(COD)(diphos)]BF_4$	7 d	14 d	NR	NR

[a] All reactions carried out in $CDCl_3$ solution unless otherwise stated. [b] NR = no reaction after 5 d (d = days). [c] Times listed refer to time required for 90% conversion of substrate.

Catalytic Rearrangements

Some of the results of metal-catalyzed Claisen rearrangements are collected in Table I. All of the reactions were run at 25 °C using 5 mol % catalyst in dilute solutions ($\sim 3 \times 10^{-4}$ mol of substrate). These data serve to illustrate, first, that a variety of catalysts can be used, second, that substituents at the 2- and 5-positions have a marked effect on the velocity of reaction, and finally that the individual catlaysts rearrange a given substrate at different rates. For consistency we have employed chloroform as a common solvent but, for the $[Pd(PPh_3)_4]$ catalyst, we found that solvents such as benzene or toluene cause a dramatic increase in catalytic turnover. Thus for the 2- and/or 5-methyl substituted substrates, the catalysis is exceedingly slow in chloroform using the palladium(0) species and we have had to use toluene as a solvent to obtain convenient rates. Even so, of all the catalysts tried, only the palladium(0) species rearranges all four of the substrates listed in Table I.

The data in Table I do not distinguish the regioselectivity of the rearrangement. This question is addressed in Table II; the most revealing results are those for the rearrangement of the 1,1-dideuterated allyl imidate. This substrate rearranges to a 1:1 mixture of Claisen and anti-Claisen products with the pallaidum(0) catalysts, exclusively to the Claisen product with the palladium(II) catalyst and to mixtures of Claisen and anti-Claisen, but predominantly anti-Claisen, products with rhodium(I) and iridium(I) catalysts. When the [3(*Z*)-^{2}H]allyl imidate substrate is used, an ^{1}H NMR analysis at 400 MHz showed that the anti-Claisen products contained the deuterium at both the *Z* and *E* positions for the palladium(0), rhodium(I), and iridium(I) catalysts. In all cases complete scrambling of the deuterium position was observed. Since the palladium(II) catalyst gives exclusively the Claisen product the question of scrambling is not resolved by the experiment. The 3-methyl and 3-phenylallyl imidates, which unlike the deuterated compounds provide steric and electronic biases to rearrangement, both give exclusively the Claisen product with the palladium(II) catalyst. With the palladium(0) catalyst, however, the phenylated substrate gives exclusively the anti-Claisen product whereas the 3-methyl analogue rearranges to an equal mixture of the two regioisomers. The same mixture is obtained by using $[Ir(COD)_2]BF_4$.

Taken as a whole these results suggest that at least two mechanisms operate for the catalytic rearrangement of allyl imidates. The mechanisms of the palladium(0) and palladium(II) catalysis are clearly different and the mechanism for the rhodium(I) and iridium(I) catalysis may differ in some respects from that of the palladium(0) species. We deal with the palladium(II) catalyzed reactions first.

Palladium(II) Catalytic Mechanism

The most obvious difference between the palladium(II) catalyst and the others is that the former always gives the Claisen product exclusively. This suggests that the mechanism of the palladium(II)

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Table II. Selectivity of the Catalytic Rearrangements of Various Allyl Imidates at 25 °C in $CDCl_3$ Solution

catalyst	[3,3] [1,3]	^{2}H isomerism?	[3,3]:[1,3]	[3,3] [1,3]
$[Pd(PPh_3)_4]$	50:50	yes	50:50 (3 h)	0:100 (<20 min)
$[PdCl_2(PhCN)_2]$	100:0		100:0 (17 h)	100:0 (30 h)
$[Rh(NBD)(diphos)]ClO_4$	15:85	yes		
$[Ir(COD)_2]BF_4$	6:94	yes	50:50 (41 h)	
$[Ir(COD)Cl]_2$	39:61	yes		
$[Ir(COD)(CH_3CN)_2]BF_4$	4:96	yes		
$[Ir(COD)(diphos)]BF_4$	19:81	yes		

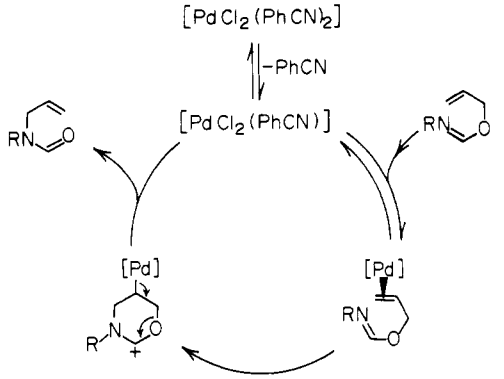


Figure 2. Outline of the catalytic cycle for palladium(II) catalyzed rearrangements of allyl imidates.

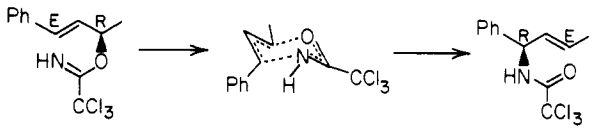


Figure 3. Thermal rearrangements of a chiral allyl imidate showing the stereocontrol via the chair intermediate.

catalyzed rearrangement may resemble the thermal concerted path. The most obvious concerted catalytic mechanism is the one originally proposed by Henry[18] for palladium(II) catalyzed acetate migration in allyl acetates and which was subsequently developed by Overman to explain the mercury(II) catalyzed rearrangements of allyl carbamates,[19] allyl imidates,[14] and the palladium(II) induced Cope rearrangements.[12] The proposed catalytic cycle is outlined in Figure 2. In this mechanism, the coordinated olefin undergoes intramolecular attack by the lone pair of the imidate nitrogen atom to the exo face of the olefin[20] to produce the metal bound six-membered cyclic carbonium ion intermediate which rapidly rearranges to the product and regenerates the catalyst. Such a mechanism will always give the Claisen product as observed. The lack of reactivity of allylic imidates wiht methyl groups at the (olefinic) 2-position (Table I) is presumably connected with the difficulty of forming a tertiary carbon–palladium bond. Although the proposed catalytic mechanism resembles the uncatalyzed thermal path, the stereocontrol in the two cases may be different because of the intervention of the palladium species in the former.

The thermal rearrangement of optically active allyl imidates has been shown to proceed with complete chirality transfer[21] via the intermediate shown in Figure 3. The suprafacial addition ensures that the (*R*, *E*)-allyl imidate will rearrange to the (*R*, *E*)-allyl amide (Figure 3). In order to compare the stereochemistry

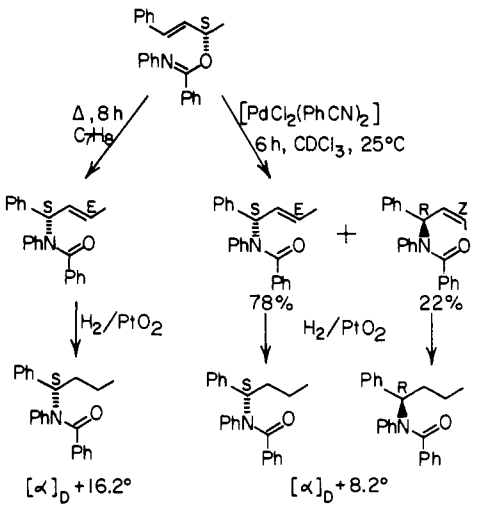


Figure 4. Products of the thermal and the catalytic palladium(II) rearrangements of the chiral allyl imidate and the products obtained after reduction of the double bonds.

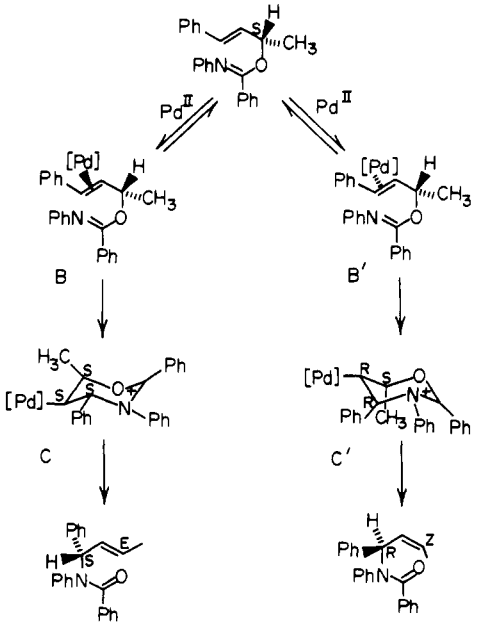
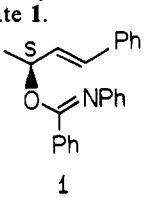


Figure 5. Proposed mechanism for the palladium(II) catalyzed rearrangement of the chiral allyl imidate.

of the catalyzed and uncatalyzed reactions, we prepared the optically active allyl imidate **1**.



1

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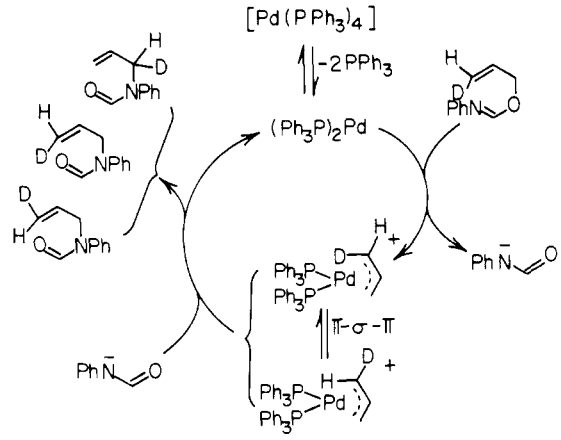

Figure 6. Proposed mechanism for the palladium(0) catalyzed rearrangement of the allyl imidates, showing how the deuterium atom is scrambled via the $\pi-\sigma-\pi$ mechanism.

Compound **1** was subjected to thermal and catalytic rearrangement under conditions outlined in Figure 4. The thermal reaction gave the pure (*E*)-allyl amide. Given this olefin geometry as well as the suprafacial addition (Figure 3), it follows that the chirality of the product is *S*. The catalytic reaction, however, gives a 78:22 ratio of *E*:*Z* olefin isomers and, moreover, the *E* and *Z* olefin isomers were of *S* and *R* chirality, respectively (Figure 4).

An explanation for the steric course of the catalytic reaction with substrate **1** is outlined in Figure 5. Because the olefin faces of **1** are diastereotopic by virtue of the adjacent chiral center, coordination of the olefin to the palladium atom can occur in two energetically distinct diastereomeric forms which are related by which of the two olefin faces is bound to the metal (B and B′). Intramolecular attack by the nitrogen atom lone pair on the exo face of the bound olefin will produce two distinct palladium six-membered ring intermediates (C and C′). We note that the chirality at the 3-phenyl-substituted carbon atom and also that of the carbon atom bound to the palladium are enantiomeric in C and C′ (Figure 5). The respective chiralities of the products are determined by which of the olefin faces is coordinated in B and B′. We assume that because of its bulk, the palladium fragment will prefer to be equatorially disposed. Given this and assuming that a chair ring is formed, intermediate C will have all of its substitutents equatorially disposed. In C′, however, the methyl group is *cis* to the palladium but the phenyl group is *trans*, hence an equatorially disposed palladium requires an axially disposed methyl group. Assuming that the transformation of C and C′ to the products is a concerted process, orbital symmetry demands that C will give the *E* olefin geometry whereas C′ will give the *Z* isomer. The chirality of each of the products is determined at the exo olefin face attack step preceding the C and C′ intermediates. Thus the intervention of the palladium catalyst changes the steric course of the Claisen rearrangement. We now turn to the palladium(0) catalysis.

Palladium(0) Catalytic Mechanism

The results in Table II show that the palladium(0) catalyzed reactions lack the regioselectivity that is displayed by the palladium(II) catalyst. Thus the 3-methylallyl imidate gives a 1:1 ratio of isomers and the 3-phenyl analogue gives exclusively the anti-Claisen product. Particularly revealing is the catalysis of 1,1-dideuterated substrate which gives a 1:1 ratio of Claisen and anti-Claisen products. This suggests that, in the absence of steric and electronic effects, the 1- and 3-positions of the allyl moiety become equivalent during the catalytic cycle. Moreover, the observation that deuterium scrambling occurs with the [3(*Z*)-^{2}H]allyl imidate suggests a nonconcerted process. The simplest mechanism which accommodates all of these observations is one involving a (π-allyl)palladium(II) intermediate. An outline of one such mechanism is given in Figure 6.

It is assumed that the palladium(0) bis(triphenylphosphine) complex oxidatively adds to the allyl imidate to give a [Pd-

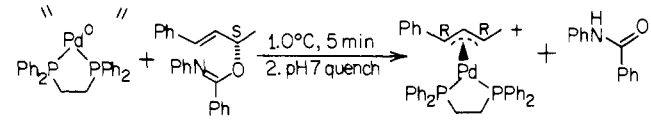

Figure 7. Oxidative addition reaction of the chiral allyl imidate with "Pd(diphos)".

$(PPh_3)_2(\pi\text{-allyl})]^+$ intermediate and the amide anion. If the π-allyl intermediate is sufficiently long lived, it will scramble the first formed anti-disposed deuterium to the syn disposition via the $\pi-\sigma-\pi$ mechanism.[22] Either of these ^{2}H syn or anti isomers is then attacked by the amide anion to give the poducts and to regenerate the palladium(0) catalyst. Ignoring deuterium effects, it is clear that the two ends of the π-allyl intermediate are equivalent and hence we expect the observed 1:1 ratio of Claisen and anti-Claisen products. Moreover, the anti-Claisen product will have the deuterium scrambled if $\pi-\sigma-\pi$ is much faster than the rate of amide anion attack, hence the observed 1:1 ratio of *Z*:*E* deuterated anti-Claisen isomers. The observed regioselectivity for the transformations of the 3-methyl and 3-phenyl substrates is controlled by the selectivity of attack on the respective π-allyl intermediates. In essence, the proposed mechanism is a form of palladium-catalyzed allylation.[23]

In order to confirm this mechansim, we require first to establish the existence of the π-allyl intermediate during the catalysis. If the π-allyl complex is indeed an intermediate, then the question of whether the amide anion attacks the coordinated π-allyl intra- or intermolecularly can be raised: i.e., does the amide anion coordinate to the (π-allyl)palladium intermediate and cause reductive elimination to the products or does a free uncoordinated amide anion attack the coordinated π-allyl group? If an optically active allyl were formed, the intramolecular mechanism would lead to retention of configuration whereas the intermolecular mechanism would lead to inversion for the nucleophilic attack step. The proposed mechanism, however, involves both oxidative addition and nucleophillic attack and in order to determine the stereochemistry of the latter we require to know that of the former. In order to do this the allyl imidate is required to have a number of characteristics which are embodied in the optically active allyl imidate **1**. Upon oxidative addition, **1** will give the chiral fragment, (1-methyl-3-phenyl-π-allyl)palladium(II), which is incapable of racemizing via the $\pi-\sigma-\pi$ mechanism.[22] Hence, the overall stereochemistry will ot be lost by racemization of the π-allyl intermediate. Further, previous work[24,25] suggests that nucleophilic attack on the $[Pd(PPh_3)_2(1\text{-methyl-3-phenyl-}\pi\text{-allyl})]^+$ ion will occur almost exclusively at the methyl bearing end of the π-allyl thus obviating complications that could arise from the production of regioisomers.

When $[Pd(diphos)(\eta^3\text{-}C_3H_5)]ClO_4$ is allowed to react with sodium dimethyl malonate in THF solution, the "Pd(diphos)" species so generated undergoes rapid oxidative addition with allyl acetates.[26] We find that this species also undergoes rapid oxidative addition to the allyl imidate **1** and by controlling the conditions, we isolated both the amide fragment as well as the [Pd(diphos)(1-methyl-3-phenyl-π-allyl)]$^+$ ion (Figure 7). The absolute configuration of this complex is known[24] and it was shown that its stoichiometric reaction with sodium dimethyl malonate leads to inversion of configuration.[24] When we performed the same reaction with the isolated [Pd(diphos)(1-methyl-3-phenyl-π-allyl)]$^+$ ion derived from the *S* allyl imidate **1**, the dimethyl malonate allyl product had the *S* configuration and the *E* olefin geometry (Figure 8). Hence, since the nucleophilic attack is known to proceed with inversion, the stoichiometric oxidative addition also proceeded with

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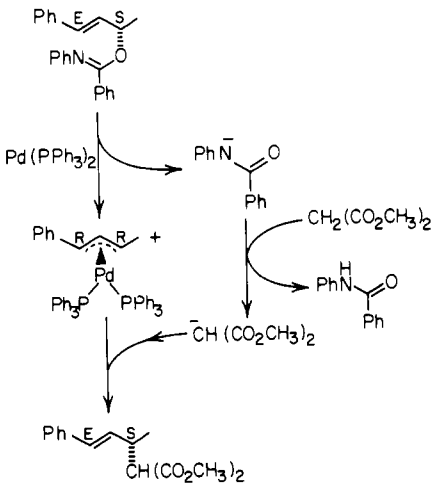

Figure 8. Mechanism for the interception of the π-allyl intermediate with dimethyl malonate anion.

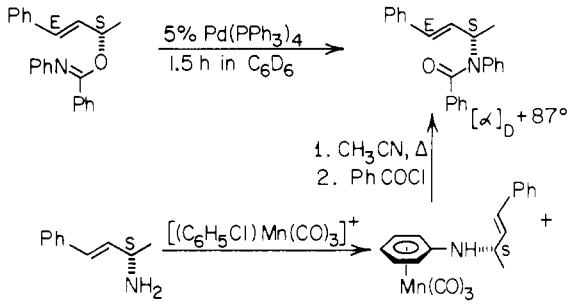

Figure 9. Method used for correlating the absolute configuration of the product of the palladium(0) catalyzed rearrangement.

inversion. We related this result to the actual catalytic reaction as follows.

Using 5% of the catalyst $[Pd(PPh_3)_4]$ and the *S* allyl imidate **1** in the presence of 3 equiv of dimethyl malonate in benzene solution, the sole products of catalysis were the dimethyl malonate allylation product and the (benzene) insoluble amide (Figure 8). The dimethyl malonate allylation product was optically and isomerically pure *S*–*E* material. Hence the oxidative addition that occurs during catalysis proceeds with inversion and the *p*-allyl intermediate has the *R*,*R* configuration (Figure 8).

The fact that the amide anion is liberated and deprotonates the dimethyl malonate strongly implicates an oxidative addition step but it does not establish that in the absence of dimethyl malonate the amide anion attacks the π-allyl intermolecularly during the Claisen rearrangement. It is still possible that the freed amide anion coordinates to the metal and then induces intramolecular reductive elimination. Since we now know that oxidative addition proceeds with inversion, we can determine the stereochemistry of nucleophilic amide attack by establishing the overall stereochemistry of the palladium(0) catalyzed Claisen rearrangement.

The $[Pd(PPh_3)_4]$ catalyzed rearrangement of the optically pure *S* allyl imidate **1** gave exclusively the anti-Claisen product which was optically active and exclusively of the *E* olefin geometry. The absolute configuration of this rearrangement product was established by the method shown in Figure 9. The resolved allyl amine, which is of known absolute configuration,[27] was phenylated by using the arylmanganese complex.[28] Subsequent removal of the metal followed by benzoylation gave the desired amide. We established by both optical rotation and by use of a chiral shift reagent in a ^1H NMR experiment that the product of catalytic rearrangement was optically pure and of *S* configuration. Thus the rearrangement proceeded with complete overall retention of

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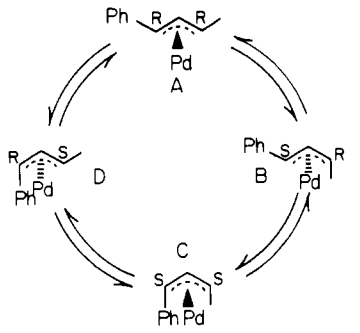

Figure 10. Epimerization cycle induced by the π-σ-π mechanism.

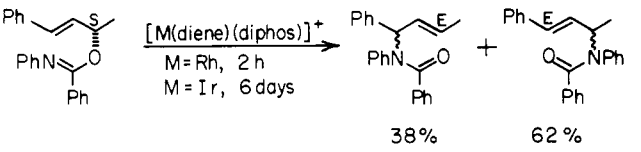

Figure 11. Rearrangement products which are formed by rhodium(I) and iridiuim(I) catalysis of the optically active allyl imidate.

configuration. Since intramolecular reductive elimination would be expected to lead to retention, and since we have shown that oxidative addition proceeds with inversion, we conclude that the nucleophilic attack step of the catalysis occurs by intermolecular attack on the exo face of the coordination π-allyl intermediate.

Although the π-σ-π mechanism will not racemize the palladium(1-methyl-3-phenyl-π-allyl) unit, the infinite epimerization cycle allows for four isomers (Figure 10). Exo attack on either A or B will lead to the observed *S* configuration and also the observed *E* geometry of the olefin. Exo or endo attack on C and D will give the wrong olefin geometry and hence endo attack on any of the four π-allyl isomers is incompatable with our observations. The results are consistent only with exo attack on A and/or B and we suppose that the majority if not all of the catalysis proceeds through A because of its greater stability[22] and the absence of evidence that attack at centers with anti-disposed groups is much faster than at centers with syn-disposed groups in allylation.[23]

Mechanism of Rhodium(I) and Iridium(I) Catalysis

The data in Tables I and II suggest that the rhodium(I) and iridium(I) catalysts proceed by a different mechanism from that proposed for either the palladium(0) or palladium(II) catalysts. Any mechanism has to account for the complete scrambling of the position of the olefin deuterium atom and it requires an explanation for the strong preference for the anti-Claisen product when the 1,1-dideuteroallyl imidate is used (Table II). In addition, the mechanism has to accomodate certain other features that we have observed. If the catalysis is carried out in the presence of dimethyl malonate, there is no incorporation of dimethyl malonate in the product as was observed for the palladium(0) catalysis. This suggests that if the amide anion is formed, it is bound to the metal. Furthermore, we find no 1,3-proton (allyl) shifts for any of the catalytic reactions which excludes the intervention of an intermediate metal–hydrido–π-allyl species. Finally, when the optically active allyl imidate **1** is allowed to rearrange catalytically with either $[Rh(NBD)(diphos)]^+$ or $[Ir(COD)(diphos)]^+$ in chloroform solution, the same ratio of Claisen to anti-Claisen products is observed (Figure 11). In both cases, however, each of the products is optically inactive.

The most obvious mechanism that could be proposed for the rhodium(I) and iridium(I) catalysis is one involving oxidative addition of the substrate to form a cis amide–(σ-allyl)metal(III) intermediate which, after stereochemical rearrangement, would reductively eliminate the substrate fragments to give the products. If oxidative addition is at all stereospecific, however, this mechanism cannot account for the complete loss of optical activity because, as we have noted, any π-allyl intermediate that may be formed from the allyl imidate **1** cannot racemize via the π–σ–π

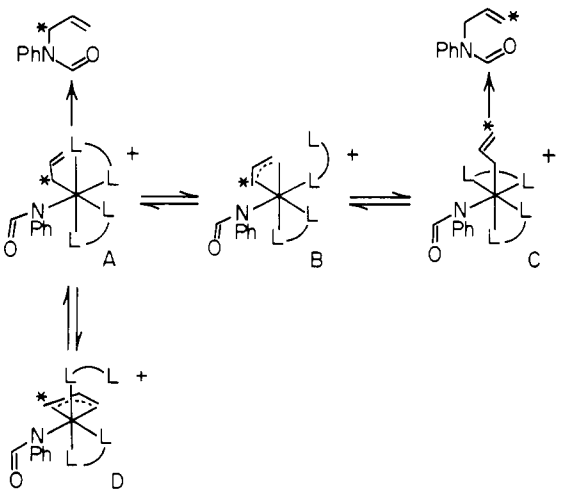

Figure 12. Some of the possible intermediates which could be formed after oxidative addition of an allyl imidate to rhodium(I) and iridium(I) complexes. Intermediate A is assumed to be the first formed product and equilibration between B, C, and D occurs via π-allyls and the partial dissociation of a bidentate ligand. Only steps involving a single act of chelate ring opening from A are considered.

mechanism. Even assuming nonstereospecific oxidative addition, this mechanism has difficulty accounting for the other characteristics of the catalysis. To account for the deuterium scrambling about the double bond via the π-σ-π mechanism a π-allyl is required to be formed in the metal(III) intermediate. A mechanism allowing for π-allyl formation is shown in Figure 12 where only transformations involving one act of bidentate ligand opening are considered. Because A and C are enantiomers, B can collapse to either A or C with equal facility and, for the same reason, A and C will reductively eliminate with equal probability. Thus in order to explain the regioselectivity observed for the 1,1-dideuterio allyl substrate we have to assume that the equilibration A $\rightleftharpoons$ D is more facile than that of A $\rightleftharpoons$ B. It is not obvious to us why this would be the case since amide ligands are not known to have a strong *trans* labilizing effect; on the contrary, because the bidentate ligands are usually phosphines or olefins, we might expect the A $\rightleftharpoons$ C equilibration to be favored.

There are other considerations which would disfavor this mechanism. All of the rhodium(I) and iridium(I) complexes used here are not expected to be effective at oxidative addition, particularly the positively charged species. We find that the complex $[Rh(PPh_3)_3Cl]$, which is known to oxidatively add allyl halides,[29] does not rearrange the allyl imidates within the window of the present conditions, although rearrangement can be induced in benzene solution at 70 °C after 12 h. Further, although rhodium(III) species tend to undergo ready reductive elimination, iridium(III) species are known to be much more stable. The data in the tables do not indicate any systematic rate difference which might reflect this. We therefore favor a superficially less appealing mechanism.

The regioselectivity of the catalysis bears a resemblance to the product distributions observed for S_N1 (nonpolar) solvolysis of allyl halides.[30] The carbonium ion intermediate forms a tight ion pair to give a so called "product spread" in the regiodirection of the starting allyl isomer irrespective of the regiostability of the carbonium ion. We therefore propose a mechanism involving carbonium ion intermediates (Figure 13). The metal(I) catalyst first coordinates to the allyl imidate which then fragments to form the carbonium ion which is partially stabilized by the metal electrons. We note that a free *delocalized* allyl carbonium ion has a rotational barrier of 17–20 kcal mol^{-1} [31] and hence we have drawn the coordinated allyl carbonium ion with a localized double

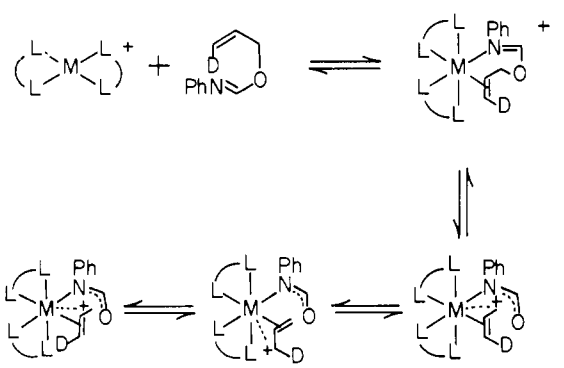

Figure 13. Proposed carbonium ion mechanism that could cause rearrangement of an allyl imidate. Shown is the fragmentation of an allyl imidate coordinated to either rhodium(I) or iridium(I). The mechanism for cis–trans olefin isomerism is shown as occurring via 1,3-carbonium ion shifts, a mechanism which also leads to loss of optical activity. The products are formed by combination of the carbonium ion with the coordinated nitrogen atom of the amide anion.

bond so as to allow rotation about the "single bond". This mechanism allows for lose of chirality and assuming a double bond shift, it also allows for scrambling of the deuterium position of the double bond. The regioselectivity would be governed by the steric constraints imposed on the system and the proximal dispositions of the allyl carbonium ion and the imidate anion. The influence of the surrounding ligands is suggested by the fact that for the structurally similar catalysts $[Rh(NBD)(diphos)]^+$ and $[Ir(COD)(diphos)]^+$ the regioselectivity is the same for the rearrangements of the allyl imidate **1** and for the deuterated substrates. Throughout the cycle (Figure 13) we assumed no formal oxidation state change in the metal, although some transference of metal electrons to the carbonium ion is expected. In this sense a quasi-π-allyl intermediate is formed but without the usual rearrangement characteristics of normal π-allyl complexes.

Discussion

The present results exemplify many of the characteristics of homogeneous metal-induced catalysis. The Claisen rearrangements appear to occur by three different mechanisms, only one of which, the palladium(II) catalyst, resembles the thermal uncatalyzed path. The other two are, characteristically, stepwise nonconcerted processes. The palladium(0) catalysis involves oxidation changes and oxidative addition followed by nucleophilic attack, and this also is typical of many group 8–10[54] metal catalysts. If, however, the proposed carbonium ion mechanism for the rhodium(I) and iridium(I) catalysts is correct then the catalysis with these metals resembles more the catalysis associated with Lewis acids. Thus because the catalytic paths are generally quite different from the uncatalyzed path, the expectation that all or many of the characteristics of the uncatalyzed process will be transferred to the catalytic reaction will seldom be realized. The use of these catalysts in synthesis requires recognition of this fact.

Experimental Section

^{1}H NMR spectra were recorded on Varian T-60, Bruker WP-80, Varian XL-200, or Bruker WH-400 spectrometers. The parameters given refer to $CDCl_3$ solutions unless specified otherwise. Chemical shifts are relative to Me_4Si. Where complex signals were obtained, the spectral parameters are given as chemical shift (multiplicity$_A$, multiplicity$_B$..., J_A, J_B...Hz, relative intensity). ^{31}P FTNMR spectra were recorded on a Bruker WP-80 spectrometer. ^{31}P chemical shifts are relative to 85% H_3PO_4. Optical rotations were determined on a Perkin-Elmer 141 polarimeter. Catalysts were prepared by previously described methods: $[Pd(PPh_3)_4]$,[32] $[PdCl_2(PhCN)_2]$,[33] $[Rh(NBD)diphos]ClO_4$,[34] $[Ir(COD)_2]BF_4$,[35] $[Ir(COD)Cl]_2$,[36] $[Ir(COD)(CH_3CN)_2]BF_4$,[37] [Ir(COD)di-

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(33) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 218.
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(35) Prepared from $[Ir(COD)Cl]_2$, COD, and $AgBF_4$: Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.

phos]BF_4.[37] The substrates allyl, 2-methylallyl, 3-methylallyl, and 3-phenylallyl *N*-phenylformimidate were prepared by methods described elsewhere.[4] The deuterium-labeled substrates were prepared from methyl *N*-phenylformimidate[38] and 1,1-dideuterioally alcohol[39] or [3(*Z*)-^{2}H]allyl alcohol[40] by the method of Roberts.[4]

Preparation of Substrates. Allyl or 2-Methylallyl *N*-Phenylacetimidate. A modification of the method of Roberts[4] using ethyl *N*-phenylacetimidate[41] (1 equiv) and allyl or 2-methylallyl alcohol (2 equiv) gave the products in 50–60% yield.

(±)-4-Phenylbut-3-en-2-ol. 4-Phenylbut-3-en-2-one[42] was reduced with $NaBH_3CN/CH_3OH$ as reported.[43] Fractional distillation gave a thick, colorless liquid (39%), bp 128–131 °C (15 mm), which slowly solidified on standing. ^{1}H NMR: δ 1.33 (d, *J* = 6 Hz, 3 H); 2.7 (br. s, 1 H); 4.57 (app q, *J* = 6 Hz, 1 H); 6.12 (dd, *J* = 16, 6 Hz, 1 H); 6.52 (d, *J* = 16 Hz, 1 H); 7.4 (s, 5 H).

(−)-*N*-Methylephedrine ((1*S*,2*S*)-1-Hydroxy-1-phenyl-2-(dimethylamino)propane). This compound was prepared from (−)-ephedrine ((1*S*,2*S*)-1-hydroxy-1-phenyl-2-(methylamino)propane, Aldrich) by the methylation procedure of Kaluszyner.[44] White needles resulted (from boiling ethanol): 90%; $[\alpha]_D$ −29.1° (*c* 5.0 CH_3OH); lit.[45b] $[\alpha]_D$ −29.1° (*c* 4.6, CH_3OH).

(2*S*)-4-Phenylbut-3-en-2-ol. This compound was prepared by the asymmetric reduction of 4-phenylbut-3-en-2-one using $LiAlH_4$ modified with the chiral auxilary *N*-methylephedrine. The reported optical rotation[45a] is less than that of the optically pure material. The procedure presented below represents a coalescence of the limited experimental details given in the references.[45]

A solution of $LiAlH_4$ in diethyl ether was prepared by refluxing $LiAlH_4$ (8.57 g, 0.226 mol) in dry ether (450 mL) under N_2 for 1.5 h. The resulting solution was cooled to room temperature and a soluton of *N*-methylphedrine (41.7 g, 0.233 mol) in ether (950 mL) was added over 2 h. After stirring for an additional 0.5 h, a solution of freshly distilled *N*-ethylaniline (56.4 g, 0.465 mol) in ether (300 mL) was added over 1.5 h. The mixture was stirred at room temperature for 2 h and was then cooled to −78 °C. A solution of 4-phenylbut-3-en-2-one[42] (10 g, 0.0684 mol) in ether (200 mL) was added dropwise over 2.25 h. After stiring for an additional 3 h at −78 °C, the mixture was hydrolyzed by the addition of H_2O (8.6 mL, the cooling bath was removed after the first 3 mL), 15% NaOH (8.6 mL), and H_2O (26 mL). Water (600 mL) was added, the layers were separated, and the aqueous layer was extracted with ether (1200 mL). The *N*-methylephedrine may be recovered from the organic layer by extraction with aqueous HCl (0.5 M, 1400 mL in 200-mL portions), carefully monitoring the pH of each wash (acid is known to racemize the alcohol[46]). Treatment of the combined acid washes with solid NaOH, extraction with benzene, removal of *N*-ethylaniline by distillation, and finally recrystallization of the solid residue from ethanol yields *N*-methylephedrine (>80% chemical yield, $[\alpha]_D$ −29.0° (*c* 5.0, CH_3OH)).

After the final acid wash, the organic layer was quickly washed with NaOH (0.5 M, 200 mL) and brine (200 mL) and was dried (Na_2SO_4). Filtration and removal of the ether under reduced pressure left 13 g of slightly yellow liquid which crystallized on cooling. This material was recrystallized six times from hot hexane (3 mL/g) to constant optical rotation to give 2.7 g of white plates: $[\alpha]_D$ −35° (*c* 5, $CHCl_3$) (lit. (+)-isomer,[21] $[\alpha]_D$ (max) +34.6°; (−)-isomer,[47] $[\alpha]_D$ −34.8°).

***N*-Phenylbenzimidoyl Chloride.**[48] A mixture of *N*-phenylbenzamide (4.54 g, 0.023 mol) and PCl_5 (4.79 g, 0.023 mol) was combined, under N_2, and slowly heated to 80 °C. This resulted in HCl evolution and the formation of a clear, yellow solution which was stirred at 80 °C for 0.5 h. The solution was allowed to cool and the $POCl_3$ was removed by distillation at reduced pressure (15 mmHg). The residue was distilled to give the product which solidifies on cooling: 4.3 g (86%); bp 123–124 °C (0.5 mmHg); lit.[48b] 175–176 °C (12 mmHg).

(±)- or (2*S*)-(4-Phenylbut-3-en-2-yl) *N*-Phenylbenzimidate. To a suspension of NaH (0.43 g, 0.011 mol, 60% in mineral oil) in dry THF (10 mL) under N_2 was added a solution of (±)-4-phenylbut-3-en-2-ol (1.58 g, 0.011 mol) in dry THF (10 mL). The mixture was stirred for 20 min and then refluxed for 2 h. The mixture was cooled to room temperature and treated with a solution of *N*-phenylbenzimidoyl chloride (2.31 g, 0.011 mol) in dry THF (10 mL). The mixture was stirred overnight and then poured into a pH 7 phosphate buffer (120 mL). The mixture was extracted with ether (4 × 30 mL) and the combined ether layers were washed with H_2O (2 × 50 mL) and brine (50 mL) and dried (Na_2SO_4). Filtration and evaporation of the solvent gave a solid residue which was crystallized from hot hexane (~10 mL) to give white needles (3 g, 86%).

When this reaction is performed with (2*S*)-4-phenylbut-3-en-2-ol, the product so obtained possesses $[\alpha]_D$ −101.6° (*c* 1.0, C_6H_6); mp 90–94 °C.

Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.26; H, 6.38; N, 4.31, ^{1}H NMR: δ 1.57 (d, *J* = 6 Hz, 3 H); 5.90 (app q, *J* = 6 Hz, 1 H); 6.2–6.8 (m, 2 H); 7.1–7.6 (m, 15 H).

4-Phenylbut-3-en-2-one oxime. A mixture of 4-phenylbut-3-en-2-one[42] (35 g, 0.24 mol) and NH_2OH·HCl (26.7 g, 0.384 mol) in 80% ethanol (120 mL) was treated with powdered NaOH (48 g, 1.2 mol) in 1–2-g portions.[49] The mixture was refluxed for 5 min and was then poured into cooled aqueous HCl (1.7 M, 700 mL). The white solid so obtained was filtered, washed with H_2O, and dried. The product was recrystallized from hot ethanol (~250 mL) by the addition of H_2O (~250 mL) to give white needles: 31.6 g (82%); ^{1}H NMR δ 2.15 (s, 3 H), 6.87 (s, 2 H), 7.2–7.6 (m, 5 H), 9.7 (br s, 1 H).

(±)-2-Amino-4-phenylbut-3-ene.[50] To an ice-cooled solution of 4-phenylbut-3-en-2-one oxime (20 g, 0.124 mol) in ethanol (160 mL) and glacial acetic acid (160 mL) was added zinc dust (80 g, 1.22 mol) in portions. The mixture was allowed to warm to room temperature and then gently warmed on a steam bath for 0.5 h. The precipitate was filtered and washed with copious quantities of ethanol. The filtrate was evaporated under reduced pressue and the solid residue was dissolved in H_2O (50 mL) and evaporated again. The residue was dissolved in H_2O (50 mL) and treated with solid NaOH. After ~30 g NaOH had been added, a yellow layer separated with concomitant formation of a white precipitate. Further addition of NaOH caused the precipate to redissolve while maintaining the presence of the oily upper layer. The amine ws extracted into ether (4 × 30 mL), and the combined ether layers were evaporated under reduced pressure. The residue was dissolved in aqueous HCl (6 M, 80 mL) and the side product, 4-phenylbutan-2-one (identified by ^{1}H NMR) was extracted into ether (4 × 25 mL). The amine was recovered from the aqueous acidic layer by treatment with solid NaOH (~50 g) and extraction with ether (4 × 30 mL). The combined ether layers were dried (BaO), filtered, and evaporated, and the residue was distilled to yield a clear colorless liquid: 4.22 g (33%); bp 111–113 °C (12 mmHg) (lit.[50] 119 °C (12 mmHg)); ^{1}H NMR δ 1.22 (d, *J* = 6 Hz, 3 H), 1.35 (s, 2 H), 3.63 (dq, *J* = 5, 6 Hz, 1 H), 6.07 (dd, *J* = 16, 5 Hz, 1 H), 6.43 (d, *J* = 16 Hz, 1 H), 7.1–7.4 (m, 5 H).

(2*S*)-2-Amino-4-phenylbut-3-ene. To a well-stirred solution of (+)-tartaric acid (4.28 g, 0.029 mol) in ethanol (140 mL) was added the racemic amine (4.22 g, 0.029 mol) in ethanol (30 mL).[51] The stirring was stopped, and from the now cloudy solution white crystals slowly formed over 24 h. These crystals were filtered and washed with a small portion of ethanol followed by hexane to yield 4.75 g. Two further crystallizations from hot ethanol (35 mL/g) gave 2.12 g of small plates of the (+)-tartrate salt of (2*S*)-2-amino-4-phenylbut-3-ene.

The resolved amine was liberated by treatment of a solution of the salt (2.12 g, 0.007 mol) in H_2O (15 mL) with solid NaOH until an oil had separated (0.85 g NaOH was required). The mixture was extracted with ether (4 × 10 mL), the combined ether layers were dried (BaO) and the clear, colorless liquid obtained by filtration and evaporation of the solvent was used without further purification: 1.0 g (100% from the tartrate salt); $[\alpha]_D$ −7.4° (*c* 10, C_6H_6), 83% optically pure.[52]

(2*S*)-*N*-Benzoyl-*N*-phenyl-2-amino-4-phenylbut-3-ene from (2*S*)-2-amino-4-phenylbut-3-ene. To a solution of (2*S*)-2-amino-4-phenylbut-3-ene (0.5 g, 0.0034 mol) in acetone (25 mL) under N_2 was added solid $[(C_6H_5Cl)Mn(CO)_3]PF_6$[28] (0.61 g, 0.00154 mol) which resulted in a clear yellow solution. After 10 min at room temperture the solvent was

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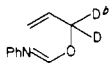
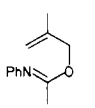
Table III. ^{1}H NMR Data of Allyl Imidates

allyl imidate	^{1}H NMR[a] data, δ
	4.73 (dt, J = 5, 1.5 Hz, 2 H), 5.2–5.6 (m, 2 H), 6.0 (ddt, J = 16, 10, 5 Hz, 1 H), 6.9–7.5 (m, 5 H), 7.7 (s, 1 H)
	4.77 (d, J = 6 Hz, 2 H), 5.26 (dt, J = 10.5, 1.2 Hz, 0.65 H), 6.04 ($dtt_{1:1:1}$, J = 10.6, 5.8, 2.6 Hz, 1 H), 6.9–7.4 (m, 5 H), 7.73 (s, 1 H)
	5.27 (dd, J = 10.4, 1.6 Hz, 1 H), 5.39 (dd, J = 17.3, 1.6 Hz, 1 H), 6.04 (dd, J = 17.3, 10.3 Hz, 1 H), 6.9–7.4 (m, 5 H), 7.72 (s, 1 H)
	1.75 (dq, J = 6, 1 Hz, 3 H), 4.69 (dm, J = 6.2, 0.9 Hz, 2 H), 5.6–6.0 (m, 2 H), 6.9–7.3 (m, 5 H), 7.7 (s, 1 H)
	1.81 (br s, 3 H), 4.7 (br s, 2 H), 5.1 (m, 2 H), 6.8–7.4 (m, 5 H), 7.7 (s, 1 H)
	4.9 (d, J = 5 Hz, 2 H), 6.0–6.9 (m, 2 H), 7.0–7.6 (m, 10 H), 7.7 (s, 1 H)
	1.83 (s, 3 H), 4.7 (br d, J = 5 Hz, 2 H), 5.1–5.6 (m, 2 H), 6.1 (ddt, J = 17, 10, 5 Hz, 1 H), 6.7–7.6 (m, 5 H)
	1.8 (overlapping s, 6 H), 4.6 (br s, 2 H), 5.0 (m, 2 H), 6.6–7.4 (m, 5 H)

[a] Obtained at 60 MHz in $CDCl_3$ unless specified otherwise. [b] Obtained at 200 MHz.

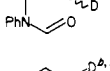
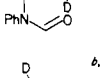
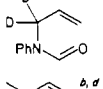
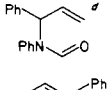
evaporated. The residue, a yellow oil, was dissolved in CH_2Cl_2 (50 mL) and was extracted with H_2O (25 mL). The CH_2Cl_2 layer was dried ($MgSO_4$), filtered, and evaporated to leave a yellow residue which was dissolved in CH_3CN (50 mL), under N_2, and was refluxed for 0.5 h. The solution was allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was triturated with ether (4 × 25 mL), the ether extracts were evaporated, and the residue was passed down a short (10 cm) alumina column in benzene collecting 100 mL of eluant. The benzene eluant was evaporated and the oily residue was benzoylated as follows.

An ice-cooled mixture of this residue and aqueous NaOH (3 mL, 5.3% solution) was treated with benzoyl chloride (0.41 mL, 0.0035 mol). After stirring for 1 h, the mixture was transferred to a separatory funnel, an additional 5 mL of H_2O was added, and the mixture was extracted with benzene (2 × 15 mL). The combined organic layers were washed with aqueous NaOH (0.2 M, 2 × 5 mL), H_2O (5 mL), and brine (5 mL) and were dried ($MgSO_4$). Filtration and evaporation gave an oil (0.57 g) which was purified by chromatography (alumna, benzene/hexane) to give 0.30 g (60% based on manganese) of the product as an oil: $[\alpha]_D$ +84.2° (c 1, C_6H_6); ^{1}H NMR (200 MHz) δ 1.29 (d, J = 7 Hz, 3 H), 5.85 (app q, J = 7 Hz, 1 H), 6.38 (dd, J = 16, 6 Hz, 1 H), 6.51 (d, J = 16 Hz, 1 H), 6.6–7.4 (m, 15 H).

Catalytic Rearrangements Monitored by ^{1}H NMR. The catalyzed rearrangements presented in Tables I and II were performed as follows. The catalyst (1.55 × 10^{-5} mol) was weighed into a 5mm ^{1}H NMR tube and was flushed with N_2 for 0.5 h. After dissolving in 0.35 mL of solvent ($CDCl_3$, C_6D_6 or toluene-d_8), the liquid imidate (3.10 × 10^{-4} mol, 20 equiv) was added by syringe and the reaction monitored periodically. Table III lists the ^{1}H NMR parameters for the allyl imidates, and Table IV contains the corresponding parameters for the rearrangment products, allyl amides.

Rearrangement of (2*S*)-(4-Phenylbut-3-en-2-yl) *N*-Phenylbenzimidate. (a) [$PdCl_2(PhCN)_2$] Catalyst. The imidate (0.1 g, 3.05 × 10^{-4} mol) and [$PdCl_2(PhCN)_2$] (6 mg, 1.56 × 10^{-5} mol) were placed in a ^{1}H NMR tube and were dissolved in $CDCl_3$ (0.35 mL). When the reaction was complete (by ^{1}H NMR, 5 h), the contents of the tube were passed down a short alumina column in benzene and the resulting colorless solution was evaporated under reduced pressure. The viscous, semisolid residue, $[\alpha]_D$ +24.3° (c 0.69, C_6H_6), proved to be a 78:22 mixture of *trans*- and *cis*-*N*-benzoyl-*N*-phenyl-1-amino-1-phenylbut-2-ene. The ratio of isomers was determined by integration of the signals of the corresponding methyl groups at 200 MHz: trans, δ 1.73 (ddd, J = 6.2, 1.3, 0.6 Hz); cis, δ 1.77 (dd, J = 6, 1.3 Hz).

Table IV. ^{1}H NMR Data of Allyl Amides

allyl amide	^{1}H NMR[a] data, δ
	4.41 (dt, J = 5.6, 1.5 Hz, 2 H), 5.17 (dq, J = 10.3, 1.5 Hz, 1 H), 5.19 (dq, J = 17.2, 1.5 Hz, 1 H), 5.85 (ddt, J = 17.2, 10.3, 5.6 Hz, 1 H), 7.2–7.5 (m, 5 H), 8.49 (s, 1 H)
	4.41 (br, 0.7 H), 5.17 (dt, J = 10.3, 1.5 Hz, 1 H), 5.19 (dt, J = 17.3, 1.5 Hz, 1 H), 5.84 (ddd, J = 17.2, 10.3, 5.5 Hz, 1 H), 7.2–7.5 (m, 5 H), 8.48 (s, 1 H)
	4.41 (dd, J = 5.6, 1.5 Hz, 2 H), 5.17 (dt, J = 10.3, 1.5 Hz, 0.7 H), 5.19 (dt, J = 17.3, 1.5, 0.7 H), 5.84 (m, 1 H), 7.2–7.5 (m, 5 H), 8.48 (s, 1 H)
	4.41 (d, J = 5.6 Hz, 2 H), 5.84 (br, 1 H), 7.2–7.5 (m, 5 H), 8.48 (s, 1 H)
	5.17 (dd, J = 10.2, 1.5 Hz, 1 H), 5.19 (dd, J = 17.3, 1.5 Hz, 1 H), 5.84 (dd, J = 17.3, 10.2 Hz, 1 H), 7.2–7.5 (m, 5 H), 8.48 (s, 1 H)
	1.28 (d, J = 7 Hz, 3 H), 5.1–5.3 (m, 3 H), 5.95 (ddd, J = 17.4, 10.4, 5.5 Hz, 1 H), 7.1–7.7 (m, 5 H), 8.27 (s, 1 H)
	1.64 (dq, J = 6, 1.2 Hz, 3 H), 4.34 (dm, J = 6, 1.2 Hz, 2 H), 5.58 (m, 2 H), 7.1–7.7 (m, 5 H), 8.43 (s, 1 H)
	1.73 (s, 3 H), 4.4 (br s, 2 H), 4.8 (m, 2 H), 7.0–7.5 (m, 5 H), 8.57 (s, 1 H)
	5.1–5.6 (m, 2 H), 5.8–6.4 (m, 2 H), 6.9–7.5 (m, 10 H), 8.4 (s, 1 H)
	4.53 (d, J = 5 Hz, 2 H), 6.1 (dd, J = 16, 5 Hz, 1 H), 6.6 (d, J = 16 Hz, 1 H), 7.0–7.6 (m, 10 H), 8.47 (s, 1 H)
	1.65 (s, 3 H), 4.32 (br d, J = 6 Hz, 2 H), 4.9–5.3 (m, 2 H), 5.92 (ddt, J = 18, 9, 6 Hz, 1 H), 6.9–7.7 (m, 5 H)
	1.68 (br s, 3 H), 1.73 (s, 3 H), 4.27 (br s, 2 H), 4.67 (m, 2 H), 6.7–7.3 (m, 5 H)

[a] Obtained at 60 MHz in $CDCl_3$ unless specified otherwise. [b] Obtained at 200 MHz. [c] Obtained at 400 MHz. [d] From [$PdCl_2(PhCN)_2$] catalyst. [e] From [$Pd(PPh_3)_4$] catalyst by subtraction of isomeric peaks. [f] From [$Pd(PPh_3)_4$] catalyst in toluene-d_8.

A portion of this unsaturated amide (0.05102 g, 1.56 × 10^{-4} mol) was hydrogenated over PtO_2 (5 mL of ethanol, room temperature, 1 h), filtered through Celite directly into a 10-mL volumetric flask, and made up to the mark with ethanol. The saturated amide possessed $[\alpha]_D$ +8.2° (c 0.5133, ethanol) and subsequent isolation confirmed that the hydrogenation was complete: ^{1}H NMR δ 0.9–2.4 (m, 7 H), 6.23 (t, J = 7.5 Hz, 1 H), 6.5–8.0 (m, 15 H).

(b) Thermal Rearrangement. The imidate (0.1 g, 3.05 × 10^{-4} mol) in toluene-d_8 (0.35 mL) in a ^{1}H NMR tube was placed in a 110 °C oil bath. When the reaction was complete (7 h) the solvent was removed under reduced pressure to leave a viscous residue: $[\alpha]_D$ +44° (c 0.53, C_6H_6). A 200-MHz ^{1}H NMR spectrum indicated that the sole product was of trans geometry: ^{1}H NMR δ 1.76 (ddd, J = 6.2, 1.3, 0.6 Hz, 3 H), 5.73 (ddq, J = 15.2, 8.3, 1.4 Hz, 1H), 5.92 (dqd, J = 15.2, 6.3, 0.5 Hz, 1 H), 6.56 (br d, J = 8.3 Hz, 1 H), 6.7–7.7 (m, 15 H).

A portion of this amide (0.05172 g, 1.58 × 10^{-4} mol) was hydrogenated as above to give the saturated amide: $[\alpha]_D$ +16.2° (c 0.5204, ethanol).

(c) [$Pd(PPh_3)_4$] Catalyst. A solution of the imidate (0.2 g, 6.11 × 10^{-4} mol) and [$Pd(PPh_3)_4$] (0.035 g, 3.05 × 10^{-5} mol) in degassed benzene (2 mL) under N_2 was stirred at room temperature for 3 h. The N_2 was removed and to the yellow solution was added Fluorosil (2 g) which adsorbs the catalyst. After 10 min, the solution was filtered and the resulting colorless filtrate was evaporated to give a viscous liquid (0.2 g):

$[\alpha]_D$ +87° (c 1.0, C_6H_6); ^1H NMR (200 MHz, C_6D_6) δ 1.29 (d, J = 6.9 Hz, 3 H), 5.85 (app q, J = 6.7 Hz, 1 H), 6.38 (dd, J = 16, 6 Hz, 1 H), 6.51 (d, J = 16 Hz, 1 H), 6.7–7.4 (m, 15 H).

(d) $[Pd(PPh_3)_4]$ Catalyst in the Presence of $CH_2(CO_2CH_3)_2$. To a solution of the imidate (0.25 g, 7.64×10^{-4} mol) and dimethyl malonate (0.26 mL, 2.29×10^{-3} mol) in degassed benzene (1 mL) under N_2 was added solid $[Pd(PPh_3)_4]$ (0.044 g, 3.82×10^{-5} mol). Cloudiness developed within the first few minutes followed by the formation of a white crystalline precipitate (PhNHCOPh, mp 164 °C, mmp 164–165 °C). After 1 h at room temperature the mixture was filtered, through a short plug of glass wool, directly into H_2O (5 mL) and was extracted with ether (2 × 10 mL). The combined ether layers were washed with H_2O (5 mL) and brine (5 mL), and then $MgSO_4$ and Fluorosil were added. After stirring for 1 h, the mixture was filtered and evaporated under reduced pressure, and the excess dimethyl malonate was removed azeotropically with toluene. Chromatography (silica, $CHCl_3$/hexane) yielded a viscous, colorless liquid: $[\alpha]_D$ −66.6° (c 0.49, $CHCl_3$); lit.[24] $[\alpha]_D$ +68.9° (c 1.0, $CHCl_3$) for the R isomer; ^1H NMR: δ 1.18 (d, J = 7 Hz, 3 H), 2.9–3.8 (m, 2 H), 3.63 (s, 3 H), 3.72 (s, 3 H), 6.05 (dd, J = 16, 7 Hz, 1 H), 6.47 (d, J = 16 Hz, 1 H), 7.3 (br s, 5 H).

(e) $[M(COD)diphos]BF_4$ Catalysts (M = Rh, Ir). A solution of the imidate of (0.15 g, 4.58×10^{-4} mol) and the catalyst (2.29×10^{-5} mol) in $CDCl_3$ (0.5 mL) in a ^1H NMR tube under N_2 was prepared. After the appropriate period of time (rhodium, 2 h; iridium, 7 days), the solution was passed down a short Fluorosil column and the eluant was evaporated under reduced pressure. The residue so obtained consisted of a mixture of N-benzoyl-N-phenyl-1-amino-1-phenylbut-2-ene (38%) and N-benzoyl-N-phenyl-2-amino-4-phenylbut-3-ene (62%) as determined by integration of the corresponding methyl signals at 200 MHz. The optical rotation of the material derived from either catalyst was $[\alpha]_D$ 0° (c 1.0, C_6H_6).

Stoichiometric Rearrangement of (4-Phenylbut-3-ene-2-yl) N-Phenylbenzimidate with $[Pd(PPh_3)_4]$ in the Presence of Acetic Acid. To a mixture of (4-phenylbut-3-en-2-yl) N-phenylbenzimidate (0.21 g, 6.4×10^{-5} mol) and $Pd(PPh_3)_4$ (0.075 g, 6.5×10^{-5} mol) in a ^1H NMR tube under N_2 was added C_6D_6 (0.4 mL) and glacial acetic acid (3.7 μL, 6.4×10^{-5} mol). This resulted (<10 min) in complete conversion of the imidate to the corresponding acetate, 4-phenylbut-3-en-2-yl acetate which was identified by comparison with an authentic sample prepared from 4-phenylbut-3-en-2-ol/THF, n-BuLi/−70 °C, and acetyl chloride. ^1H NMR (C_6D_6): δ 1.23 (d, J = 6 Hz, 3 H), 1.72 (s, 3 H), 5.57 (app q, J = 6 Hz, 1 H), 6.05 (dd, J = 16, 6 Hz, 1 H), 6.57 (d, J = 16 Hz, 1 H), 7.0–7.4 (m, 5 H).

(1R,3R)-[(1-Methyl-3-phenylallyl)Pd(diphos)]ClO_4 and Its Reaction with Sodium Dimethyl Malonate. A standard solution of sodium dimethyl malonate (0.197 M) in THF was prepared as follows. A suspension of NaH (0.1 g, 0.0025 mol, 60% in mineral oil) in dry THF (15 mL) under N_2 was treated with dimethyl malonate (0.31 mL, 0.00275 mol). After 20 min, the solution was filtered through Celite by cannulation and the resulting clear, colorless solution was standardized by quenching a 1-mL aliquot in standard HCl (25 mL, 0.2 M) and back-titration with standard NaOH (0.2 M).

To a solution of $[(C_3H_5)Pd(diphos)]ClO_4$[53] (0.25 g, 3.87×10^{-4} mol) in dry THF (90 mL) under N_2 was added (2S)-(4-phenylbut-3-en-2-yl) N-phenylbenzimidate (0.19 g, 4.28×10^{-4} mol). The solution was cooled to 5 °C and sodium dimethyl malonate (2.16 mL, 0.197 M) was added over 2 min. The solution became yellow after the first drops of the anion solution had been added and subsequently turned amber. After 10 min the solution was quenched with a phosphate buffer (200 mL, pH 7). The homogeneous yellow solution was extracted with CH_2Cl_2 (2 × 40 mL). The combined organic layers were washed with H_2O (3 × 50 mL) and dried (Na_2SO_4). Filtration and evaporation of the solvent gave an orange oil. Trituration of this oil in ether resulted in a powdery solid, 0.23 g (82%). Analysis of this solid (^1H NMR) showed that it consisted of the desired π-allyl complex (72%) and $[(C_3H_5)Pd(diphos)]ClO_4$ (28%): ^1H NMR (200 MHz) δ 1.63 (dt, J = 6.3, 9.4 Hz, 3 H), 2.2–2.7 (m, 4 H), 4.43 (m, 1 H), 5.15 (t, J = 12 Hz, 1 H), 6.17 (t, J = 12 Hz, 1 H), 6.6–7.7 (m, 25 H).

This mixture of π-allyl complexes (0.23 g) was suspended in benzene (4 mL) and was treated with a suspension of sodium dimethyl malonate in benzene (prepared from NaH (0.38 g, 9.5×10^{-4} mol) and dimethyl malonate (0.14 mL), 1.22×10^{-3} mol) in benzene (6 mL) and transferred by using a large diameter cannula). The mixture was vigorously stirred overnight and then quenched with H_2O (20 mL) and extracted with ether (3 × 25 mL). The combined organic laves were washed with H_2O (2 × 30 mL), and brine (30 mL) and dried ($MgSO_4$). The solution was filtered and evaporated, and the excess dimethyl malonate was removed azeotropically with toluene. Finally, an ether solution of the residue was passed down a short Fluorosil column and the eluant was evaporated to leave a clear, colorless liquid: $[\alpha]_D$ −51.4° (c 1.75, $CHCl_3$), 75% ee.

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada who also awarded T.G.S. a scholarship.

Registry No. 1, 95190-90-2; $Pd(PPh_3)_4$, 14221-01-3; $PdCl_2(PhCN)_2$, 14220-64-5; $[Rh(NBD)(diphos)]ClO_4$, 32799-34-1; $[Ir(COD)_2]BF_4$, 35138-23-9; $[Ir(COD)Cl]_2$, 12112-67-3; $[Ir(COD)(CH_3CN)_2]BF_4$, 32679-03-1; $[Ir(COD)(diphos)]BF_4$, 34692-04-1; $PhN{=}CHOCH_2CH{=}CH_2$, 85021-15-4; $PhN{=}C(CH_3)OCH_2CH{=}CH_2$, 95121-78-1; $PhN{=}CHOCH_2C(CH_3){=}CH_2$, 85021-17-6; $PhN{=}C(CH_3)OCH_2C(CH_3){=}CH_2$, 95121-79-2; (?,E)-$PhN{=}CHOCH_2CH{=}CHPh$, 95121-80-5; (?,E)-$PhN{=}CHOCH_2CH{=}CHCH_3$, 95121-81-6; $PhN{=}C(CH_3)OEt$, 19655-72-2; $CH_2{=}CHCH_2OH$, 107-18-6; $CH_2{=}C(CH_3)CH_2OH$, 513-42-8; (±)-(E)-$PhCH{=}CHCH(OH)CH_3$, 84519-62-0; $PhCH{=}CHC(O)CH_3$, 122-57-6; (S)-(E)-$PhCH{=}CHCH(OH)CH_3$, 81176-43-4; PhC(Cl)=NPh, 4903-36-0; PhC(O)NHPh, 93-98-1; (±)-(?,E)-$PhN{=}C(Ph)OCH(CH_3)CH{=}CHPh$, 95121-82-7; (?,E)-$PhCH{=}CHC(CH_3){=}NOH$, 61210-87-5; (±)-(E)-$PhCH{=}CHCH(NH_2)CH_3$, 57128-68-4; (S)-(E)-$PhCH{=}CHCH(NH_2)CH_3$, 57128-66-2; (S)-(E)-$PhCH{=}CHCH(NH_2)CH_3$·(+)-tartrate, 57128-67-3; (S)-(E)-$PhCH{=}CHCH(CH_3)N(Ph)C(O)Ph$, 95121-83-8; (±)-(E)-$PhCH{=}CHCH(CH_3)N(Ph)C(O)Ph$, 95190-92-4; $[(PhCl)Mn(CO)_3]PF_6$, 57812-91-6; (S)-(E)-$PhCH{=}CHCH(CH_3)NHPh$, 95121-84-9; (S)-(E)-$PhC(O)N(Ph)CH(Ph)CH{=}CHCH_3$, 95121-85-0; (±)-(E)-$PhC(O)N(Ph)CH(Ph)CH{=}CHCH_3$, 95190-91-3; (R)-(Z)-$PhC(O)N(Ph)CH(Ph)CH{=}CHCH_3$, 95121-86-1; (S)-$PhC(O)N(Ph)CH(Ph)(CH_2)_2CH_3$, 95121-87-2; (R)-$PhC(O)N(Ph)CH(Ph)(CH_2)_2CH_3$, 95121-88-3; $CH_2(CO_2CH_3)_2$, 108-59-8; (S)-(E)-$PhCH{=}CHCH(CH_3)CH(CO_2CH_3)_2$, 88057-04-9; $[Rh(COD)(diphos)]BF_4$, 34664-29-4; (1R,3R)-$[(PhCH{=}CHCH(CH_3))Pd(diphos)]ClO_4$, 95190-93-5; $CH_2(CO_2CH_3)_2$·Na, 18424-76-5; $[(C_3H_5)Pd(diphos)]ClO_4$, 92342-86-4; (±)-(E)-$PhCH{=}CHCH(CH_3)OAc$, 82045-04-3; (−)-N-methylephedrine, 552-79-4; (−)-ephedrine, 299-42-3; (+)-tartaric acid, 87-69-4.

(53) Prepared as described in ref 38.

(54) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.