Molecular Mechanics Predictions and Experimental Testing of Asymmetric Palladium-Catalyzed Allylation Reactions Using New Chiral Phenanthroline Ligands

Eduardo Peña-Cabrera,[1a] Per-Ola Norrby,*,[1b] Magnus Sjögren,[1c] Aldo Vitagliano,[1d] Vincenzo De Felice,[1e] Johan Oslob,[1c] Shingo Ishii,[1a] David O'Neill,[1a] Björn Åkermark,*,[1c] and Paul Helquist*,[1a]

Contribution from the Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, Department of Medicinal Chemistry, Royal Danish School of Pharmacy, Universitetsparken 2, DK-2100 Copenhagen, Denmark, Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden, Dipartimento di Chimica, Università di Napoli "Federico II", via Mezzocannone 4, I-80134 Napoli, Italy, and Facoltà di Agraria, Università del Molise, via Tiberio 21/A, I-86100 Campobasso, Italy

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Abstract: Molecular mechanics calculations were used to probe the conformational properties of a number of substituted phenanthrolines and their η^3-allylpalladium complexes. Special attention was focused on phenanthrolines bearing chiral, terpene-derived, alkyl and alkenyl groups at C(2). Based upon these calculations, predictions could then be made regarding the suitability of the several ligands for use in asymmetric palladium-catalyzed substitution reactions of allylic acetates. Each of the substituted phenanthrolines was prepared by straightforward means. Use of these ligands in catalytic allylations gave results which were in good agreement with the calculation-based predictions. The highest levels of asymmetric induction were predicted and were obtained with a readily available 2-(2-bornyl)phenanthroline ligand **13**. The results were compared with previously reported data obtained using other ligands. Overall, this work provides further indication of the potential utility of a combined calculational/experimental approach for the design of chiral catalysts.

Introduction

Several approaches have been developed for the asymmetric synthesis of nonracemic organic compounds. Among the most common strategies is the use of reactions promoted by metal catalysts bearing chiral ligands.[2] Many of the highly successful ligand systems that have been developed have arisen largely by a trial-and-error approach. Our laboratories wished to explore the feasibility of using molecular mechanics calculations[3] as a basis for the rational design of new chiral ligands. These calculations would be used to predict the stereoselectivity of metal complex formation and the stereoselectivity of the subsequent reactions of the complexes. If this approach were to prove feasible, then actual laboratory efforts could be invested in the synthesis of only the most promising candidates for use as ligands in asymmetric synthesis.

We have previously published some of our studies directed toward developing molecular mechanics parameter sets for η^3-allylpalladium complexes.[4] Likewise, the Pregosin and Albinati laboratories have employed molecular mechanics calculations in related studies of chiral palladium complexes.[3u,w] However, to meet the longer-term goals stated above, we next needed to test the usefulness of our parameter sets in predicting the stereochemical outcomes for the formation and reactions of η^3-

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(1) (a) University of Notre Dame. (b) Royal Danish School of Pharmacy. (c) Royal Institute of Technology. (d) Università di Napoli. (e) Università del Molise.

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allylpalladium complexes.[5] In this paper, we report studies in which we have made these predictions for use of several new ligands, and we report the results of testing these predictions experimentally.

Results

Molecular Mechanics Studies of the Proposed Ligands and Their Palladium Complexes: Basic Approach. We begin this discussion by describing our general molecular mechanics-based approach and its inherent limitations. As a starting point for our calculational approach to catalyst design, we chose to explore the possible conformations of η^3-allylpalladium complexes containing various proposed chiral ligands. The molecular mechanics calculations give us two types of relevant information for each conformation of the complexes, namely the steric energy and the geometry, both of which have been shown to be well represented in the case of η^3-allylpalladium complexes with substituted phenanthroline ligands.[4] When all conformations on the reaction pathway have been found, the product distribution is determined by two factors: the relative populations and the intrinsic reactivity of the respective intermediates. Under Curtin-Hammett conditions,[6] the population is simply scaled by the intrinsic reactivity in order to obtain the product isomeric ratio. When conformational equilibration in the intermediate is slower, the intrinsic reactivity is mainly important in determining which of the allyl termini is attacked by the nucleophile. Thus, as a very tentative first approximation, the product distribution can be predicted from the populations of the respective intermediates, but, in most cases, at least a qualitative assessment of the reactivity is necessary. Several structural factors influencing the reactivity have been identified previously, and therefore a reasonable initial prediction of the products can usually be made if not only the energies but also the structures of the intermediates are considered. This is especially important in locally symmetric cases when attack at the two different termini on one single conformation will lead to opposite enantiomers (*e.g.*, in cyclohexenyl complexes). Here any selectivity can arise *only* from reactivity differences within conformations. These points will be discussed further (*vide infra*).

There are some readily recognized limitations in this approach, especially if a generalization to other catalytic systems is sought. First of all, the required molecular mechanics parameter sets for metals are still in an early stage of development. The specific η^3-allyl palladium force field employed in the present study has been validated both for structures and energies,[4] but for most other synthetically interesting metal complexes, only generalized parameter sets are available. Attempts to use some of the general parameter sets that are now becoming available in commercial programs indicated that these nonspecific force fields would not yield the accuracy necessary for our purposes. The present study serves as an additional test of the usefulness of the parameters that we have developed to date.[4]

Secondly, and of even more fundamental concern, when Curtin-Hammett considerations are taken into account, there is no firm basis for believing that the energy-minimized complexes that we may identify will be the actual reactive species in the allylic substitution reactions of interest. Instead, higher energy complexes that would not be considered in our approach may be the kinetically more important intermediates in these reactions.[6] This Curtin-Hammett factor is, in general, a potential pitfall in studies based upon the experimental detection or calculational prediction of reaction intermediates. Our tentative solution to this problem is to retain high energy species in the conformational search of the intermediates and to try to identify any that might have exceptional reactivity. Thorough kinetic studies coupled with identification of intermediates, their rates of interconversion, and their involvement in actual reaction pathways would be required to address this point in greater detail. However, these further, more elaborate studies lie beyond the scope of our initial efforts aimed at developing a molecular mechanics-based approach for the identification of possible candidates to serve as chiral ligands. Caution must therefore be exercised in drawing conclusions from our initial results.

Thirdly, a number of reaction parameters can greatly affect the stereochemical outcome of a given reaction. Among these factors are the properties of the other reactants such as the nucleophiles present in a given reaction, the nature of coreagents such as the bases used to generate reactive intermediates, the reactivity of leaving groups, the properties of the counterions present with the reagents and intermediates, and variations in solvent. Although these variables can have a great bearing on enantioselectivities of reactions, these factors are not addressed by the molecular mechanics approach employed in the present work.

In full recognition of the need to go beyond the present level of analysis, we have also begun, in parallel work, to address some of the required reactivity considerations in considerable detail. For example, in studies to be reported separately,[7] we have developed an approach for quantifying the intrinsic reactivity based on the structure of several complexes of the types discussed in the present paper and also based on the steric effects of the nucleophile itself as it approaches the allyl ligand.

Selection and Study of Ligand Systems. Some of our earlier work indicated the special role that substituted phenanthroline ligands play in controlling the stereochemistry of formation and reactions of η^3-allylpalladium complexes.[8] For example, the use of phenanthrolines bearing various substituents at C-2 and C-9 showed an altered *syn,anti*-stereoselectivity in allyl complex formation and important differences in the reactivity of *anti*- and *syn*-substituted termini. This earlier work

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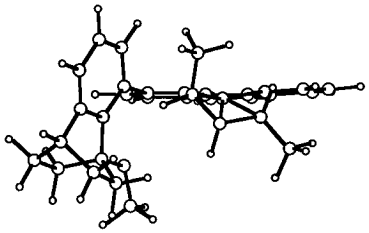
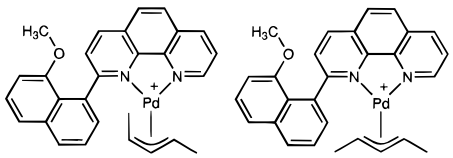


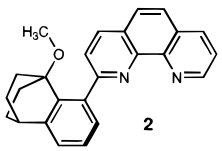
Figure 1. Two views of a minimized structure of *anti,syn*-**3**.

prompted our initial development of new parameter sets for performing molecular mechanics calculations on these and other related palladium-containing systems.[4] One of our earlier, key results was that 2-(8-methoxy-1-naphthyl)phenanthroline forms (η^3-1,3-dimethylallyl)palladium complexes for which the *anti,syn*-**1** and *syn,syn*-**1** isomers exist in a ratio of 80:20. An initial consideration was that an increase in the steric demands of the phenanthroline substituent should lead to an enhanced *anti,syn*:*syn,syn* ratio. Furthermore, these types of ligands should be resolvable due to greatly restricted rotation about the bond joining the phenanthroline to the methoxy-substituted naphthyl group, in which case these ligands should induce asymmetry in the resulting allyl complexes.

After brief molecular mechanics analysis of various derivatives of this system, the benzobicyclo[2.2.2]octane derivative **2** was chosen for more detailed studies. This choice was based upon (1) prediction of high *anti,syn*:*syn,syn* ratios in the formation of allyl complexes and (2) the potential ease of preparation of this ligand compared to other possible choices.



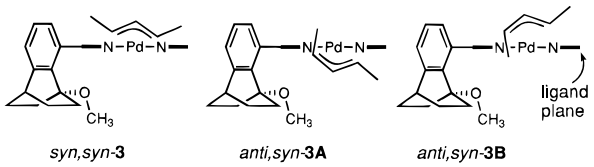
anti,syn -**1** *syn,syn* -**1**



2

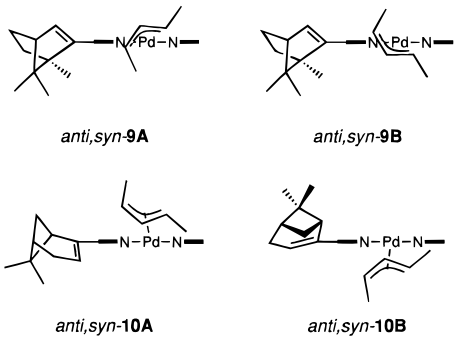
In particular, molecular mechanics calculations were performed on the (η^3-1,3-dimethylallyl)palladium complexes **3** containing ligand **2**. Figure 1 shows a minimized conformation of *anti,syn*-**3**. Formation of the *syn,syn* isomer would be expected to be unfavorable due to interaction of a *syn*-methyl group with the benzobicyclooctyl substituent.

High *anti,syn* preference is not a sufficient condition for a high level of asymmetric induction in subsequent additions to the allyl ligand. A brief experimental examination of the reaction of the racemic ligand **2** with a preformed (η^3-1,3-dimethylallyl)palladium trifluoroacetate complex **4** showed that a 20:1 mixture of *anti,syn* and *syn,syn* complexes **3** is formed based upon ^{1}H NMR analysis of the product mixture (eq 1). However, the *anti,syn* product consists of a 3:1 mixture of two diastereomers which can be explained by nondiastereofacial selective coordination of the 1,3-dimethylallyl ligand to palladium (Figure 2). The fact that the two *anti,syn* isomers are formed suggests that the benzobicyclooctyl group can rotate away from the *anti*-methyl group in order to minimize steric interactions in the second *anti,syn* isomer depicted in Figure 2. Even if a nucleophile were to attack selectively at either an *anti*-substituted or a *syn*-substituted terminus of the allyl system,



syn,syn-**3** *anti,syn*-**3A** *anti,syn*-**3B**

Figure 2. Proposed structures of the (η^3-allyl)Pd complexes **3** formed from the ligand rac-**2**.

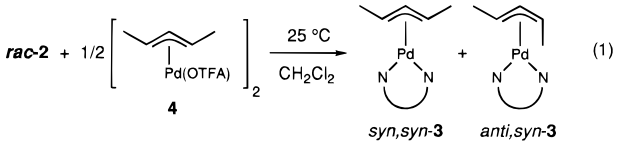


anti,syn-**9A** *anti,syn*-**9B**

anti,syn-**10A** *anti,syn*-**10B**

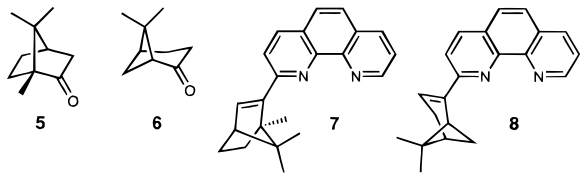
Figure 3. Two diastereomeric forms each of **9** and **10**.

the fact that a mixture of diastereomeric complexes is present is likely to lead to a low degree of asymmetric induction. These results clearly indicated the need to probe the question of diastereofacial selectivity in the more detailed molecular mechanics calculations to be performed on each of the further proposed allyl complexes.



(1)

We therefore chose to investigate a series of additional chiral phenanthroline ligands. Ideally, the ligands would be readily available in nonracemic form without a need for resolution. Consideration was given to the substitution of phenanthroline with groups directly obtainable from naturally occurring terpene hydrocarbons. After preliminary consideration of several possible systems, we focused on the use of readily available (1*R*)-camphor **(5)** and (1*R*)-nopinone **(6)**.



5 **6** **7** **8**

We initially chose to consider the conversion of ketones **5** and **6** into alkenyl derivatives for attachment to phenanthroline to give ligands **7** and **8**, respectively. With our previously developed molecular mechanics parameter set, the structures of the *anti,syn*- and *syn,syn*-1,3-dimethylallylpalladium complexes **9** and **10** were subjected to an initial minimization.[9] The minimized structures for the *anti,syn* complexes are shown in Figure 3.

From Figure 3, we see that the *exo* face of the allyl group in both isomers is rather distant from the terpene-derived group.

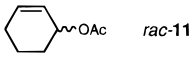
(9) All the minimizations were performed using the MM2 program, utilizing the parameter set described in ref 6. MM2(91), version for Macintosh: MacMimic/MM2(91), InStar Software AB, IDEON Research Park, S-223 70 Lund, Sweden. MM2 versions for platforms other than Macintosh are available from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405.

Consequently, the achievement of high asymmetric induction may be thought to be unlikely since the chiral center of the ligand is on the face of the allyl ligand opposite the *exo* face which an incoming nucleophile would attack.[5] However, an interesting feature of the minimized structures is that the allylic plane does not lie perpendicular to the phenanthroline plane, but it is rotated and/or pushed away from the coordination plane. This feature has been observed experimentally by others when bulky ligands are employed.[10] Differences in reactivities of the allylic termini may therefore result from a more pronounced distortion caused by the terpene-derived group upon one of the allylic termini preferentially or from inherent differences in reactivity of the *anti* and *syn* termini (see above),[8] provided that there is good diastereofacial selectivity in the coordination of the allylic group to the metal.

Initial MM2 calculations on the diastereomeric forms of *anti,syn*-**9** depicted in Figure 3 show that their energy difference is very small (0.1 kcal/mol). Also, the calculations indicate that there is a *syn,syn* isomer with a steric energy slightly lower (ca. 0.6 kcal/mol) than that of the *anti,syn* isomers. A total of nine different conformers were found within 2 kcal/mol of the global minimum (a *syn,syn* isomer). With these small energy differences, we would predict poor asymmetric induction in subsequent reactions of the dimethylallyl ligand with nucleophiles.

A similar situation arises for *anti,syn*-**10**. Our initial calculations indicate an energy difference of only 0.2 kcal/mol between the two diastereomeric forms depicted in Figure 3. The calculations also indicate the existence of two *syn,syn* diastereomers with steric energies ca. 1 kcal/mol less than their *anti,syn* counterparts. The calculated energy difference between the two *syn,syn* isomers is only 0.3 kcal/mol. Here we find a total of six conformers within 2 kcal/mol of the lowest *syn,syn* isomer. Therefore, we would again predict poor asymmetric induction in reactions of **10**.

In attempting to reduce the number of factors that affect the enantioselectivity of the reactions of the allyl complexes, we decided to consider the use of *rac*-1-acetoxy-2-cyclohexene (**11**) since the question of *syn,anti* isomerism would not occur in this cyclic system. The key factor that would govern enantioselectivity in this case would be the regiochemistry of nucleophilic attack on the coordinated cyclic allyl system.



rac-**11**

Molecular mechanics calculations on the corresponding allylpalladium complex of the camphor-derived ligand leads to energy minima corresponding to **12A** and **12B** (Figure 4) having an energy difference of 1.3 kcal/mol. In order for nucleophilic addition to take place with significant asymmetric induction, there must be some factor, either structural or electronic, that sufficiently differentiates the two allylic termini. As an additional complication, complexes of symmetric allyls (*e.g.*, **12**) are expected to show very rapid equilibration between all possible forms due to fast *syn,syn*-*anti,anti*-isomerization (apparent rotation of the allyl moiety).[8c] According to the Curtin-Hammett principle,[9] the rate of addition to any allylic carbon is a product of the Boltzmann population of that conformer and the inherent reactivity of the specific allyl terminus.

Analysis of these structures indicates, as in the acyclic cases, that the terpene-derived substituent would not be expected to interact sterically with an incoming nucleophile. Also, the allylic moiety is seen to lie considerably off of the coordination plane formed by the palladium atom and the phenanthroline nitrogen atoms. Of further interest in **12A** is that the two Pd−N

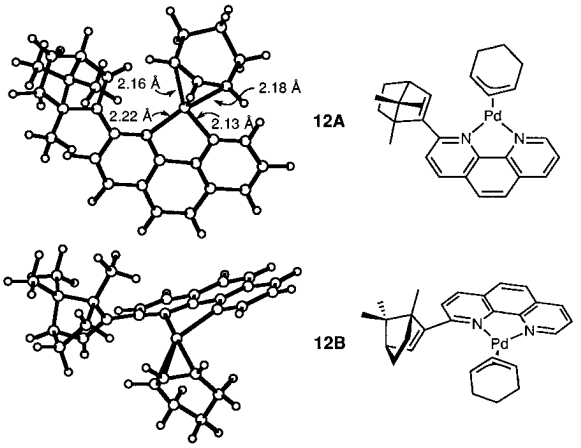


Figure 4. Two diastereomeric forms of complex **12**. Calculated bond distances shown for form **12A**. Distance differences are smaller in **12B**, the global minimum energy conformation.

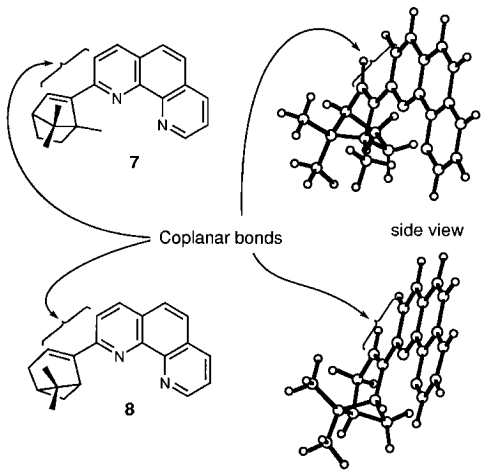


Figure 5. Minimized structures of ligands **7** and **8** showing coplanarity between the phenanthroline ring and the olefinic bond of the terpene unit.

bond distances are unequal, and the two terminal C−Pd distances are also unequal. These calculated distances are shown in Figure 4. The slightly greater Pd−N_1 distance is likely due to the closeness of the bulky terpene-derived group at C_2. The somewhat closer interaction between N_{10} and Pd (increased electron-donation) may tend to shorten the bond between palladium and the allylic carbon atom trans to N_{10} (assuming the allyl fragment to be an electron-accepting species). If this perturbation were sufficiently great, it would create greater carbocation character at the other allylic carbon atom *trans* to N_1. Therefore, the incoming nucleophile may be expected to attack preferentially at this latter terminus. Unfortunately, the difference between the termini in **12B** is much smaller, and the high energy of **12A** precludes any dominating influence of this conformer unless the reactivity of one terminus is extraordinarily large. Thus, only low asymmetric induction is predicted for this system.

Further calculations on each of the above allyl systems leads to additional minimized conformations in addition to those already discussed, but in no case could a prediction of good asymmetric induction be made using ligands **7** and **8**. These additional calculations did lead to another important point, however. Minimized structures of just the noncoordinated ligands **7** and **8** by themselves are depicted in Figure 5. In these structures, the olefinic bond of each terpene residue is coplanar with the phenanthroline ring. The barrier to rotation of the terpene moiety (calculated to be ca. 7 kcal/mol) would

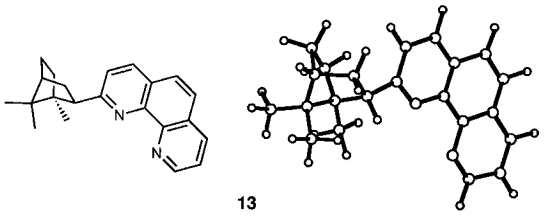


Figure 6. Two conformers of ligand **13**. The ground state (left) is hindered at the coordination site, but the low energy conformer to the right is relatively unhindered.

Figure 7. Minimized diastereomeric forms of complex **14**.

necessitate a high energy expenditure upon formation of a metal complex of either of these ligands. This barrier may reduce the rate of complexation, or it may destabilize the intermediate metal complexes and lead to early decomposition of the catalyst. In either case, these effects may be reflected in low overall rates of reaction and/or a low yields of the final allylic substitution products.

These results indicated the need to modify the structure of the chiral substituent on the phenanthroline so as to allow free interaction of the nitrogen atoms with the palladium. Examination of various modified ligands led us to the dihydro, or bornyl, analogue **13** of the previously studied bornenylphenanthroline **7**. The minimum energy structure of **13** (Figure 6) still shows severe interaction with the coordination site, but formation of rotamers with less crowding is much less costly for **13** than for the previously studied analogue **7**.

The first complexes of **13** to be subjected to molecular mechanics calculations were those of the 1,3-dimethylallyl system **14**. Energy minimization leads to two isomers, namely *syn,syn*-**14** and *anti,syn*-**14** as depicted in Figure 7, having an energy difference of only 0.03 kcal/mol. Among the key structural features of these complexes is the distortion of the allyl group coordination caused by the terpenyl group. The net result of this interaction is a displacement of the allyl group out of the N−Pd−N coordination plane as well as a slight rotation about the centroid of the allyl group. Another important feature is the placement of the *anti*-methyl group in *anti,syn*-**14** below the unsubstituted carbon ring of the phenanthroline ligand. Presumably, the methyl group at C-1 of the terpenyl group prevents placement of the *anti*-methyl group below the substituted A ring of the phenanthroline ligand.

Upon addition of nucleophiles to either of these isomers of **14**, the initial steric interaction between the incoming nucleophile and the dimethylallyl ligand would not appear to play an important role in determining enantioselectivity. However, other important differences may be expected to arise at a later stage of bond formation. Once nucleophilic addition occurs, the η^3-complex becomes a transient η^2-complex by rotation of the allylic fragment.[11] A search of the Cambridge database reveals that η^2-olefin complexes of Pd(0) strongly prefer a trigonal planar coordination with the olefin parallel to the coordination plane.[12] Thus, if nucleophilic attack were to occur at the allylic terminus of *syn,syn*-**14** proximal to the substituted phenanthroline ring, the allylic fragment would rotate counterclockwise in order to align the newly formed olefin with the coordination plane, as depicted in Figure 8. This rotation would produce a strong steric interaction between the methyl group at this terminus and the terpenyl group. On the other hand, if nucleophilic attack were to occur on the allylic terminus proximal to the unsubstituted phenanthroline ring, the subsequent clockwise rotation would not lead to any significant steric interactions. Therefore, attack at this latter position and subsequent formation of the *R* enantiomer (assuming highest Cahn−Ingold−Prelog priority for the nucleophile moiety) of the allylation product would be favored.

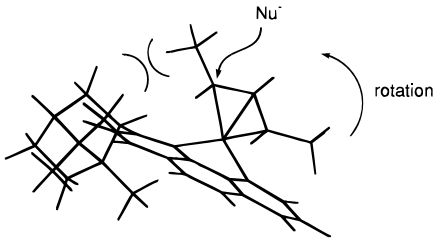


Figure 8. Steric interactions produced by nucleophilic attack at the allylic center proximal to the substituted phenanthroline ring of *syn, syn*-**14**.

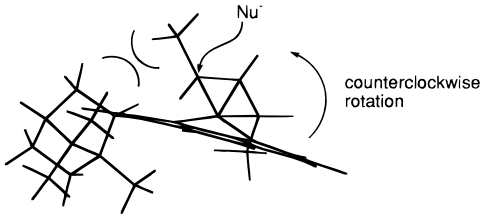


Figure 9. Steric interactions that arise from nucleophilic attack at the *syn*-substituted allylic C atom of *anti,syn*-**14**.

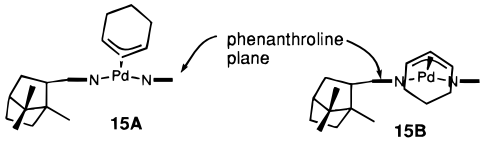


Figure 10. Bottom view of two diastereomeric forms of **15**.

Similar reasoning in the case of *anti,syn*-**14**, would predict formation of the *S* enantiomer of the allylation product due to unfavorable interactions in formation of the *R* product (Figure 9). However, because *syn,syn*-**14** would preferentially afford the *R* enantiomer, and because the energy difference between *syn,syn*-**14** and *anti,syn*-**14** is estimated to be only 0.03 kcal/mol, poor overall asymmetric induction would be predicted for this dimethylallyl system.

We next studied the cyclic allyl complexes **15** to be derived from 1-acetoxy-2-cyclohexene (**11**). Energy minimization leads to the two structures **15A** and **15B** (Figure 10), with the latter being only 0.2 kcal/mol lower in energy than the former. No significant differences in N−Pd or terminal allylic C−Pd distances are observed in either structure. However, a key difference in the two structures is that in **15A** the cyclic allyl group and the terpenyl group lie on opposite sides of the phenanthroline plane, whereas in **15B**, the cyclic allyl group is much closer to the bulky terpenyl group.

Nucleophilic attack on the allylic terminus closer to the terpenyl group of **15A** would induce clockwise rotation of the

(10) Experimentally, a similar phenomenon has been observed in a related compound. See: Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; Baker-Dirks, J. D. J. *J. Chem. Soc., Chem. Commun.* **1979**, 670.

(11) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organometallic Chemistry*; University Science Books: Mill Valley, California, 1987; p 417.

(12) Cambridge Structural Database codes for η^2-olefin-Pd(0) complexes: BPBZAP, BZYLPD, CARJOU, CUTZAS, DBZACP10, FICBIC, FMEACA10, GENJAK, HADSIO, SOLTAO, VUFNUF. Only in the case of the geometrically constrained $Pd_2(dba)_3$ (DBZACP10) does any olefin deviate significantly from the coordination plane of palladium.

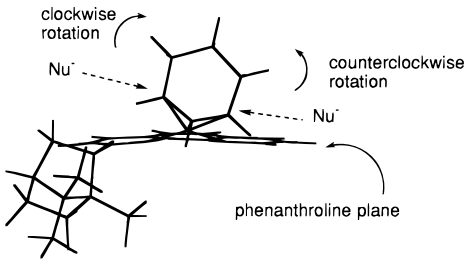


Figure 11. Effect of rotation of the six-membered ring upon nucleophilic attack at either end of the allylic fragment of **15A**.

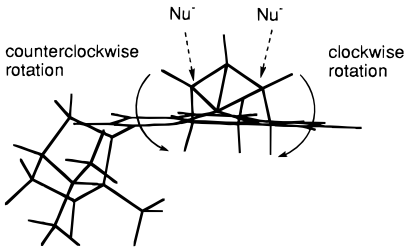


Figure 12. Modes of rotation of the six-membered ring upon nucleophilic attack on **15B**.

cyclic allyl unit, whereas attack at the other terminus would induce counterclockwise rotation (Figure 11). However, in neither case would significant steric interactions arise between the allyl residue and the substituted phenanthroline ligand, and therefore poor asymmetric induction would be predicted for reaction of **15A**.

On the contrary, attack on the allylic terminus proximal to the terpenyl group of **15B** and subsequent counterclockwise rotation would reposition the cyclohexenyl residue away from the terpenyl group, whereas attack at the other terminus accompanied by clockwise rotation would move the cyclohexenyl group toward the bulky substituent (Figure 12). To the extent that isomer **15B** undergoes reaction, good asymmetric induction would thus be predicted, but this outcome would be attenuated by competing reaction of **15A**. Therefore, at most, only modest overall asymmetric induction would be predicted for this cyclic allyl system.

For the purpose of studying a system that would perhaps exhibit greater interactions between the allylic substituents and the substituted phenanthroline ligand, we next examined complexes containing the 1,3-diphenylallyl ligand. This allyl system has been studied extensively in asymmetric allylations by several other investigators (*vide infra*). We considered only *syn,syn* isomers since this geometry is greatly favored in this case (as also confirmed in NMR studies below). Molecular mechanics calculations lead to two minimized forms, **16A** and **16B** (Figure 13), having an energy difference of 1.8 kcal/mol, with **16B** having the lower energy. With this energy difference, **16B** may therefore be favored by as much as 95% over **16A** at equilibrium, although Curtin-Hammett considerations[6] must still be borne in mind. Among the complexes that we have studied, this system also exhibits the greatest distortion of the allylic group away from the N−Pd−N coordination plane.

For either of these forms, nucleophilic attack would be expected to occur at the allylic terminus proximal to the unsubstituted phenanthroline ring because of the subsequent rotation of the diphenylallyl group away from the bulky terpenyl substituent. If the assumption were valid that the more stable form **16B** would also be the principal participant in this reaction, then we could predict good enantioselectivity to give the *R* enantiomer of the allylation product (Figure 14).

As a final case, we chose to study the unsymmetrically substituted 1-methyl-3-phenylallyl system. The minimized

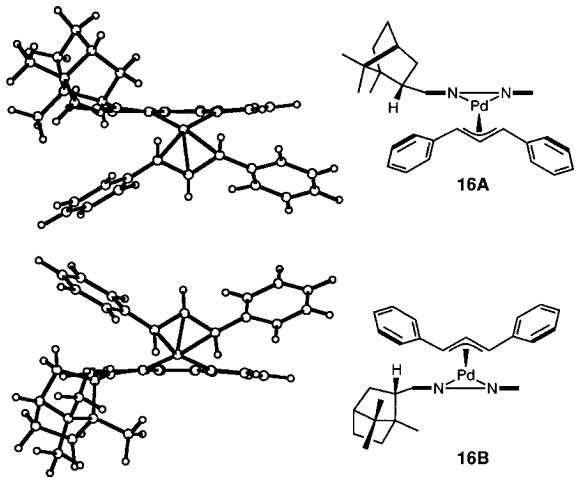


Figure 13. Two diastereomeric forms of *syn,syn*-**16**.

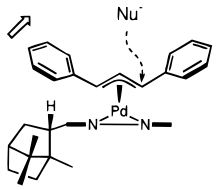


Figure 14. Predicted regiochemistry for nucleophilic attack on *syn,syn*-**16B**.

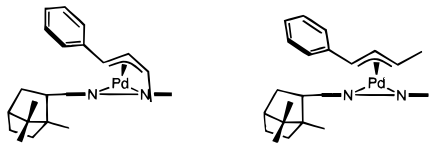


Figure 15. Two diastereomeric forms of **17**.

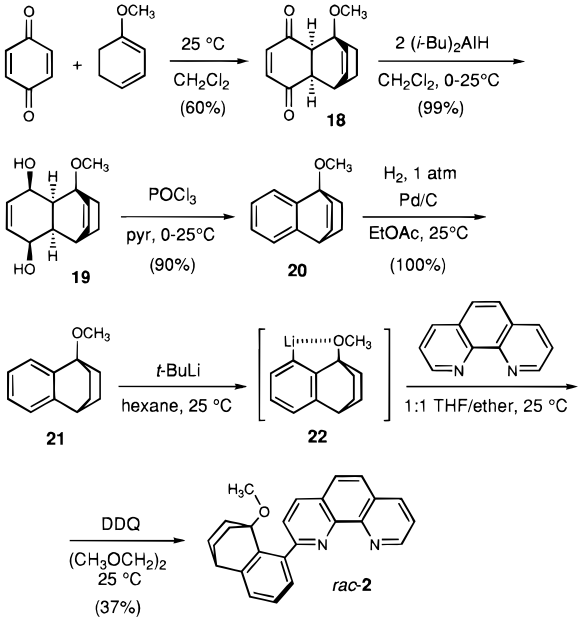
structures *anti,syn*-**17** and *syn,syn*-**17** were found with an energy difference of only 0.1 kcal/mol slightly favoring the *anti,syn* isomer (Figure 15). The forms having the phenyl group proximal to the terpenyl-substituted phenanthroline ring were unexpectedly found to be approximately 2 kcal/mol lower in energy than the forms having the phenyl group proximal to the unsubstituted phenanthroline ring. A detailed examination of the possible conformers reveals that the phenyl and methyl groups experience a comparable number of repulsive van der Waals interactions (*e.g.*, C−H distances < 2.9 A in the MM2 force field) in the proximal position, whereas the phenyl group in this position is also stabilized by a large number of attractive van der Waals interactions (*e.g.*, C−H distances > 3.0 A). Slight rotation of the allyl causes increased crowding between the *syn* position and H_9 on the phenanthroline, thus favoring the *anti*-methyl isomer. In unsubstituted phenanthroline, where there is very little rotation of the allyl, the *syn/anti* ratio is 9/1.[8]

For either form, we would anticipate at least some preference for nucleophilic attack at the methyl-substituted terminus of the allylic system and subsequent rotation of the phenyl-substituted terminus away from the terpenyl group. Because the two forms have opposite *syn,anti* configurations at this site of attack, they would give opposite configurations of the final allylation product. However, our prior studies[8] indicate the greater reactivity of *anti*-substituted allylic termini and, therefore, the *anti,syn* isomer may react at the methyl terminus more rapidly than the *syn,syn* isomer, thus leading to a modest asymmetric induction for this site of attack. On the other hand, both forms have the same *syn* configuration at the phenyl-substituted terminus and, therefore, to the extent that reaction may occur at this position, both forms would give the same configuration

Table 1. Experimental and Calculated Diastereomeric Ratios of Some Pd−Allyl Complexes with Chiral Phenanthroline Ligands

Ligand	Allyl	Diastereomeric Ratio	
		Exptl	Calcd
7	$(CH_3)_2C$	1:1	2:1
7	$(Ph)_2C$	2:1	3:1
8	$(CH_3)_2C$	2:1	2:1
13	PhCH=CHPh	4:1	19:1
13		4:1	2:1
13	CH_3CH=$CHPh$	5:2:1	6:3:1:0
13	$(CH_3)_2C$	3:1	1:1
13	$(Ph)_2C$	11:1	11:1

Scheme 1



of the final product. The overall prediction would therefore be modest asymmetric induction for the major regioisomer but much higher asymmetric induction for the minor regioisomer.

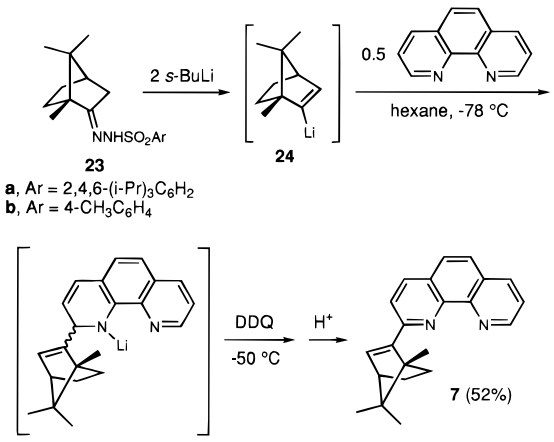
Our predictions for each of the preceding systems are summarized later along with experimental results of actual catalytic allylation reactions (Table 2).

Synthesis of the Chiral Ligands. The synthesis of **2** proceeds relatively straightforwardly (Scheme 1). The benzobicyclo[2.2.2]octene unit is prepared according to a modification of the route previously reported by Schmid and Rabai.[13] Diels−Alder reaction of 1,4-benzoquinone with 1-methoxy-1,3-cyclohexadiene affords the tricyclic adduct **18**. Reduction with diisobutylaluminum hydride (DIBALH) produces the allylic diol **19**. Aromatization with phosphoryl chloride and pyridine gives the benzo-fused derivative **20**. Hydrogenation of the alkene bridge provides the benzobicyclo[2.2.2]octene **21**. Linking of **21** to phenanthroline is accomplished by methoxy-directed lithiation[14] of **18** with *tert*-butyllithium to generate the presumed

(13) Schmid, G. H.; Rabai, J. *Synthesis* **1988**, 332.

(14) Shirley, D. A.; Cheng, C. F. *J. Organomet. Chem.* **1969**, *20*, 251.

Scheme 2



intermediate **22** followed by reaction with phenanthroline. Rearomatization with dichlorodicyanoquinone (DDQ) then gives the desired ligand **2** in racemic form.

Several approaches were studied for the preparation of the chiral terpene-based phenanthroline derivatives, but only the most successful routes are summarized here. A route quite different from ours was reported previously by Gladiali *et al.*, but in an approach more closely related to ours, the coupling of a camphor sultam with halophenanthroline derivatives was reported by Steckhan *et al.*[15]

Based upon the work of Bond,[16] the hydrazone **23a** obtained from (1*R*)-camphor and 2,4,6-triisopropylbenzenesulfonylhydrazide[17] undergoes a Shapiro reaction upon treatment with *sec*-butyllithium to generate the alkenyllithium derivative **24** (Scheme 2); the simpler *p*-toluenesulfonylhydrazone **23b** was shown to be useful in subsequent work described below. Direct reaction[18] of **24** with phenanthroline at −78 °C followed by DDQ-induced rearomatization at −50 °C gives the desired ligand **7** in 52% yield. Careful temperature control is necessary during the addition reaction in order to prevent alkene double bond migration/rearomatization of the intermediate adduct, which leads to varying amounts of the dihydro, or bornyl, derivative **13** (*vide infra*).

As an alternative approach, we studied the use of the corresponding alkenyl iodide. Based upon a literature procedure,[19] the parent hydrazone derivative **25**[20] of (1*R*)-camphor (**5**) undergoes reaction with iodine in the presence of triethylamine to give a 1:1 mixture of the desired iodide **26** and the regioisomeric product **27** (Scheme 3). The literature procedure[19] describes the separation of these two products through use of spinning-band distillation, but we have found the use of column chromatography employing $AgNO_3$-impregnated silica gel[21] to be a practical option.

Lithium/iodide exchange[22] of **26** with *tert*-butyllithium followed by addition of the resulting alkenyllithium **24** to phenan-

(15) (a) Gladiali, S.; Chelucci, G.; Soccolini, F.; Delogu, G.; Chessa, G. *J. Organomet. Chem.* **1989**, *370*, 285. (b) Kandzia, C.; Steckhan, E.; Knoch, F. *Tetrahedron: Asymm.* **1993**, *4*, 39.

(16) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147.

(17) Cusack, N. J.; Reese, C. B.; Risius, A. C.; Roozpeikar, B. *Tetrahedron* **1976**, *32*, 2157.

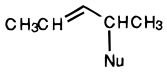
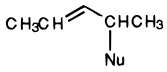
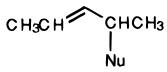
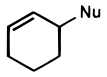
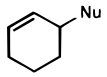
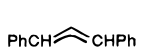
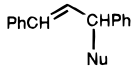
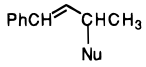
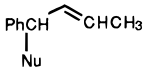
(18) For related reports of organolithium addition to phenanthroline and rearomatization with MnO_2, see: (a) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. *Tetrahedron Lett.* **1982**, *23*, 5291. (b) Lam, F.; Chan, K. S.; Liu, B.-J. *Tetrahedron Lett.* **1995**, *36*, 6261.

(19) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 989.

(20) Reush, W.; DiCarlo, M. W.; Traynor, L. *J. Org. Chem.* **1961**, *26*, 1711.

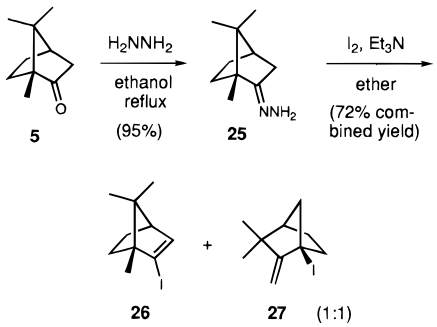
(21) Loev, B.; Bender, P. E.; Smith, R. *Synthesis* **1973**, *6*, 362.

Table 2. Summary of Predicted Enantioselectivities and Experimental Results of Allylation Reactions

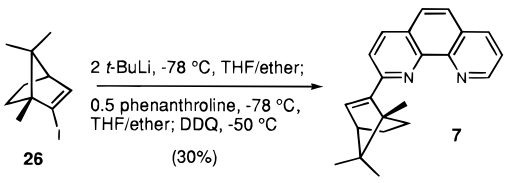
Entry	Phenanthroline Derivative as Ligand	Allyl Ligand	Nucleophile[a]	Product(s)	Predicted e.e.	Exptl e.e. (%)	Exptl Yield(%)
1	 **7**		$HC(Me)(CO_2Et)_2$		low	0	10
2	 **8**		$HC(Me)(CO_2Et)_2$		low	3	50
3	 **13**		$H_2C(CO_2Me)_2$		low	24	80
4			$HC(Me)(CO_2Et)_2$			12	75
5	**7**		$HC(Me)(CO_2Et)_2$		low	8	45
6	**13**		$H_2C(CO_2Me)_2$		modest	16	70
7			$HC(Me)(CO_2Et)_2$			55	80
8	**13**		$H_2C(CO_2Me)_2$		high	80 92[b]	80
9			$HC(Me)(CO_2Et)_2$			38	85
10	**13**		$H_2C(CO_2Me)_2$	 	modest high	33 95 96[b]	68 17

[a] Unless otherwise noted, the nucleophile was generated from the malonate + NaH. [b] Obtained using the BSA procedure.

Scheme 3



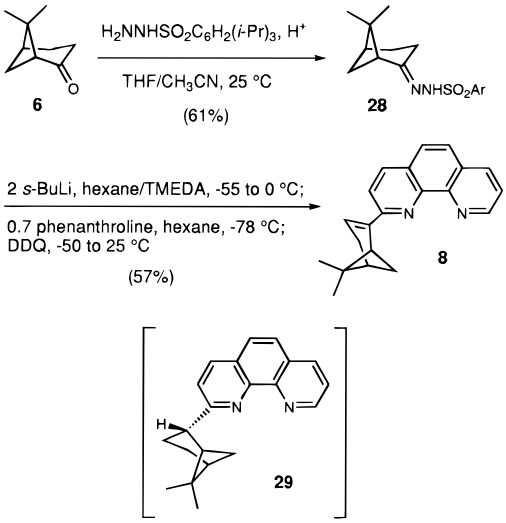
throline and treatment with DDQ gives the desired ligand **7** in 30% yield (eq 2). Although the overall yield of **7** is much lower by this route, this preparation is considerably less expensive than the first one employing 2,4,6-triisopropylbenzenesulfonylhydrazide (Scheme 2).



(2)

For incorporation of (1*R*)-nopinone (**6**) into the corresponding ligand **8**, we again proceeded via the Shapiro reaction of the corresponding arenesulfonylhydrazone **28**. The desired ligand

Scheme 4

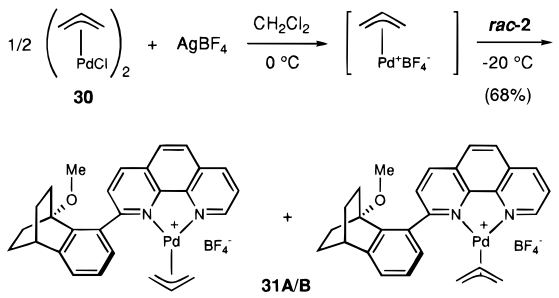


8 is obtained in 57% yield (Scheme 4), but if low temperature is not properly maintained, this compound is again contaminated by a side product **29**[15] resulting from alkene double bond migration/rearomatization.

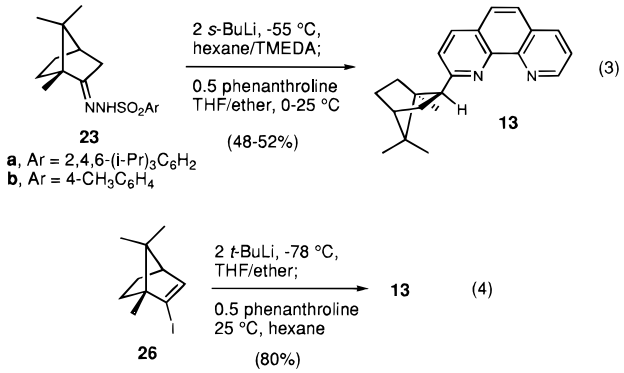
The spontaneous alkene double bond migration/rearomatization could be used to advantage in the synthesis of the bornyl-substituted ligand **13** by simply changing the reaction temperature for the addition of the alkenyllithium **24** to phenanthroline.

(22) Seebach, D.; Neumann, H. *Chem. Ber.* **1974**, *107*, 847.

Scheme 5



Use of an arenesulfonylhydrazone **23** or the alkenyl iodide **26** as a precursor gives the ligand **13** in overall yields of 50 or 80%, respectively (eqs 3 and 4). In this case, we investigated the use of the triisopropylbenzenesulfonylhydrazone **23a** and the less expensive *p*-toluenesulfonylhydrazone **23b**, both of which give **13** in yields of approximately 50%. Furthermore, *p*-toluenehydrazone **23b** is commercially available as either the (*R*)- or the (*S*)-enantiomer, thus permitting facile synthesis of either enantiomeric series of ligands. Detailed ^{1}H NMR analysis of the product **13** reveals the presence of only the *endo*-bornyl isomer, which indicates that the alkene double bond migration/rearomatization is highly stereoselective.



The synthesis of 2,9-disubstituted phenanthrolines was briefly investigated. Addition of bornenyllithium **24** to the monosubstituted ligand **7** followed by rearomatization with DDQ gives the bis(bornenyl)phenanthroline but in a yield of only 15%. Likewise, the nopinone-derived ligand **8** may be converted into the corresponding disubstituted phenanthroline but in a yield of only 6%.

Structural Studies of Palladium Complexes. The feasibility of forming characterizable η^3-allylpalladium complexes containing phenanthroline ligands described in this paper was first tested with the benzobicyclo[2.2.2]octenyl derivative **2**. Reaction of bis[η^3-allyl(chloro)palladium(II)] **30** with silver(I) tetrafluoroborate followed by ligand **2** gives the desired complex **31** in 68% yield as a 1:1 mixture (NMR determination) of diastereomeric forms **31A** and **31B** (Scheme 5). Crystallization from methylene chloride affords material enriched in **31A** as crystals suitable for X-ray diffraction. Figure 16 depicts the structure deduced from the X-ray data, because this complex does not bear substituents at the terminal positions of the allyl group; however, it was not intended for use in our studies of asymmetric allylation reactions. Rather, it served as an initial test case for formation and structural studies of our series of substituted phenanthroline complexes.

^{1}H NMR measurements of the diastereomeric ratios of some palladium allyl complexes containing our substituted phenanthroline ligands were performed and compared to the molecular mechanics-based predictions. We have already described the

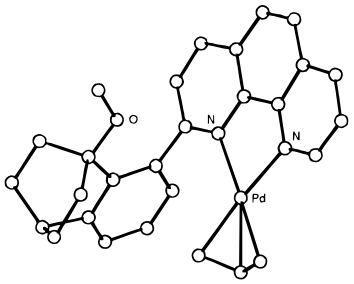
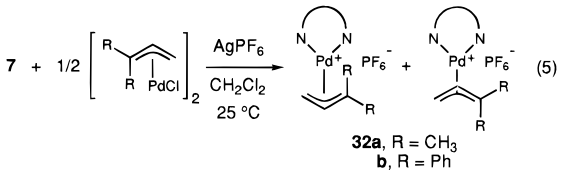


Figure 16. X-ray structure of **31A**. Non-carbon atoms are labeled. Hydrogens are not shown.

NMR studies of a complex **3** containing the 2-benzobicyclo-[2.2.2]octenylphenanthroline ligand **2** (*vide supra*). The low 3:1 diastereofacial selectivity (*vide supra*) prompted our study of the terpene-derived ligands.

For 2-bornenylphenanthroline (**7**), the molecular mechanics calculations predict poor potential utility in asymmetric allylation reactions. The first experimental examination of this system was the preparation of η^3-1,1-dimethylallyl and η^3-1,1-diphenylallyl) complexes **32a** and **32b** (eq 5). ^{1}H NMR showed them to exist as 1:1 and 2:1 diastereomer mixtures, respectively, most likely having their substituted allylic termini remote from the bornenyl substituent but differing in diastereofacial coordination of their allyl groups. No attempts were made to distinguish these isomers. Also, due to their substitution patterns, the terminal positions of these complexes cannot function as prochiral centers for nucleophilic addition.



These results together with the NMR studies using the other chiral ligands are shown in Table 1. The NMR experimental values agree well with the calculated ratios. The largest error (19:1 vs. 4:1 for the fourth entry) corresponds to an energy difference of less than 1 kcal/mol. In other studies, it has recently been shown that the average error for simple, *non-organometallic*, organic compounds with some of the best force fields in use today is approximately 0.5 kcal/mol.[23] A maximum error of 1 kcal/mol in less fully developed organometallic systems represents a relatively good level of agreement.

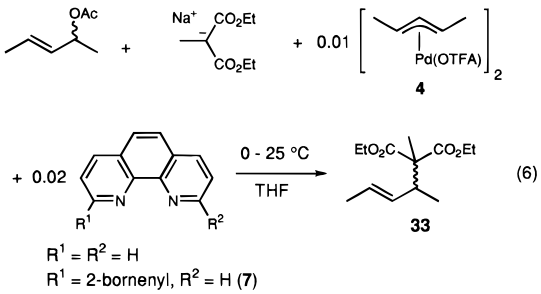
From the perspective of asymmetric allylation reactions, the results with the 1,3-diphenylallyl, 1-methyl-3-phenyl, and cyclohexenyl systems are the most interesting. The results of studying these allyl systems with the chiral ligand **13** are especially promising for asymmetric addition reactions. Also, from the measurements of the diastereomeric ratios of the complexes, the apparent rotation of the allyl ligands is slow on the NMR time scale when PF_6^- or BF_4^- is used as the counterion.

Catalytic Allylation Reactions. All of the chiral ligands and allyl systems that had been the subject of calculations were employed in catalytic allylation reactions using malonate nucleophiles. The systems that were studied calculationally provided a wide range of predicted outcomes, varying from very low levels up to relatively high levels of asymmetric induction. If these wide-ranging predictions could be confirmed experimentally, then some assurance would be provided for the

(23) Gundertofte, K.; Liljefors, T.; Norrby, P.-O.; Pettersson, I. *J. Comput. Chem.* In press.

viability of employing this molecular mechanics approach in additional future efforts directed toward chiral catalyst design.

The conditions of the catalytic allylations are typified by a control reaction of *rac*-(*E*)-4-acetoxy-2-pentene, diethyl sodiomethylmalonate, (η^3-1,3-dimethylallyl)palladium trifluoroacetate **4**, and *unsubstituted* phenanthroline. The product **33** is obtained, obviously in racemic form, in 84% yield and 100% consumption of the starting acetate after 14 h at 0 °C (eq 6). Alternative conditions for generation of the nucleophile entail *in situ* treatment of the malonate ester with *O*,*N*-bis(trimethylsilyl) acetamide (BSA) and potassium acetate or potassium fluoride, either in the absence or in the presence of 18-crown-6.[24−32]



When the experiment is repeated with bornenylphenanthroline **7** as the ligand, one difference is a much slower rate of reaction which may be due to the steric interaction of the bornenyl substituent with the metal moiety as discussed above. After 29 h at 0 °C, only 17% of the allylic acetate is consumed, and the yield of **33** is only 10%. Also, the enantiomeric excess (ee) of the product is 0%, as measured by ^{1}H NMR using the chiral shift reagent, tris{3-[heptafluoropropyl)hydroxymethylene]-(+)-camphorato]europium, Eu(hfc)$_3$.[33] This outcome is also consistent with the very low level of asymmetric induction predicted by the calculations. A further decrease in reaction rate is seen upon use of the 2,9-bis(bornenyl)phenanthroline ligand whereby only 8% of the allylic acetate is consumed after 29 h at 0 °C to give racemic product in a yield of 4%. Therefore, use of disubstituted ligands was not pursued further. Emphasis was instead placed upon use of the bornylphenanthroline ligand **13** for which the previous molecular mechanics studies had indicated less hindrance toward palladium coordination. The overall results obtained with the monosubstituted, terpene-derived phenanthroline ligands are summarized in Table 2 along with the prior predictions of asymmetric induction.

Discussion

The predicted and the experimentally observed ee values are in close agreement for the products of the palladium-catalyzed allylation reactions employing our chiral phenanthrolene ligands. Those systems that had been predicted to give poor asymmetric induction do, in fact, give zero or very small ee values. Most gratifying are the two systems that had been predicted to give significantly higher ee values. Use of the bornylphenanthroline ligand **13** in the reaction of dimethyl malonate with the 1,3-diphenylallyl system gives an ee of up to 92% (entry 8). The (*R*)-enantiomer is the predominant product as predicted (see Figure 14). Also of significance is that different levels of asymmetric induction had been predicted for the cyclohexenyl system, depending upon the choice of ligand **7** or **13**, and again these predictions are consistent with the experiments (entries 5−7). Very important are the results with the 1-methyl-3-phenylallyl system for which significantly different outcomes had been predicted for reactions occurring at the two termini. Reaction at the methyl-substituted terminus, which is the major pathway, gives an ee of 33%, whereas reaction at the phenyl-substituted terminus gives an ee of up to 96% (entry 10). Although these results are gratifying, an explanation for the asymmetric induction in this latter case is far from complete. The substrate for this reaction was the corresponding racemic allylic acetate. Therefore, if a simple, direct, two-step mechanism were invoked, consisting of π-allyl complex formation and nucleophilic attack with inversion of configuration of the allylic positions in both steps, the products would be racemic. However, the two enantiomers of the starting allylic acetate would afford diastereomeric π-allyl complexes of different energies, and if stereochemical interconversion were to occur in this system, net asymmetric induction could result. Various mechanisms, including π-σ-π rearrangement, *anti* displacement of coordinated palladium by external palladium, and reversible nucleophilic attack, have been proposed previously for stereochemical interconversion of allyl systems.[5j−t,8c,41] Although our results are consistent with a palladium exchange pathway as proposed in very similar work of others,[41] we have insufficient data to claim a specific stereochemical interconversion pathway in the present case.

Our results must also be considered in a broader context. Of the several metal-promoted reactions that have been the subject of investigations in asymmetric synthesis,[2] palladium-catalyzed allylations[5,24−32,35−41] have been under especially intense scrutiny. A large number of chiral ligands have been studied with great success in these reactions (Figure 17). In order to place our work in proper perspective, we have compiled representative results in Table 3 for several of these chiral ligands in comparison with the use of bornylphenanthroline **13**.

Our ligands have functioned well for the originally stated purpose of studying the correlation of predicted and experimental results. This key, initial goal has been met, but we do not lay claim to superiority of our ligands compared to the best of the ligands developed previously. However, our results are at least comparable in some selected cases, and our ligands are relatively easily prepared in enantiomerically pure form. Also, in comparison of different conditions for employing malonate derivatives, our results are consistent with the prior finding of

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(38) Yamazaki, A.; Morimoto, T.; Achiwa, K. *Tetrahedron: Asymm.* **1993**, *4*, 2287.
(39) Togni, A. *Tetrahedron: Asymm.* **1991**, *2*, 683.
(40) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 4089.
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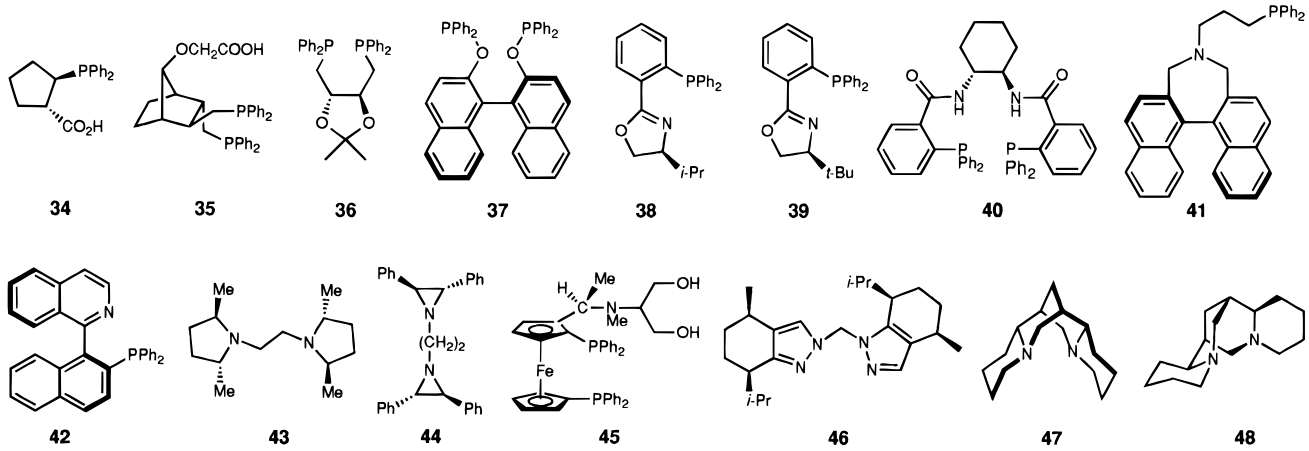
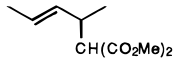
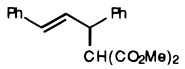
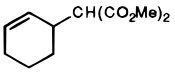
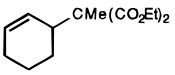
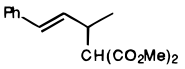
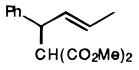


Figure 17. Examples of previously reported chiral ligands for palladium-catalyzed asymmetric allylation reactions.

Table 3. Comparison of Ligand **13** with Other Previously Reported Chiral Ligands for Palladium-Catalyzed Asymmetric Allylation Reactions

Product	Results with **13** %ee	Results with other ligands Ligand	% e.e.	lit. ref.
	24	(+)-DIOP	22	34
		36		
		39	71	24
	92	BINAPO	55	25
		37		
		34	85	35
		45	48	26
		38	98	26
		46	84	28
		44	>99	37
		47	88	29
		43	91	38
		35	49	38
		41	96	30
		42	98	31
	16	**48**	50	39
		40	96	40
	55	(no prior examples found)	-	-
	33	**48**	21	39
	96	**48**	85	39

Trost and others that the use of the alternative BSA conditions gives superior ee values compared to more traditional conditions.[24−32] We have not employed the tetraalkylammonium malonate derivatives that have also been reported to give improved results.[40]

Another point is that in the past, most ligands used in these reactions were phosphine or phosphite derivatives, but several nitrogen-based ligands **38**−**48** have been developed more recently. Our results give an additional indication of the potential for further development of nitrogen donor ligands in these reactions.

Conclusion

The studies described in this paper lend support to the notion that molecular mechanics may be one of various useful tools for assisting the rational design of asymmetric catalysts. Clearly, much remains to be done to improve this approach. More complete development of parameter sets for metal complexes is an obvious need. At an even more fundamental level, we must return to key comments in the introduction. The calculational prediction and experimental detection of relatively stable intermediates are not sufficient indicators for successful catalyst design. The reactivity characteristics and the equilibria between several species must also be taken into account.[6] Other concerns may again be raised about the effects of other reaction parameters such as solvents, counterions, and specific selections of bases, nucleophiles, and leaving groups employed in these reactions.

With the realization that our present results are only a first step in this direction, we are actively pursuing some of these further considerations. We are reporting separately our next step which takes into account the intrinsic reactivity of distorted allyls and the steric demands of an approaching nucleophile.[7] However, all of the above concerns must be addressed if the molecular mechanics approach is to be developed into a generally useful tool for catalyst design. Chiral ligands are of importance in many other synthetically useful, palladium-catalyzed reactions including couplings (e.g., the Stille[42] and the Suzuki[43] reactions), vinylations (e.g., the Heck reaction[44]), heteronucleophilic additions to alkenes,[45] 3 + 2 cycloadditions,[46] and alkene polymerizations.[47] Also, nitrogen donor ligands are of use in complexes involved in other reactions such as the well-established alkene oxidations promoted by osmium[48] and

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(43) (a) Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419. (b) Martin, A. R.; Yang, Y. *Acta Chem. Scand.* **1993**, *47*, 221.

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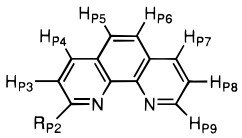
(47) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641.

manganese compounds,[49] the rich organometallic chemistry of copper,[50] cobalt-promoted alkylations,[51] iron-mediated triene carbocyclizations,[52] and nickel-catalyzed conjugate additions to enones.[53] These and many other reactions will continue to attract the attention of investigators concerned with the rational design of methods for asymmetric synthesis.

Experimental Section

General Methods. All manipulations of air-sensitive compounds were performed in oven-dried glassware under a nitrogen atmosphere. Solutions were transferred with hypodermic syringes or with double-ended needles (cannulas). GC analyses were performed on a Hewlett-Packard 5890A chromatograph equipped with a capillary column (methyl silicone gum, 25 m × 0.31 mm). HPLC analyses were performed using an ISCO Model 2360 gradient programmer, a Model 2350 pump, a V4 variable wavelength UV detector, and a Brownlee silica Spheri-5 HPLC analytical 4.6 mm x 22 cm cartridge column. Flash column chromatography and MPLC were performed using EM Science silica gel 60 (230−400 mesh) or Aldrich neutral aluminum oxide, Brockmann I (150 mesh). MPLC purifications were performed as described by Baeckström *et al.*[54] Analytical TLC was performed using Whatman AL SIL G/UV(254) silica gel plates (250 μm thick) or E. Merck 60 F_{254} neutral (type E) aluminum oxide sheets (0.2 mm thick). Preparative TLC was performed using Analtech silica gel thin-layer chromatography plates (250 μm) or E. Merck 60 F_{254} neutral (type E) aluminum oxide sheets (0.2 mm thick).

Proton (^{1}H) nuclear magnetic resonance (NMR) spectra were obtained with a Magnachem A-200 (200 MHz), a Bruker ACF-250 (250 MHz), a General Electric GN-300 (300 MHz), or a Bruker AM-400 (400 MHz) spectrometer. Carbon (^{13}C) NMR spectra were recorded on the Bruker or General Electric spectrometers at 62.5, 75, or 100 MHz. $CDCl_3$ containing 5% (v/v) TMS was the solvent unless otherwise indicated. NMR assignments were made with both COSY and homodecoupling programs. The subscript $_P$ is used to identify the protons in the phenanthroline ligands according to following numbering scheme:



Infrared spectra were recorded on a Perkin-Elmer Model 1420 spectrophotometer. Mass spectral data were obtained on a Finnigan MAT 8430 spectrometer. HRMS data were obtained by electron impact, and low resolution data were obtained by isobutane chemical ionization. Optical rotations were determined with a Rudolph Research Autopol III polarimeter at 546 nm. Elemental analyses were performed by M-H-W laboratories (Phoenix, AZ) and are reported when they agree with the calculated values within ±0.4%. Melting points were determined in Pyrex capillaries with a Thomas Hoover Unimelt apparatus and are corrected.

Anhydrous THF, ethyl ether, and dimethoxyethane (DME) were freshly distilled under nitrogen from dark blue or purple solutions of sodium-benzophenone ketyl/dianion. Hexane and CH_2Cl_2 used for chromatography and workup were distilled form calcium hydride. Pentane (reagent grade) utilized for chromatography was used directly without purification. Ethyl ether used for workup was distilled from ferrous sulfate. Ethyl acetate was distilled from calcium chloride. Tetramethylethylenediamine (TMEDA) was freshly distilled under nitrogen from sodium. Hexane was distilled under nitrogen from calcium hydride. Triethylamine, pyridine, and diisopropylamine were distilled under nitrogen from sodium hydroxide. 1,10-Phenanthroline was heated at 60 °C under vacuum (0.01 mm Hg) for 12 h and was stored under nitrogen. The racemic allylic acetates were obtained by acetylating the alcohols with acetic anhydride under standard conditions. All other chemicals were purchased from Aldrich Chemical Co. unless otherwise stated. 1-Acetoxy-2-cyclohexene was kindly donated by Dr. Sverker Hansson (Royal Institute of Technology). (1,2,3-η)-Propenylpalladium chloride dimer,[55] bis(μ-trifluoroactetato)bis[(2,3,4-η)-3-pentenyl]dipalladium,[56] and $Pd(dba)_2$[57] were synthesized using literature procedures.

1-Methoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (21). 1,4-Benzoquinone (2.0 g, 18,5 mmol) and 1-methoxy-1,3-cyclohexadiene (1.9 g, 17.6 mmol) in CH_2Cl_2 (50 mL) were stirred for 12 h at 25 °C. The solvent was then evaporated to give a dark solid which was stirred in CCl_4. The mixture was passed through a sintered glass funnel, the solvent was removed under reduced pressure, and the yellow solid was recrystallized from EtOAc/pentane to give **18** (2.3 g, 60.2%) as pale yellow needles: mp 118−119 °C. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.53; H, 6.47. Found: C, 71.67; H, 6.58. To a solution of **18** (5.0 g, 22.9 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added a solution of DIBAL (48.16 mmol) via syringe. The mixture was stirred at 25 °C for 1 h and was quenched with 1:1 H_2O/MeOH and aqueous sodium potassium tartrate. The mixture was extracted with ether, and the extracts were dried, treated with activated charcoal, and concentrated. Recrystallization from EtOAc gave **19** (5.03 g, 99%) as colorless prisms: mp 128−129 °C. A solution of **19** (3.68 g, 16.6 mmol), pyridine (40 mL), and phosphoryl chloride (6.8 mL, 73.2 mmol) at 0 °C was warmed to 25 °C. After completion of the reaction (TLC), the mixture was poured into ice−water and extracted with ether. The extracts were washed with 5% HCl and water, treated with activated charcoal, dried, concentrated, and purified by column chromatography (silica gel, 2% EtOAc/pentane) to give **20** (2.76 g, 90%) as a colorless oil. HRMS *m/e* calcd for $C_{11}H_{10}O$ ($M^+ - C_2H_4$) 158.0732, found 158.0736 ($M^+ - C_2H_4$). Anal. Calcd for $C_{13}H_{14}O$: C, 83.82; H, 7.58. Found: C, 84.00; H, 7.74. **20** (0.173 g, 0.93 mmol) and 10% Pd/C (0.1 g) in EtOAc were stirred under hydrogen (1 atm) at 25 °C and monitored by GC. The mixture was passed through a cotton plug. The filtrate was concentrated to give **21** (0.174 g, 99%) as a colorless oil: ^{1}H NMR (300 MHz) δ 7.5−7.0 (m, Ar*H*), 3.53 (s, C*H*$_3$O), 2.93 (m, bridgehead H), 2.0−1.8 (m, $CH_3OC(CH_2)_2$), 1.6−1.4 (m, $CH_3OC(CH_2CH_2)_2$); ^{13}C NMR (75 MHz) δ 143.38, 142.50, 125.90, 125.77, 123.21, 120.15 (Ar), 76.58 (*C*OCH$_3$), 51.17 (CO*C*H$_3$), 33.71 (*C*H), 29.25 (CH_3OCCH_2), 26.64 ($CH_3OCH_2CH_2$); IR (neat) 3050 (Ar), 2950, 2850 (CH), 1330 (C-O-C) cm^{-1}. HRMS *m/e* calcd for $C_{13}H_{16}O$ 188.1201, found 188.1187. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.79; H, 8.56.

2-[(1-Methoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-8-yl)]-1,10-phenanthroline (*rac*-2). To a solution of *t*-BuLi (5.3 mmol) and TMEDA (0.62 g, 5.3 mmol) in hexane (1.0 mL) at 25 °C under nitrogen was added **21** (0.5 g, 2.7 mmol) over 30 min. The lithiation stopped at 56% conversion (GC analysis of an aliquot methylated with CH_3I). The solvent was then evaporated to give a dark oil which was dissolved in THF (2.0 mL) and added to 1,10-phenanthroline (0.96 g, 5.3 mmol) in 1:1 ether/THF (10.0 mL) at 25 °C. After 12 h, DDQ (1.2 g, 5.3 mmol) in DME (5.0 mL) was added at 25 °C. After 12 h, the reaction was quenched with aqueous NH_4Cl. The CH_2Cl_2 extracts were passed Celite, dried, concentrated, and purified by MPLC (neutral alumina, EtOAc/hexane gradient) to give *rac*-**2** (0.36 g, 37%) which was recrystallized from EtOAc/pentane: mp 219−222 °C; ^{1}H NMR (300 MHz) δ 9.2 (dd, J = 4.3, 1.8 Hz, H_{P9}), 8.25 (dd, J = 8.1, 1.8 Hz, H_{P7}), 8.1 (d, J = 8.3 Hz, H_{P4}), 7.9−7.7 (two d, $J_{P5,6} = J_{P6,5}$ = 8.8 Hz, H_{P5} and H_{P6}), 7.8 (d, J = 8.3 Hz, H_{P3}), 7.6 (dd, J = 8.1, 4.3 Hz, H_{P8}), 7.5 (dd, J = 7.6, 1.5 Hz, H_p), 7.25 (dd, J = 7.5, 7.3 Hz, H_m), 7.2 (dd, J =

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7.4, 1.5 Hz, H_o), 3.05 (bs, bridgehead H), 2.5 (s, CH_3O), 2−1.5 (broad shoulder, 4 CH_2); ^{13}C NMR (75 MHz) δ 162.02, 150.23, 146.49, 145.02, 143.43, 140.10, 136.66, 135.84, 132.77, 130.33, 128.66, 127.12, 126.86, 126.48, 125.80, 125.78, 123.89, 122.47 (phen and Ar), 78.45 (*C*OCH$_3$), 50.65 (CO*C*H$_3$), 34.59 (*C*H), 32.93, 28.42, 26.81, 25.56 (bs *C*H2); IR (CH_2Cl_2) 3060 (Ar), 2900 (CH), 1250 (C-O-C), 900 (C-H Ar) cm^{-1}. HRMS *m/e* calcd for $C_{25}H_{22}N_2O$ 366.1732, found 366.1703. Anal. Calcd for $C_{25}H_{22}N_2O$: C, 81.83; H, 6.06. Found: C, 81.81; H, 6.16.

(1*R*)-2-Iodo-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene (26) and 2,2-Dimethyl-3-methylene-4-iodobicyclo[2.2.1]heptene (27).[21] To a (1*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one hydrazone (**25**)[20] (7.0 g, 42.1 mmol), Et_3N (10.0 mL), and ether (50.0 mL) was added dropwise iodine in ether until the yellow color persisted for about 30 s. The crude product consisted of a 1:1 mixture (8.0 g, 72% combined yield) of **26** and **27** which was separated by column chromatography (silica gel/10% silver nitrate,[21] pentane) to give **26** (3.2 g, 29%) as a pale yellow oil: ^{1}H NMR (300 MHz) δ 6.4 (d, J = 3.4 Hz, C*H*=C), 2.36 (t, J = 3.4 Hz, H-4), 1−2 (m, 4 H, ring protons), 0.96 (s, CH_3 at C-1), 0.85 (s, CH_3 at C-7), 0.84 (s, CH_3 at C-7) (lit.[21] ^{1}H NMR); **27** (3.5 g, 43%) as a pale yellow oil: ^{1}H NMR (300 MHz) δ 5.17 (s, C=C*H*H), 4.82 (s, C=CH*H*), 2.5−1.5 (m, 7 H, ring protons), 1.13 (s, CH_3), 1.08 (s, CH_3) (lit.[21] ^{1}H NMR).

2-[(1*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl]-1,10-phenanthroline (7). **Method I**.[16] To a suspension of triisopropylbenzenesulfonylhydrazone **23a** (1.0 g, 2.3 mmol) in 1:1 hexane/TMEDA (20.0 mL) at −55 °C was added a solution of *s*-BuLi (5.1 mmol) dropwise. The solution was stirred at −55 °C for 1.5 h and at 0 °C for 30 min and was then added to a suspension of 1,10-phenanthroline (0.19 g, 1.04 mmol) in hexane (5.0 mL) at −78 °C. After 12 h, DDQ (0.52 g, 2.3 mmol) in DME (5.0 mL) was added at −50 °C. After 6 h at 25 °C, the reaction was quenched with aqueous NH_4Cl solution and the CH_2Cl_2 extracts were passed through Celite, dried, concentrated, and purified by MPLC (neutral alumina, EtOAc/hexane gradient) to give **7** (0.17 g, 52%) as a yellow crystalline solid which was recrystallized from EtOAc/pentane: mp 182−184 °C; $[\alpha]^{25}_D$ −129.4° (*c* 0.05, CH_2Cl_2); ^{1}H NMR (300 MHz) δ 9.2 (dd, J = 4.3, 1.7 Hz, H_{P9}), 8.2 (dd, J = 8.1, 1.7 Hz, H_{P7}), 8.1 (d, J = 8.4 Hz, H_{P4}), 7.75−7.70 (two d, J = 8.8 Hz, H_{P5} and H_{P6}), 7.72 (d, J = 8.4 Hz, H_{P3}), 7.6 (dd, J = 8.0, 4.3 Hz, H_{P8}), 6.8 (d, J = 3.4 Hz, H-3), 2.51 (app. t, J = 3.4 Hz, H-4), 2.0 (m, H-5$_{exo}$), 1.8 (m, H-6$_{endo}$), 1.6 (m, H-5$_{endo}$), 1.56 (s, CH_3 at C-1), 1.15 (m, H-6$_{exo}$), 0.96 (s, CH_3 at C-7), 0.90 (s, CH_3 at C-7); ^{13}C NMR (75 MHz) δ 157.08, 150.28, 149.41, 146.69, 145.93, 137.66, 126.96, 126.91, 126.42, 125.42, 122.49, 121.01 (phen), 135.83, 135.49 (C-2 and C-3), 57.00, 55.12, 52.06 (C-1, C-4, and C-7), 31.89, 25.76 (C-5 and C-6), 19.92 (*C*H$_3$ at C-7), 19.65 (*C*H$_3$ at C-7), 13.02 (*C*H$_3$ at C-1); IR (CH_2Cl_2) 3030 (Ar, Cd=C), 2980 (C-H), 1420 (CH) cm^{-1}. HRMS *m/e* calcd for $C_{22}H_{22}N_2$ 314.1783, found 314.1775. Anal. Calcd for $C_{22}H_{22}N_2$: C, 84.03; H, 7.06. Found: C, 84.31; H, 7.13.

Method II.[22] A solution of **26** (0.5 g, 1.9 mmol), 4:1 THF/ether (10 mL), and *t*-BuLi (4.2 mmol) was stirred at −78 °C for 1 h and was added to phenanthroline (0.17 g, 0.95 mmol) in 4:1 THF/ether (10 mL) at −78 °C . After 7 h, DDQ (0.43 g, 1.9 mmol) in DME (2.0 mL) was added at −50 °C. After 6 h at 25 °C, product isolation as in Method I gave **7** (0.09 g, 30%) as a yellow crystalline solid.

2-[(1*R*)-2-*endo*-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl]-1,10-phenanthroline (13). Using Method I as above, the alkenyllithium from **23a** (1.0 g, 2.3 mmol) *s*-BuLi (5.1 mmol) was stirred with 1,10-phenanthroline (0.210 g, 1.15 mmol) in hexane (20.0 mL) at 25 °C for 60 h. Purification with MPLC (neutral alumina, EtOAc/hexane gradient) gave **13** (0.19 g, 52%) as a yellow crystalline solid which was recrystallized from EtOAc/pentane. Alternatively, (*R*)-camphor *p*-toluenesulfonylhydrazone (1.25 g, 3.90 mmol) in 1:1 hexane/TMEDA (10 mL) and a cyclohexane solution of *s*-BuLi (7.8 mmol) followed by reaction with phenanthroline (0.345 g, 1.91 mmol) in hexane (10 mL) gave **13** (0.29 g, 48%) as a yellow crystalline solid: mp 157−159 °C; $[\alpha]^{25}_D$ −64.5° (*c* 0.03, CH_2Cl_2); ^{1}H NMR (300 MHz) δ 9.2 (dd, J = 4.3, 1.8 Hz, H_{P9}), 8.15 (dd, J = 8.1, 1.8 Hz, H_{P7}), 8.1 (d, J = 8.4 Hz, H_{P4}), 7.70−7.65 (two d, J = 8.8 Hz, H_{P5} and H_{P6}), 7.6 (d, J = 8.4 Hz, H_{P3}), 7.55 (dd, J = 8.0, 4.4 Hz, H_{P8}), 3.8 (ddd, J = 11.5, 5.3, 2.4 Hz, H-2$_{exo}$), 2.3 (m, H-3$_{exo}$), 2.05 (dd, J = 13.1, 5.3 Hz, H-3$_{endo}$) 1.85 (m, H-4 and H-5$_{endo}$), 1.60 (m, H-5$_{exo}$), 1.35 (m, H-6$_{endo}$), 1.25 (m, H-6$_{exo}$), 1.12 (s, CH_3 at C-1), 0.95 (s, 2 CH_3 at C-7); ^{13}C NMR (75 MHz) δ 163.81, 150.08, 146.36, 145.00, 135.60, 134.90, 128.57, 126.70, 126.20, 125.26, 122.64, 122.24 (phen), 52.76, 50.84 (C-2 and C-3), 50.29 (C-7), 45.60 (C-4), 33.74 (C-1), 29.24, 28.27 (C-5 and C-6), 19.47, 18.93, 14.57 (methyl groups); IR (CH_2Cl_2) 3060 (Ar), 2900 (CH), 900 (C-H Ar) cm^{-1}. HRMS *m/e* calcd for $C_{22}H_{24}N_2$ 316.1940, found 316.1954. Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.49; H, 7.65. Found: C, 83.26; H, 7.85.

Method II. 26 (0.5 g, 1.9 mmol) in 1:1 THF/ether (10 mL), *t*-BuLi (4.2 mmol), and phenanthroline (0.17 g, 0.95 mmol) in hexane (10 mL) gave **13** (0.24 g, 80%) as a yellow crystalline solid.

2-{(1*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl}-1,10-phenanthroline (8). Hydrazone **28** was obtained from reaction of 2,4,6-triisopropylbenzenesulfonylhydrazide (5.2 g, 17.4 mmol), (1*R*)-6,6-dimethylbicyclo-[3.1.1]heptan-2-one (2.2 g, 15.8 mmol), and concentrated aqueous HCl (1.5 mL) in 3:1 CH_3CN/THF (40.0 mL) at 25 °C for 14 h to give 4.0 g (61%) of colorless crystals: mp 162−163 °C (dec.). HRMS *m/e* calcd for $C_{24}H_{38}N_2O_2S$ 419.2748, found 419.2740. Anal. Calcd for $C_{24}H_{38}N_2O_2S$: C, 68.86; H, 9.16. Found: C, 68.59; H, 8.92. By use of Method I, **28** (0.5 g, 1.2 mmol) in 1:1 hexane/TMEDA (10.0 mL), *s*-BuLi (2.6 mmol), phenanthroline (0.14 g, 0.79 mmol) in hexane (5.0 mL), and DDQ (0.27 g, 1.2 mmol) in DME (3.0 mL) and purification with MPLC (neutral alumina, EtOAc/hexane gradient) gave **8** (0.14 g, 57%) as a yellow crystalline solid which was recrystallized from EtOAc/pentane: mp 169−171 °C; $[\alpha]^{25}_D$ +25° (*c* 0.04, CH_2Cl_2); ^{1}H NMR (300 MHz) δ 9.2 (dd, J = 4.4, 1.8 Hz, H_{P9}), 8.2 (dd, J = 7.8, 1.8 Hz, H_{P7}), 8.1 (d, J = 8.3 Hz, H_{P4}), 7.75 (d, J = 8.6 Hz, H_{P3}), 7.7 (two d, J = 8.7 Hz, H_{P5} and H_{P6}), 7.55 (dd, J = 8.4, 4.4 Hz, H_{P8}), 6.91 (m, H-3), 3.5 (dt, J = 5.6, 1.6 Hz, H-1), 2.65−2.5 (m, H-7$_{exo}$, H-4$_{exo}$, H-4$_{endo}$), 1.45 (s, CH_3 at C-6), 1.42 (d, J = 8.6 Hz, H-7$_{endo}$), 0.92 (s, CH_3 at C-6); ^{13}C NMR (75 MHz) δ 157.33, 150.16, 147.28, 146.34, 135.97, 135.91, 129.00, 126.89, 126.28, 125.43, 122.47 (phen), 145.60 and 118.91 (C-2 and C-3), 42.47 (C-1), 40.62 (C-5), 38.04 (C-6), 32.25, 31.68 (C-7 and C-4), 26.31 (*C*H$_3$ at C-6), 21.02 (*C*H$_3$ at C-6); IR (CH_2Cl_2) 3030 (Ar and C=C), 2980 (CH), 1420 (CH) cm^{-1}. HRMS *m/e* calcd for $C_{21}H_{20}N_2$ 301.1705, found 301.1730. Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.95; H, 6.72. Found: C, 83.76; H, 6.77.

2,9-bis-[(1*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl]-1,10-phenanthroline. **Method I.** The alkenyllithium from **23a** (0.21g, 0.48 mmol) in 1:1 hexane/TMEDA (8.0 mL) and *s*-BuLi (1.0 mmol) was stirred with **7** (0.1 g, 0.32 mmol) in hexane (5.0 mL) at −78 °C for 16 h followed by DDQ (0.11 g, 0.48 mmol) in DME (3.0 mL) at 25 °C for 4 h. Purification with MPLC (neutral alumina, ethyl acetate/hexane gradient) gave the disubstituted phenanthroline (0.017 g, 17%) as a pale yellow crystalline solid which was recrystallized from ethyl acetate/pentane: mp 169−171 °C; $[\alpha]^{25}_D$ −333.3° (*c* 0.03, CH_2Cl_2); ^{1}H NMR δ 8.03 (d, J = 8.4 Hz, H_{P3} and H_{P8}), 7.71 (d, J = 8.4 Hz, H_{P4} and H_{P7}), 7.61 (s, H_{P5} and H_{P6}), 6.56 (d, J = 3.3 Hz, H-3), 2.52 (app. t, J = 3.4 Hz, H-4), 2.00 (m, H-5$_{exo}$), 1.9−1.5 (m, H-6$_{endo}$, H-5$_{endo}$), 1.75 (s, CH_3 at C-1), 1.3−1.1 (m, H-6$_{exo}$), 0.96 (s, CH_3 at C-7), 0.93 (s, CH_3 at C-7); ^{13}C NMR (75 MHz) δ 157.03, 150.22, 145.71, 126.91, 125.18, 120.56 (phen), 137.29 and 135.32 (C-2 and C-3), 56.21 (C-7), 55.52 (C-1), 52.18 (C-4), 31.51 (C-6), 26.08 (C-5), 19.77 (*C*H$_3$ at C-7), 19.58 (*C*H$_3$ at C-7), 12.53 (*C*H$_3$ at C-1); IR (CH_2Cl_2) 3030 (Ar, C=C), 2980 (C-H), 1420 (CH) cm^{-1}. HRMS *m/e* calcd for $C_{32}H_{36}N_2$ 448.2878, found 448.2873.

Use of Method II with **26**, *t*-BuLi, **7**, and DDQ gave the disubstituted phenanthroline (14%) as a yellow crystalline solid.

Simple Bis(*μ*-chloro)bis[η^3-allyl]dipalladium Complexes.[55] **Bis(*μ*-chloro)bis[(1,2,3-η)-1-methyl-3-phenyl-2-propenyl]dipalladium.** Trifluoroacetic anhydride (920 mg, 4.38 mmol) was added to *trans*-4-phenyl-3-buten-2-ol[58] (500 mg, 3.37 mmol) and ether (35 mL) at 0 °C. The mixture was stirred at 25 °C for 12 h, and the ether was removed by rotary evaporation. Pd(dibenzylideneacetone)$_2$ (1.4 g, 2.55 mmol), acetonitrile (9 mL), and THF (36 mL) were added, and the mixture was stirred at 25 °C for 15 min. The mixture was extracted with 90:10 H_2O:CH_3CN followed by filtration and rotary evaporation. The residue was dissolved in anhyd acetone (50 mL), and LiCl (340 mg, 8 mmol) was added. The reaction mixture was stirred at 25 °C for 30 min and was then filtered though silica gel and evaporated to give 348 mg (50%) of yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 7.3 Hz, 2 H), 7.31 (m, 1 H), 7.25 (m, 2 H), 5.64 (app t, J = 10.7 Hz, 1 H), 4.41 (d, J = 10.7 Hz, 1 H), 3.94 (m, 1 H), 1.29 (d, J = 6.2 Hz, 3 H).

Bis(μ-chloro)bis[(1,2,3-η)-cyclohexenyl]dipalladium. By the above procedure, 2-cyclohexen-1-ol gave a 20% yield: ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.48 (app t, J = 6.0 Hz, 1 H), 5.18 (app t, J = 6.0 Hz, 2 H), 1.90−1.68 (br m, 4 H), 1.11−1.00 (br m, 2 H).

Bis(μ-chloro)bis[(1,2,3-η)-1,3-diphenyl-2-propenyl]dipalladium. By the above procedure, 1,3-diphenyl-2-propen-1-ol gave a 60% yield as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.26 (br m, 10 H), 4.67 (br s, 1 H), 4.15 (br s, 2 H).

{2-[(1-Methoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-8-yl)]-1,10-phenanthroline}[(1,2,3-η)-propenyl]palladium(II) Tetrafluoroborate (31). (1,2,3-η)-Propenylpalladium[58] chloride dimer (0.006 g, 0.026 mmol) in CH_2Cl_2 (0.5 mL) was added to a suspension of $AgBF_4$ (0.0062 g, 0.032 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C. After 20 min, *rac*-**2** (0.012 g, 0.032 mmol) in CH_2Cl_2 (0.5 mL) was added. After 30 min at 25 °C, the mixture was passed through a cotton plug and magnesium sulfate. Evaporation gave 0.014 g (68%) of off-white solid whose ^{1}H NMR spectrum showed a 1:1 mixture of diastereomers. Recrystallization from CH_2Cl_2/hexane gave **31** as colorless prisms: mp > 230 °C; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.15 (dd, J = 5.0, 1.5 Hz, 1 H, H_{P9}), 8.72 (dd, J = 8.3, 1.4 Hz, 1 H, H_{P7}), 8.5 (app. t, J = 8.2 Hz, 1 H, H_{P4}), 8.2−8.0 (two d, J = 8.8 Hz, 2 H, H_{P5} and H_{P6}), 8.0−7.9 (m, 2 H, H_{P8} and H_{P3}), 7.5−7.0 (m, 3 H, Ar-*H*), 5.62 (m, 1 H, central allylic H, one diastereomer), 5.49 (m, 1 H, central allylic H, other diastereomer), 4.3 (bd, J = 7.0 Hz, 2 H, H_{syn}), 3.55 (d, J = 12.1 Hz, 2 H, H_{anti}, one diastereomer), 3.45 (d, J = 12.3 Hz, 2 H, H_{anti}, other diastereomer), 3.15 (m, 1 H, bridgehead H), 2.78 (s, 3 H, C*H*$_3$O, one diastereomer), 2.62 (s, 3 H, C*H*$_3$O, other diastereomer), 2.3−1.75 (m, 4 H, $CH_3OC(CH_2)_2$), 1.75−1.2 (m, 4 H, $CH_3OC(CH_2CH_2)_2$); IR (CH_2Cl_2) 3060 (ArH), 2900 (CH), 1420 (C=C allylic), 1250 (C-O-C), 1050 (C=C allylic), 900 (CH Ar) cm^{-1}. HRMS (FAB)*m/e* calcd for the cation $C_{28}H_{27}N_2OPd$ 513.1169, found 513.1167.

X-ray Structure Determination of {2-[(Methoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-8-yl)]-1,10-phenanthroline}[(1,2,3-η)-propenyl]palladium(II) Tetrafluoroborate (31A). The structure shown in Figure 16 was solved by standard methods.[59−63] Full details and tables of data are available as supporting information.

Synthesis of Complexes with Other Phenanthroline Ligands. General Procedure. $AgBF_4$(s) or $AgPF_6$(s) (0.06 mmol) was added to $[(allyl)PdCl]_2$ (0.06 mmol) in CH_2Cl_2 (3 mL) at 0 °C. After 20 min, the substituted phenanthroline (0.06 mmol) was added. After 5 min at 20 °C, the mixture was filtered through cotton and Celite. The solvent was evaporated, and the product was recrystallized twice from CH_2Cl_2/hexane.

NMR Determination of Diastereomeric Ratios. Equilibrium between the diastereomers of the complexes was ensured by ^{1}H NMR integration of the isomers at regular intervals (ca. 2 days) and by adding a catalytic amount of CF_3CO_2H 24 h before the last measurement. The ratios were independent of the use of the BF_4^- or PF_6^- counterions.

{2-[(1*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl]-1,10-phenanthroline}[1,1-diphenyl-(1,2,3-η)-2-propenyl]palladium Tetrafluoroborate. Obtained as a 2:1 mixture of diastereomers. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (dd, J = 8.0 Hz, J = 1.4 Hz, 1 H, H_{P9}), 8.46 (d, J = 8.6 Hz, 1 H, H_{P4}), 7.95 (d, J = 9.0 Hz, 1 H, $H_{P5\ or\ 6}$), 7.91 (d, J = 8.8 Hz, 1 H, $H_{P5\ or\ 6}$), 7.79 (d, J = 8.6 Hz, 1 H, H_{P3}), 7.53 (d, J = 8.0 Hz, 1 H, H_{P8}), 6.48 (d, J = 3.2 Hz, 1 H), 6.05 (dd, $J_{2,1a}$ = 12.7 Hz, $J_{2,1s}$ = 7.6 Hz, 1 H, H_2), 4.47 (d, 1 H, H_{1s}), 3.48 (d, 1 H, H_{1a}), 2.36 (t, J = 3.4 Hz, 1 H), 1.90 (m, 1 H), 1.58 (m, 1 H). Minor isomer: 8.55 (dd, J = 7.9 Hz, J = 1.5 Hz, 1 H, H_{P9}), 8.46 (d, J = 8.6 Hz, 1 H, H_{P4}), 7.96 (d, J = 8.8 Hz, 1 $H_{P5\ or\ 6}$), 7.93 (d, J = 8.7 Hz, $H_{P5\ or\ 6}$), 7.79 (d, J = 8.6 Hz, H_{P3}), 7.54 (d, J = 7.9 Hz, 1 H, H_P), 6.65 (d, J = 3.3 Hz, 1 H), 6.22 (dd, $J_{2,1a}$ = 12.7 Hz, $J_{2,1s}$ = 7.6 Hz, 1 H, H_2), 3.54 (d, 1 H, H_{1a}), 2.53 (t, J = 3.5 Hz, 1 H), 1.79 (m, 1 H), 1.43 (m, 1 H). Unassigned signals: 7.51−7.45 (br m), 7.38−7.24 (br m), 7.16 (t, J = 7.8 Hz), 7.08 (m), 3.62 (d, J = 5.9 Hz), 2.04 (m), 1.11 (m), 0.90−0.70 (br m).

{2-[(1*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-en-2-yl]-1,10-phenanthroline}[1,1-dimethyl-(1,2,3-η)-2-propenyl]palladium Tetrafluoroborate. Obtained as a 1:1 mixture of diastereomers. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (dd, $J_{P9,8}$ = 5.0 Hz, 1 H, $J_{P9,7}$ = 1.4 Hz, H_{P9}), 8.68 (dd, $J_{P7,8}$ = 8.3 Hz, 1 H, H_{P7}), 8.55 (d, $J_{P4,3}$ = 8.6 Hz, 1 H, H_{P4}), 8.19 (dd, 1 H, H_{P8}), 8.02 (br s, 2 H, $H_{P5,6}$), 7.87 (d, 1 H, H_{P3}), 6.93 (d, J = 3.3 Hz, 1 H), 5.26 (dd, $J_{2,1a}$ = 13.0 Hz, $J_{2,1s}$ = 7.6 Hz, 1 H, H_2), 4.19 (dd, $J_{1s,2}$ = 7.6 Hz, $J_{1s,1a}$ = 1.1 Hz, 1 H, H_{1s}), 3.46 (dd, 1 H, H_{1a}), 2.75 (t, J = 3.3 Hz, 1 H). Minor isomer: 9.08 (dd, $J_{P9,8}$ = 5.0 Hz, $J_{P9,7}$ = 1.4 Hz, 1 H, H_{P9}), 8.71 (dd, $J_{P7,8}$ = 8.2, 1 H, H_{P7}), 8.56 (d, $J_{P4,3}$ =8.5 Hz, 1 H, H_{P4}), 8.18 (dd, 1 H, H_{P8}), 8.04 (br s, 2 H, $H_{P5,6}$), 7.86 (d, J = 8.5 Hz, 1 H, H_{P3}), 6.86 (d, J = 3.4 Hz, 1 H), 5.47 (dd, $J_{2,1a}$ = 13.4 Hz, $J_{2,1s}$ = 7.7 Hz, 1 H, H_2), 4.32 (dd, $J_{1s,1a}$ = 1.0 Hz, 1 H, H_{1s}), 3.46 (dd, 1 H, H_{1a}), 2.75 (t, J = 3.4 Hz, 1 H). Unassigned signals: 2.13 (m), 1.85 (m), 1.82 (s), 1.74 (s), 1.53 (m), 1.50 (s), 1.42 (m), 1.27 (s), 1.26 (s), 1.24 (s), 1.17 (s), 1.06 (s), 1.03 (s), 0.94 (d, J = 5.1 Hz), 0.87 (m).

{2-[(1*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl]-1,10-phenanthroline}[1,1-dimethyl-(1,2,3-η)-2-propenyl]palladium Hexafluorophosphate. Obtained as a 2:1 mixture of diastereomers. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (d, $J_{P9,8}$ = 4.3 Hz, 1 H, H_{P9}), 8.64 (d, $J_{P7,8}$ = 8.2 Hz, 1 H, H_{P7}), 8.56 (d, $J_{P4,3}$ = 8.5 Hz, 1 H, H_{P4}), 8.10 (dd, 1 H, H_{P8}), 7.98 (m, 2 H, $H_{P5,6}$), 7.65 (d, 1 H, H_{P3}), 5.23 (dd, $J_{2,1a}$ = 12.9 Hz, $J_{2,1s}$ = 7.6 Hz, 1 H, H_2), 4.06 (dd, 1 H, $J_{1s,1a}$ = 1.0 Hz, H_{1a}), 3.36 (dd, 1 H, H_{1s}). Minor isomer: 9.00 (d, $J_{P9,8}$ = 4.4 Hz, 1 H, H_{P9}), 8.66 (d, $J_{P7,8}$ = 8.4 Hz, 1 H, H_{P7}), 8.57 (d, $J_{P4,3}$ = 8.5 Hz, 1 H, H_{P4}), 8.10 (dd, 1 H, H_{P8}), 7.99 (m, 2 H, $H_{P5,6}$), 7.67 (d, 1 H, H_{P3}), 5.58 (dd, $J_{2,1a}$ = 13.3 Hz, $J_{2,1s}$ = 7.6 Hz, 1 H, H_2), 4.36 (d, 1 H, H_{1a}), 3.62 (d, 1 H, H_{1s}). Unassigned signals: ^{1}H NMR(400 MHz, $CDCl_3$): δ 2.97 (m), 2.72 (m), 2.61 (m), 2.30 (s), 1.83 (m), 1.71 (s), 1.61 (s), 1.59 (s), 1.56 (s), 1.51 (s), 1.29−1.12 (br m), 0.90 (m).

{2-[(1*R*)-2-*endo*-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl]-1,10-phenanthroline}[1,1-dimethyl-(1,2,3-η)-2-propenyl]palladium Hexafluorophosphate. Obtained as a 3:1 mixture of diastereomers. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (d, $J_{P9,8}$ = 4.0 Hz, 1 H, H_{P9}), 8.65 (d, $J_{P4,3}$ = 8.2 Hz, 1 H, H_{P4}), 8.64 (d, $J_{P7,8}$ = 8.5 Hz, 1 H, H_{P7}), 8.11 (dd, 1 H, H_{P8}), 8.06 (d, $J_{P5,6}$ = 8.8 Hz, 1 H), 8.01 (d, 1 H, H_{P3}), 8.00 (d, 1 H), 5.32 (dd, $J_{2,1a}$ = 12.7 Hz, $J_{2,1s}$ = 7.6 Hz, 1 H, H_2), 4.13 (d, 1 H, H_{1a}), 3.47 (d, 1 H, H_{1s}). Minor isomer: 9.03 (d, J = 5.5 Hz, 1 H, H_P), 8.70 (d, J = 8.2 Hz, 1 H, H_P), 8.17 (d, J = 5.5 Hz, 1 H, H_P), 8.03 (d, J = 8.2 Hz, 1 H, H_P), 5.55 (dd, $J_{2,1a}$ = 13.4 Hz, $J_{2,1s}$ = 7.7 Hz, 1 H, H_2), 4.54 (d, 1 H, H_{1a}), 3.61 (d, 1 H, H_{1s}). Unassigned signals: 8.58 (m), 5.09 (m), 3.80 (m), 2.49 (m), 2.00−1.89 (br m), 1.85−1.78 (br m), 1.72 (s), 1.58 (s), 1.56−1.47 (br m), 1.46−0.68 (br m).

{2-[(1*R*)-2-*endo*-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl]-1,10-phenanthroline}[1,1-diphenyl-(1,2,3-η)-2-propenyl]palladium Hexafluorophosphate. Obtained as an 11:1 mixture of diastereomers. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, $J_{P4,3}$ = 8.8 Hz, 1 H, H_{P4}), 8.62 (dd, $J_{P9,8}$ = 8.2 Hz, $J_{P9,7}$ = 1.4 Hz, 1 H, H_{P9}), 8.03 (m, 2 H, $H_{P5,6}$), 7.98 (d, 1 H, H_{P3}), 6.22 (dd, $J_{2,1a}$ = 12.4 Hz, $J_{2,1s}$ = 7.5 Hz, 1 H H_2), 4.38 (d, 1 H, H_{1s}), 3.64 (d, 1 H, H_{1a}). Minor isomer: 6.40 (dd, $J_{2,1a}$ = 13.4 Hz, $J_{2,1s}$ = 7.6 Hz, 1 H H_2), 4.95 (d, 1 H, H_{1s}), 3.74 (d, 1 H, H_{1a}). Unassigned signals: 7.59−7.51 (m), 7.50−7.46 (m), 7.42 (m), 7.36 (m), 2.40 (m), 2.10 (m), 1.76 (m), 1.45 (m), 1.25 (s), 1.12 (m), 1.01 (s), 0.95 (m), 0.87 (s), 0.83 (s), 0.27 (s), 0.07 (s).

{2-[(1*R*)-2-*endo*-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl]-1,10-phenanthroline}[(1,2,3-η)-2-cyclohexenyl]palladium Hexafluorophosphate. Obtained as a 4:1 mixture of diastereomers. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.39 (dd, J_1 = 4.9 Hz, J_2 = 1.3 Hz, 1 H, H_P), 8.65 (app. t, J = 8.3 Hz, 2 H, H_P), 8.10 (d, J = 5.0 Hz, 1 H, H_P), 8.08 (d, J = 5.0 Hz, 1 H, H_P), 8.03 (d, J = 8.8 Hz, 1 H, H_P), 8.02 (d, J = 8.8 Hz, 1 H, H_P), 6.04 (t, J = 6.7 Hz, 1 H, H_2), 5.75 (quintet, J_1 = 11.5 Hz, J_2 = 6.2 Hz, 2 H, $H_{1,3}$), 4.00 (dd, J_1 = 11.4 Hz, J_2 = 3.4 Hz, 1 H, H_T), 2.55 (m, 1 H, H_T), 1.23 (s, 3 H, Me), 1.02 (s,

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3 H, Me), 0.78 (s, 3 H, Me). Minor isomer: 9.32 (d, $J = 4.5$ Hz, 1 H, H_P), 8.58 (m, 2 H, H_P), 5.90 (d, $J = 6.8$ Hz, 1 H, H_2), 5.54 (m, 2 H, $H_{1,3}$), 3.87 (m, H_T). Unassigned signals: 2.15 (m), 1.70 (m), 1.58 (m), 1.28 (m), 0.83 (m).

{2-[(1*R*)-2-*endo*-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl]-1,10-phenanthroline}[1-phenyl-3-methyl-(1,2,3-η)-2-propenyl]palladium Hexafluorophosphate. Obtained as a 5:2:1 mixture of diastereomers. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, $J =$ 8.5 Hz, 1 H, H_P), 8.05 (m, 2 H, H_P), 7.95 (d, $J = 8.8$ Hz, 1 H, H_P), 6.02 (t, $J = 11.3$ Hz, 1 H, H_2), 5.23 (d, $J = 12.5$ Hz, 1 H, H_1), 4.23 (m, 1 H, H_3), 3.73 (dd, $J_1 = 10.9$ Hz, $J_2 = 3.3$ Hz, 2 H, H_T), 2.51 (m, 1 H, H_T), 1.55 (s, 3 H, Me_T), 1.21 (s, 3 H, Me_T), 1.02 (s, 3 H, Me_T). Minor isomer: 8.47 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.3$ Hz, 1 H, H_P), 5.60 (t, $J = 7.7$ Hz, 1 H, H_2), 4.67 (m, 2 H, $H_{1,3}$), 3.23 (m, 1 H, H_T). Minor isomer: 5.60 (dd, $J_{2,1} = 12.8$ Hz, $J_{2,3} = 9.2$ Hz, 1 H, H_2), 5.20 (d, $J =$ 12.8 Hz, 1 H, H_1), 4.35 (m, 1 H, H_3), 3.85 (m, 1 H, H_T). Unassigned signals: 8.56 (m), 7.17−7.89 (br m), 6.95 (d), 2.05 (t), 1.95 (d), 1.92 (d), 0.95−1.25 (br m).

{2-[(1*R*)-2-*endo*-1,7,7-Trimethylbicyclo[2.2.1]hept-2-yl]-1,10-phenanthroline}[1,3-diphenyl-(1,2,3-η)-2-propenyl]palladium Hexafluorophosphate. Obtained as a 4:1 mixture of diastereomers. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (d, $J = 3.2$ Hz, 2 H, H_P), 8.63 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.4$ Hz, 2 H, H_P), 8.55 (d, $J = 8.4$ Hz, 2 H, H_P), 7.92 (dd, $J_1 = 8.1$ Hz, $J_2 = 4.5$ Hz, 2 H, Ph), 6.12 (t, $J =$ 10.8 Hz, 1 H, H_2), 5.23 (d, $J = 12.1$ Hz, 1 H, H_1), 5.01 (d, $J = 10.6$ Hz, 1 H, H_3), 3.25 (m, 1 H, H_T), 2.94 (m, 3 H, H_T), 1.14 (s, 3 H, Me_T), 0.98 (s, 3 H, Me_T), 0.92 (s, 3 H, Me_T). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, $J = 8.5$, 2 H, H_P), 6.23 (t, $J = 11.9$ Hz, 1 H, H_2), 5.37 (d, 1 H, H_1), 5.08 (d, $J = 10.4$ Hz, 1 H, H_3), 3.50 (m, 1 H, H_T), 3.03 (t, $J = 8.0$ Hz, 2 H, H_T). Unassigned signals: ^{1}H NMR(400 MHz, $CDCl_3$): δ 7.20−8.10 (m), 1.20−1.85 (m), 0.52 (s), 0.04 (s).

General Procedure for Allylations. The allylic acetate (0.10 mmol) was added to the ligand (typically 0.005 mmol), Pd(0) complex (0.001 mmol in Pd), and THF (5.0 mL) at 25 °C. After 15 min, the suspension from reaction of the dialkyl malonate (0.15 mmol) and NaH (0.17 mmol) in THF (5.0 mL), or alternatively, the malonate (0.15 mmol), *N*,*N*-bis(trimethylsilyl) acetamide (BSA, 0.15 mmol), anhydrous KOAc (0.01 mmol) and, in some cases, 18-crown-6 (0.01 mmol) were added at 0 °C. The mixture was stirred at 25 °C and monitored by GC or TLC. After completion, satd aq NH_4Cl was added, the ether extracts were dried and concentrated, and the product was purified by MPLC (silica gel, ether/pentane gradient). The % ee was determined by ^{1}H NMR using 8−10% tris[3-heptafluoropropyl)hydroxymethylene]-(+)-camphorato]europium [Eu(hfc)$_3$] in $CDCl_3$.[33] Absolute configurations were not assigned unless otherwise indicated.

Reaction of *rac*-(*E*)-2-Acetoxy-3-pentene with Dimethyl Malonate. Ligand **13** (0.0056 g, 0.018 mmol), [(MeCHCHCHMe)Pd(O_2CCF_3)]$_2$[56] (0.0026 g, 0.005 mmol), *rac*-(*E*)-2-acetoxy-3-pentene (0.1 g, 0.9 mmol), dimethyl malonate (0.17 g, 1.3 mmol), and NaH (0.035 g, 1.4 mmol) in THF (10 mL) gave 0.13 g (71% yield) of colorless oil: ^{1}H NMR (300 MHz) δ 5.56 (ddq, $J = 15.2$, 6.2, 0.8 Hz, CH_3CH═H), 5.34 (ddq, $J = 15.2$, 8.1, 1.4 Hz, CH_3CH═C*H*), 3.70 and 3.65 (two s, (CH_3OC(═O))$_2$C), 3.25 (d, $J = 9.1$ Hz, (CH_3OC(═O))$_2$C*H*), 2.9 (m, CH═CHC*H*), 1.63 (dd, $J = 6.4$, 1.5 Hz, CH_3-CH═CH), 1.06 (d, $J = 6.8$ Hz, CH═CHCHCH_3). With Eu(hfc)$_3$, the signal at 1.06 ppm was split into two doublets (24% ee).

Reaction of *rac*-1-Acetoxy-2-cyclohexene with Diethyl Methylmalonate. **13** (0.0090 g, 0.028 mmol), [(MeCHCHCHMe)Pd(O_2CCF_3)]$_2$[56] (0.004 g, 0.007 mmol), *rac*-1-acetoxy-2-cyclohexene (0.20 g, 1.4 mmol), diethyl methylmalonate (0.36 g, 2.1 mmol), and NaH (0.054 g, 2.2 mmol) in THF (10 mL) gave 0.28 g (80% yield) of colorless oil: ^{1}H NMR (300 MHz) δ 5.75 (m, C*H*═CH), 5.5 (m, CH═C*H*), 4.2 (m, 2 CH_3CH_2), 3.05 (m, CH═CHC*H*), 2.0−1.4 (m, −(CH_2)$_3$−), 1.32 (s, CH_3C), 1.24 (two overlapping t, $J = 8.0$ Hz, 2CH_3-CH_2). With Eu(hfc)$_3$, the signal at 1.32 ppm was split into two singlets (55% ee).

Reaction of *rac*-(*E*)-1-Acetoxy-1,3-diphenyl-2-propene with Dimethyl Malonate. **13** (0.0025 g, 0.008 mmol), [(MeCHCHCHMe)-Pd(O_2CCF_3)]$_2$[56] (0.0023 g, 0.0004 mmol), *rac*-(*E*)-1-acetoxy-1,3-diphenyl-2-propene (0.1 g, 0.4 mmol), dimethyl malonate (0.078 g, 0.6 mmol), and NaH (0.0015 g, 0.6 mmol) in THF (10 mL) (or use of BSA as in the alternative procedure) gave 0.1 g (80% yield) of colorless oil: $[\alpha]^{25}_D$ +14.6° (*c* 0.01, $CHCl_3$) [lit.[26] calcd for the (*S*)-enantiomer of 100% ee, $[\alpha]^{25}_D$ −22.4° (*c* 1.80, $CHCl_3$)]; ^{1}H NMR (300 MHz) δ 6.5 (d, $J = 15.7$ Hz, PhC*H*═CH), 6.3 (dd, $J = 15.7$, 8.6 Hz, PhCH═C*H*), 4.25 (dd, $J = 11.0$, 8.8 Hz, PhCH═CHC*H*), 3.95 (d, $J =$ 11.0 Hz, (CH_3OC(C═O))$_2$C*H*), 3.7 and 3.52 (two s, 2 CH_3O(C═O)). With Eu(hfc)$_3$, the signal at 3.7 ppm was split into two singlets (80% ee with the NaH procedure; up to 92% ee with the BSA procedure). The absolute configuration was assigned as *R* by comparing the sign of its optical rotation with that of known product.[26]

Reaction of *rac*-(*E*)-2-Acetoxy-4-phenyl-3-butene with Dimethyl Malonate. **13** (0.010 g, 0.03 mmol), [(MeCHCHCHMe)Pd(O_2CCF_3)]$_2$[56] (0.009 g, 0.016 mmol), *rac*-(*E*)-2-acetoxy-4-phenyl-3-butene (0.30 g, 1.6 mmol), dimethyl malonate (0.30 g, 2.4 mmol), and NaH (0.062 g, 2.6 mmol) in THF (10 mL) gave 0.31 g (75%) of colorless oil: ^{1}H NMR showed an 80:20 inseparable mixture of **A** from attack at C-2 (33% ee) and **B** from attack at C-4 (95% ee with NaH; up to 96% using the BSA procedure), respectively: ^{1}H NMR (300 MHz) δ (**A**) 7.5−7.0 (m, 5 H, Ar*H*), 6.48 (d, $J = 15.0$ Hz, PhC*H*═CH), 6.2 (dd, $J =$ 15.1, 9.0 Hz, PhCH═C*H*), 3.75 and 3.67 (two s, 2 CH_3OC(═O)), 3.4 (d, $J = 9.0$ Hz, (CH_3OC(═O))$_2$C*H*), 3.1 (m, PhCH═CHC*H*), 1.2 (d, $J = 6.8$ Hz, CH_3CH); δ (**B**) 7.5−7.0 (m, 5 H, Ar*H*), 5.7−5.4 (m, C*H*═C*H*), 4.1 (m, PhC*H*), 3.8 (d, $J = 11.0$ Hz, (CH_3OC(═O))$_2$C*H*), 3.73 and 3.48 (two s, 2 CH_3OC(═O)), 1.63 (bd, $J = 4.5$ Hz, CH_3-CH═CH) (lit.[5k] ^{1}H NMR). With Eu(hfc)$_3$, the signal of **A** at 1.2 ppm was split into two doublets, and the signal of **B** at 1.63 ppm was split into two doublets.

Computational Details. Energy minimizations were performed using the MacMimic/MM2(91) package,[9] augmented by a parameter set for (η^3-allyl)palladium complexes.[4a,c] Calculations were done on a Macintosh Quadra 800. Analysis of structures and drawings in wire frame format were performed with MacMimic.

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Supporting Information Available: Full details of the crystal structure determination for **31A** and five tables of crystal data and intensity data collection parameters, interatomic distances, interatomic angles, torsional angles, fractional triclinic coordinates, and isotropic displacement parameters for the non-hydrogen atoms of **31A** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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