Tetrahedron: Asymmetry Vol. 2, No. 7, pp. 569-592, 1991
Printed in Great Britain

0957-4166/91 $3.00+.00
Pergamon Press plc

New Chiral Phospholanes; Synthesis, Characterization, and Use in Asymmetric Hydrogenation Reactions

Mark J. Burk*, John E. Feaster, and Richard L. Harlow

Contribution No. 5883; Central Research & Development Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, DE 19880-0328

(*Received* 29 *April* 1991)

Abstract: We describe the practical synthesis of enantiomerically pure *trans*-2,5-disubstituted-1-phenylphospholanes which are then employed in the preparation of a new series of C_2-symmetric bis- and C_3-symmetric tris(phospholane) ligands. A versatile three-step route to the important chiral 1,4-diol intermediates, used in the phosphine syntheses, is outlined. Rhodium complexes bearing the new phosphine ligands were prepared and shown to act as efficient catalyst precursors for the enantioselective hydrogenation of various unsaturated substrates.

Introduction

Asymmetric catalysis has been and remains a primary goal of modern organic and organometallic chemistry. The great interest in asymmetric catalysis largely stems from the capacity to generate a very large amount of enantiomerically-enriched material from a small amount of a chiral catalyst. This catalytic approach is by far the most efficient use of chirality transfer. Many useful transition metal-based catalytic reactions are known.[1] Crucial to the development of practical asymmetric versions of these catalytic reactions is the design and synthesis of new chiral ligands which coordinate to transition metals.

Literally hundreds of chiral phosphines have been described in the literature.[2] The great utility of many of these phosphines as ligands in asymmetric catalysis has been amply demonstrated.[2a,3] In several instances, enantiomeric excesses (*ee*'s) approaching 100% have been observed. Despite these successes, our understanding of the requirements necessary for the generation of efficient catalysts which provide high *ee*'s remains rather limited. Valuable information can be gleaned from some of the more successful chiral phosphines which, in general, are rigid chelating (bidentate) ligands possessing a C_2 symmetry axis. In certain instances, like the useful series of ferrocenyl phosphine ligands,[4] the introduction of heteroatom-containing substituents into the ligand backbone has been shown to be a key element for the attainment of high ee's. Also, most of the successful chiral phosphines bear at least two aryl substituents on the

phosphorus center, and the chirality usually exists within the bridging backbone of a diphosphine ligand or at the phosphorus atoms. The mechanism of chirality transfer using many of these phosphines has been associated with a manifestation of the backbone chirality (and thus conformation) in the proper orientation of the phenyl substituents on phosphorus.[3] As a result, there is the common belief that phenyl groups on phosphorus are an indispensible feature of new ligand design and the realization of high enantioselectivities.

Our research has been directed toward the design and synthesis of new types of chiral phosphine ligands which may be used in asymmetric catalysis.[5] The electronic properties of phosphine ligands are known to dramatically influence the reactivity and selectivity of transition metal centers.[1] The phenyl substituents present in most chiral phosphines render the phosphorus atoms, and thus the attached metal centers, relatively electron-poor. Our first objective was to prepare new electron-rich (peralkyl) chiral phosphines.[5a] To date, the use of electron-rich chiral phosphines remains relatively unexplored,[6] and for transition metal phosphine complexes, high enantioselectivity in catalytic reactions has been limited mainly to chiral phosphines which bear phenyl substituents.

Secondly, ligand chelation is believed to play an important role in stereochemical control by restricting the number of competing asymmetric conformations surrounding the metal center. Most known chiral chelating phosphines are bidentate ligands where the backbone enforces a *cis*-relationship between the phosphorus centers on the metal. We sought to design chiral polydentate (three or more potential binding groups) phosphines which could enforce a *trans*-relationship between the phosphorus moieties, thereby enveloping the metal center with an asymmetric environment.

Finally, the use of chiral polydentate phosphine ligands in transition metal-based asymmetric catalysis has received little attention. While much research has been devoted to chiral ligands possessing a C_2 symmetry axis, chiral ligands possessing higher symmetry elements have been largely ignored.[7] The proper introduction of chirality into polydentate ligands should provide novel systems with high order symmetry. Along these lines, our third goal was the preparation and study of new chiral C_3-symmetric tripodal phosphine ligands.[5b]

Herein we report the preparation and characterization of a series of new electron-rich chiral phosphines. A practical synthesis of enantiomerically pure *trans*-2,5-disubstituted-1-phenylphospholanes, and their use in the preparation of various C_2-symmetric bis- and C_3-symmetric tris(phospholane) ligands will be outlined. A versatile three-step route to the important chiral 1,4-diol intermediates, used in the phospholane syntheses, will be detailed. Rhodium complexes bearing several of the new phosphine ligands were characterized by X-ray crystallography. The use of these new ligands in rhodium-catalyzed enantioselective hydrogenation reactions will be described.

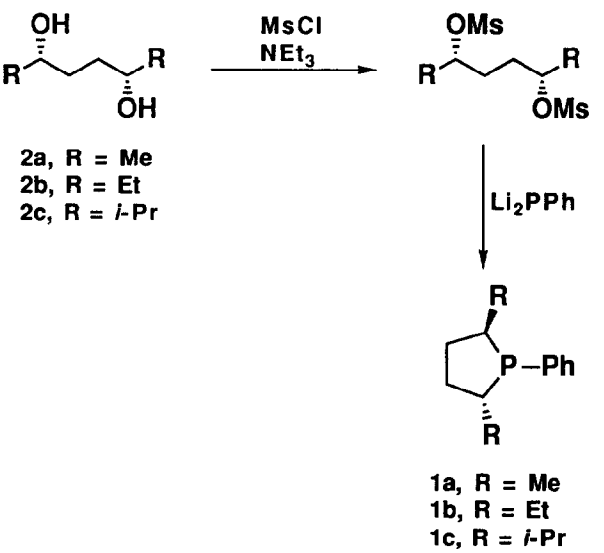
Results

I. Phosphine Syntheses

Phenylphospholanes. Our initial efforts were directed toward the development of an efficient route to the enantiomerically pure phenylphospholanes **1**. Such chiral *trans*-2,5-disubstituted phospholanes are analogous to a variety of known C_2-symmetric heterocycles which are well-documented to be good sources of asymmetric induction.[8] In contrast to chiral acyclic and phenyl-containing phosphines, the chirality in **1** exists in a rigid five-membered ring which should restrict the conformational mobility of this system.

Our original procedure[5a] for the preparation of (2*R*,5*R*)-2,5-dimethyl-1-phenylphospholane (*R*,*R*)-**1a** involved the known[9] enzymatic reduction of 2,5-hexanedione which provided the key intermediate (2*S*,5*S*)-2,5-hexanediol (*S*,*S*)-**2a**. Subsequent transformation of (*S*,*S*)-**2a** to the corresponding bis(mesylate),[10] followed by reaction with Li_2PPh·THF, led to closure of the ring and afforded the desired phosphine (*R*,*R*)-**1a** in 83% isolated yield (Scheme I).

Scheme I



2a, R = Me
2b, R = Et
2c, R = *i*-Pr

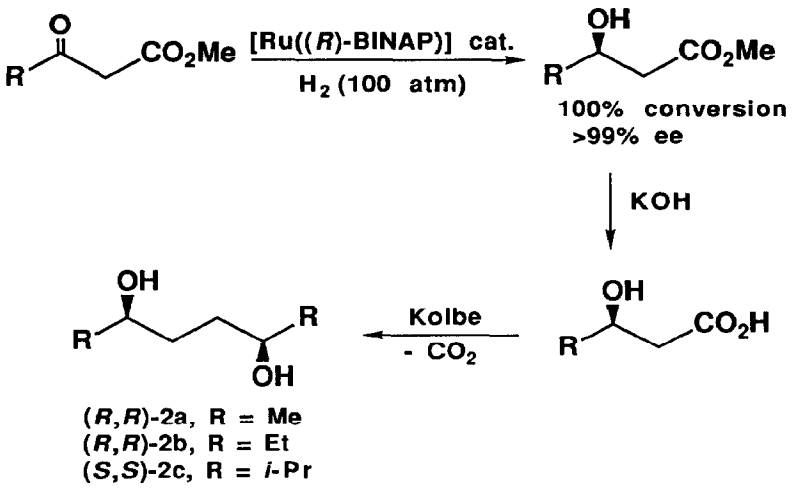
1a, R = Me
1b, R = Et
1c, R = *i*-Pr

By this route, 10-20 g of (*R*,*R*)-**1a** could be prepared in a reasonable timeframe. The major limitation of this synthesis, however, is the step involving baker's yeast reduction. In addition to the low overall product yields, long reaction times (3-7 days), and tedious isolation procedures which are often associated with enzymatic reductions,[11] we also were limited to the production of only one enantiomer of the important diol intermediate **2a**, and the synthesis could not be extended to derivatives containing other substituents on the phospholane ring. The development of a general

route to chiral phospholanes of type **1** required an alternative procedure for the preparation of the valuable chiral 1,4-diol intermediates **2**.

Chiral 1,4-diols. We have devised a versatile three-step synthesis of the chiral 1,4-diols **2** (Scheme II).

Scheme II



The first step of the process involves asymmetric catalysis and currently is based on the Ru(BINAP) catalyst system developed by Noyori and coworkers[12] for the reduction of β-keto esters to the corresponding β-hydroxy esters. It is this step that introduces the required chirality. As reported, for the cases studied thus far, we have observed excellent conversion to β-hydroxy esters with extremely high enantiomeric excesses (>99% ee). Hydrolysis of the esters to the corresponding β-hydroxy acids was readily accomplished with aqueous KOH. The obtained chiral β-hydroxy carboxylic acids then were directly subjected to an electrochemical Kolbe-coupling procedure[13] which provided the desired enantiomerically pure 1,4-diols **2** (R = Me, Et, *i*-Pr) as crystalline solids in reasonable overall yield (40-50%). The procedure outlined in Scheme II demonstrates the use of the ruthenium catalyst containing the diphosphine (*R*)-(+)-BINAP. Consistent with the expected β-hydroxy ester absolute configurations,[12] the 1,4-diols (*R,R*)-**2a** (R = Me), (*R,R*)-**2b** (R = Et), and (*S,S*)-**2c** (R = *i*-Pr) were obtained; the opposite diol enantiomers were obtained when (*S*)-(-)-BINAP was used in the hydrogenation step. This method utilizes commercially available materials and provides a practical, efficient route to relatively large quantities of either 1,4-diol antipode. The only apparent limitations of the current process are associated with the efficiency and enantioselectivity of the first step involving the Ru(BINAP) catalysts. Since many β-keto ester substrates are known to be reduced in high enantiomeric purity,[12] wide application of this method for the synthesis of enantiomerically pure 1,4-diols may be expected. Ultimately, we would like to

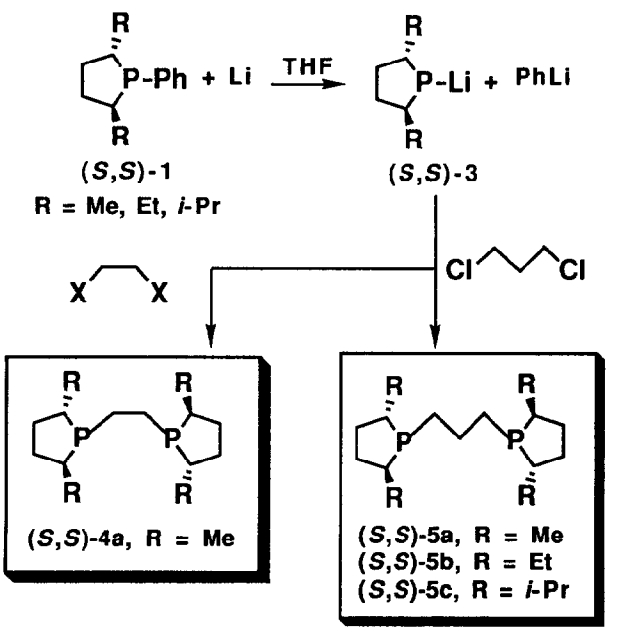
generate a phospholane-based catalyst for this reduction, effectively leading to self-generation (breeder cycle)[14] of our own phosphines.

The ready availablity of enantiomerically pure 1,4-diols **2a-c** provided access to the series of corresponding homochiral *trans*-2,5-disubstituted phenylphospholanes **1a-c** (Scheme I). No epimerization or racemization was observed during the preparation of the phospholanes **1**, and each new phosphine was ascertained to be optically pure (within the limits of detection) by reacting each with (R)-[(dimethyl-(α-methylbenzyl)-aminato-C,N]palladium(II) chloride dimer[15] and monitoring the ^{31}P NMR spectrum which in all cases showed the presence of a single complex. Comparisons were made with the spectrum of the opposite phosphine enantiomer.

C_2-Symmetric Bis(phospholanes). While the phenylphospholanes **1** were desirable in their own right, we were very interested in using just the phospholane moiety of **1** for the synthesis of other potentially more useful chelating derivatives. The employment of the phospholane core in this capacity critically relied on our ability to selectively cleave the P-phenyl bond of **1** without stereoisomerization. While P-Ph cleavage with lithium metal is well-known, dialkylphenylphosphines have been shown to undergo cleavage of both the phenyl as well as the alkyl groups under similar conditions.[16] Cleavage of the alkyl ring in **1**, even transiently, probably would lead to epimerization or ultimately racemization of the phospholane moiety.

We were pleased to discover that reaction of phospholane (*S,S*)-**1a** with clean lithium metal in THF produced a mixture of the lithium phosphide (*S,S*)-**3a** and phenyllithium (Scheme III).

Scheme III



It is notable that the use of lithium metal which did not have the usual gray (presumably oxide or hydroxide) coating removed manually from the surface resulted in the epimerization of **1a**, leading eventually to substantial quantities (40-50%) of *meso*-phosphide product. It currenly is unclear what role the lithium oxide/hydroxide coating plays in this process.

Given the expected high nucleophilicity of lithium phosphide **3a** and the relatively low nucleophilicity of PhLi, especially in C-C bond forming reactions, we have found that reaction of the cleavage mixture directly with 1,2-dichloroethane or ethylene glycol di-*p*-tosylate (0.5 equiv.) provided the C_2-symmetric bis(phospholane) (*S,S*)-**4a** in moderate isolated yield. The PhLi remaining after the coupling reaction subsequently was reacted with methanol. The opposite enantiomer, (*R,R*)-**4a**, was analogously prepared from (*R,R*)-**1a**. The low isolated yield of pure **4a** is due to the competitive formation of substantial quantities (30-40%) of the P-P bonded diphospholane dimer which must be separated from **4a** by careful fractional distillation. Reactions involving electron-rich dialkylphosphides and 1,2-bis(electrophiles) are known to be particularly prone to electron transfer or metal-halogen exchange pathways which result in P-P dimer formation.[6,16a,17] While the ethyl derivative **4b** was formed in the analogous reaction between **3b** and 1,2-dichloroethane, attempts to isolate and purify significant quantities of this compound were unsuccessful. In contrast, reaction between **3a** and 1,3-dichloropropane proceeded with no P-P dimer formation, and the C_2-symmetric propano-bridged bis(phospholane) (*S,S*)-**5a** was obtained in good yield (Scheme III). Likewise, the antipode (*R,R*)-**5a** was prepared from (*R,R*)-**1a**. The propano-bridged ethyl-substituted bis(phospholane) **5b** was obtained in a similar fashion.

Implementation of the above methodology for preparation of the *iso*-propyl-substituted analogues **4c** and **5c**, however, was not as fruitful. Regardless of the apparent purity of the lithium metal used, we consistently observed 10-15% isomerization in the Ph cleavage step. Although the minor isomer has not been characterized, presumably *meso*-**3c** is generated in a competing epimerization process. The production of an isomeric mixture of **3c**, coupled with the overall low yield in the reaction with 1,2-dichloroethane, made this route to **4c** impractical. Upon proceeding with the coupling reaction involving 1,3-dichloropropane as usual, however, we obtained a mixture of diastereomeric bis(phospholanes), with the major product being the desired C_2-symmetric (*S,S*)- or (*R,R*)-**5c**. The two isomeric propano-bridged analogs, C_2-symmetric (*R,R*)-**5c** and C_1-symmetric **5c'**, were obtained in ca. 4:1 ratio. While these compounds could not be separated as the free phosphines, recrystallization of a mixture of rhodium complexes of (*R,R*)-**5c** and **5c'** allowed isolation of the isomerically pure C_2-symmetric complex of (*R,R*)-**5c** (vide infra).

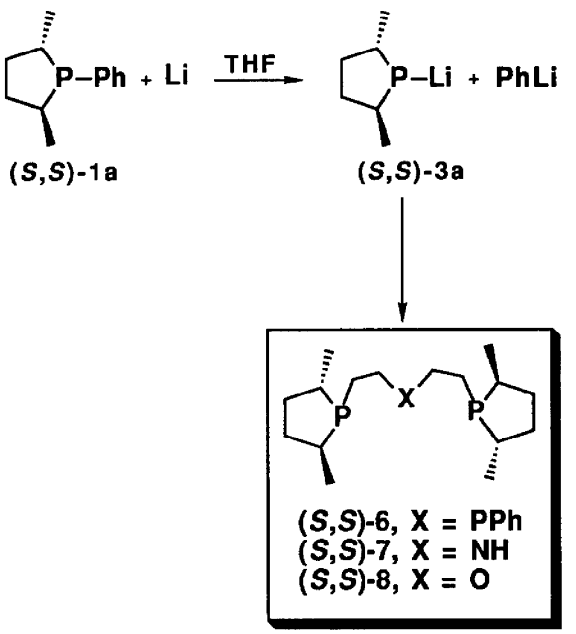
Polydentate Phosphines

Polydentate phosphine ligands have attracted considerable recent interest,[18] particularly with respect to potential utility in homogeneous catalysis.[19] Their versatile yet well-defined donor set and rigid chelating nature can provide substantial control on the coordination number, electronic properties, and stereochemistry of attached metals. Furthermore, novel systems possessing high order symmetry (ie. C_3- and C_4-symmetric) should be accessible through the

proper introduction of chirality into polydentate phosphine ligands. Our intent in this area was to design a series of new chiral polydentate phosphine ligands which are capable of, and are often restricted to, binding transition metals in specific coordination modes (ie. meridinal vs facial).

Chiral Tridentate Diphospholane Ligands. We have prepared several examples of new chiral diphospholane ligands as shown in Scheme IV.

Scheme IV



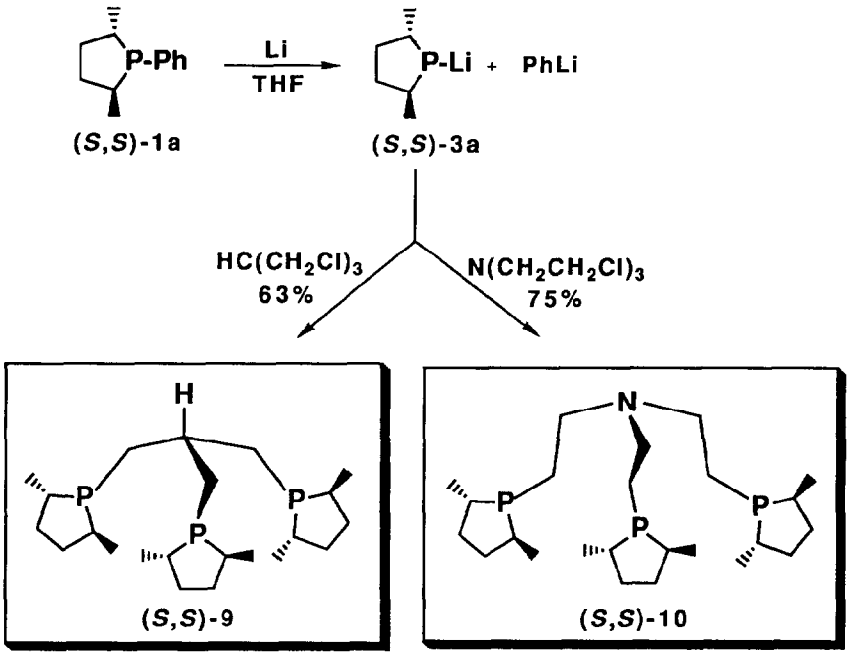
The synthetic pathway followed the standard protocol based on the generation of (*S,S*)-**3a**, which upon reaction with divinylphenylphosphine, bis(2-chloroethyl)trimethylsilylamine,[20] or bis(2-chloroethyl)ether provided the corresponding phosphine ligands (*S,S*)-**6** (X = PPh), (*S,S*)-**7** (X = NH), or (*S,S*)-**8** (X = O), respectively. In the preparation of (*S,S*)-**6**, MeOH (1.2-1.3 equivs.) was added prior to divinylphenylphosphine addition in order to completely remove phenyllithium as benzene. The base-catalyzed nature of phosphide addition to the vinylphosphine moiety,[21] assured complete consumption of any secondary phosphine generated. After the addition of bis(2-chloroethyl)trimethylsilylamine in the synthesis of (*S,S*)-**7**, a THF solution of n-BuN_4F (1.2 equivs.) was added in order to remove the trimethylsilyl amine protecting group. Surprisingly, attempted removal of Me_3Si by the addition of excess MeOH led to a mixture of products due to incomplete silyl cleavage. As usual, the antipodes (*R,R*)-**6**, (*R,R*)-**7**, and (*R,R*)-**8** could be prepared by starting with (*R,R*)-**1a**.

Placement of a heteroatom in the backbone of these phosphine ligands is expected to dramatically affect the mode of binding to transition metals. For example, coordination of the two phophorus groups as well as the heteroatom affords a tridentate ligand array where the chiral phospholane moieties may be placed in a *trans* disposition, effectively surrounding the metal with chirality. To our knowledge, such coordination would constitute the first example of a chiral *trans*-spanning bis(phosphine) ligand, and may impart unique properties on the attached metal centers (such as high enantioselectivity in catalytic reactions). Recently, the first examples of related tridentate chiral bis(oxazolinyl)pyridine ligands were reported to provide high enantioselection in hydrosilylation reactions.[22]

Chiral C_3-Symmetric Tripodal Phosphines. In simple terms, the great success of chiral chelating C_2-symmetric ligands in asymmetric catalysis can been ascribed to the equivalent asymmetric environments imposed above and below the plane of an intermediate square-planar metal complex.[3,8,23] Ligands possessing a C_2 symmetry axis apparently limit the "available quadrants"[3b] on a square-planar metal center to two, thereby providing high facial selectivity in the binding of prochiral unsaturated substrates. It is believed that this leads to a reduction in the number of possible diastereomeric transition states, thus giving rise to the high enantioselectivities observed. Often, however, the situation is more complex and cannot be explained by simple facial selectivity arguments. For example, it has been shown in certain hydrogenation systems that the critical factor in determining enantioselectivity is the relative rates of hydrogen addition to the intermediate diastereomeric complexes containing the substrate; the less prevalent intermediate reacts much faster and provides the predominant product enantiomer.[24] Furthermore, in addition to square-planar species, octahedral intermediates are known to be involved in many transition metal-catalyzed reactions.[25] An octahedral intermediate bearing a chiral bidentate C_2-symmetric ligand offers two inequivalent (diastereotopic) coordination sites (axial and equatorial) for substrate binding. In contrast, a similar octahedral intermediate with a facially-coordinated chiral tridentate C_3-symmetric ligand offers only one type of site for substrate coordination; all sites opposite such a C_3-symmetric tripodal ligand are equivalent or homotopic. The reduced number of competing asymmetric environments may provide good absolute stereocontrol in catalytic reactions involving metal centers possessing chiral C_3-symmetric tripodal ligands. Furthermore, high enantioselectivities are often restricted to substrates which can chelate to the catalytic metal center. Our hope is to obviate this requirement through the use of C_3-symmetric tripodal ligands which enforce binding of a chiral phosphine moiety in the coordination site usually occupied by the secondary donor group on the substrate. Ultimately, this approach could lead to high enantioselectivities in notoriously difficult asymmetric catalytic reactions such as those involving nonchelating or unfunctionalized substrates.

We have prepared the first examples of chiral C_3-symmetric tris(phosphine) ligands as shown in Scheme V.

Scheme V



Initial attempts to prepare a tris(phosphine) in a typical manner through treatment of (*S,S*)-**3a** with 1,1,1-tris(chloromethyl)ethane led not to the expected product, but to a mixture containing the P-P diphospholane dimer as the major product. We reasoned that the neopentyl-like nature of the substrate chloromethyl groups resulted in slow nucleophilic attack, and electron transfer or metal-halogen exchange chemistry dominated. In an effort to remove these unfavorable steric interactions, we used the less hindered 1,3-dichloro-2-chloromethylpropane.[26] The desired C_3-symmetric tris(phospholane) (*S,S*)-**9** (only one set of phospholane symmetry labels are required for these compounds since the other two are defined by the operation of a C_3-symmetry axis) was produced as a colorless crystalline solid in 63% yield. In a similar manner, the novel C_3-symmetric tris(phospholano)amine (*S,S*)-**10** was prepared upon reaction between (*S,S*)-**3a** and tris(2-chloroethyl)amine. Analogously, the antipodes (*R,R*)-**9** and (*R,R*)-**10** were readily prepared by starting with (*R,R*)-**1a**. The C_3-symmetry of **9** and **10** was clearly indicated by ^{31}P NMR spectra, which exhibited singlets at δ -8.0 and -3.4, respectively. Rhodium complexes containing the C_3-symmetric ligands **9** and **10** have been characterized by X-ray crystallography.[5b]

Transition Metal Complexes

With a series of new chiral phosphines in hand, it became desirable to obtain structural information concerning the asymmetric environment imposed by these ligands. Since our initial catalytic studies have focussed on hydrogenation reactions, we prepared the rhodium complexes $[(COD)Rh(P)_2]^+SbF_6^-$ which could be used as catalyst precursors. The most convenient method found for the preparation of these complexes was based on the reaction between $[(COD)_2Rh]^+SbF_6^-$ and phosphine ligands. The molecular structure of the complex $[(COD)Rh((R,R)\text{-}\mathbf{4a})]^+SbF_6^-$ has been reported.[5a] In an effort to confirm the structure of the *iso*-propyl-substituted diphospholane (*R,R*)-**5c**, we prepared the analogous rhodium complex.

As described above, our method for diphospholane synthesis led to a distereomeric mixture of (*R,R*)-**5c** and **5c'** (ca. 4:1 ratio). Consequently, a mixture of rhodium compexes (4:1) were obtained upon reaction with $[(COD)_2Rh]^+SbF_6^-$. The C_2-symmetric nature of the major complex containing (*R,R*)-**5c** was indicated by the ^{31}P NMR spectrum which showed a single resonance at δ 15.1 (J_{RhP} = 146 Hz). That the diastereomer **5c'** lacked a symmetry axis was similarly evidenced by the ^{31}P NMR spectrum of the minor rhodium complex which exhibited two resonances at δ 14.3 (J_{RhP} = 145 Hz, J_{PP} = 23 Hz) and 17.2 (J_{RhP} = 147 Hz, J_{PP} = 23 Hz). Separation of these complexes was readily accomplished by recrystallization from CH_2Cl_2/Et_2O which afforded pure $[(COD)Rh((R,R)\text{-}\mathbf{5c})]^+SbF_6^-$ as an orange-red crystalline solid. The structure of this complex was ascertained by X-ray crystallography and the ORTEP diagram is shown in Figure 1. Selected interatomic bond distances and angles are provided in Table I. The asymmetric unit consists of two crystallographically independent molecules which mainly differ by the conformation of the propane backbone of the diphospholane ligand. That two different conformations are observed in the solid state suggests that the propane backbone is quite flexible in these systems. Such flexibilty also explains the relatively low enantioselectivity observed in hydrogenation reactions when using the propano-bridged diphospholane ligands **5** (vide infra). Only one molecule is depicted in Figure 1; the conformation of the second molecule is shown in the supplementary material. Interestingly, one of the four *i*-Pr groups adopts a very different conformation compared to that of the others. The reason for this is unclear. Of particular importance is the large dihedral angle (24.6°) between the P-Rh-P plane and the plane defined by the COD olefin midpoints and Rh. A similar phenomenon was observed in the complex $[(COD)Rh((R,R)\text{-}\mathbf{4a})]^+SbF_6^-$.[5a] This distortion from the expected square-planar Rh geometry appears to result from steric interactions between the *i*-Pr groups of (*R,R*)-**5c** and the COD olefinic carbons C2 and C6. Interestingly, the chemically equivalent dihedral angle in the second rhodium cation (see supplementary material) is only 13.6 deg., indicating that the backbone conformation of the bis(phospholanes) strongly influences the steric environment imposed by these ligands. The enantiomorphic structure refined to slightly larger R values, consistent with the *R,R*-configuration for the phospholane moieties of the ligand.

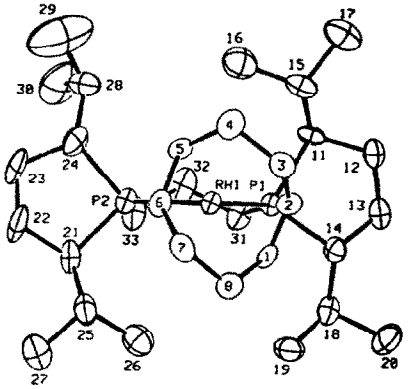


Figure 1. ORTEP diagram of [(COD)Rh((*R,R*)-**5c**)]$^+$SbF$_6^-$

Table I. Selected Interatomic Distances (Å) and Intramolecular Angles (deg) for [(COD)Rh((*R,R*)-**5c**)]$^+$SbF$_6^-$

Interatomic Distances (Å)	
Rh(1)-P(1)	2.317 (2)
Rh(1)-P(2)	2.336 (2)
Rh(1)-C(1)	2.181 (8)
Rh(1)-C(2)	2.253 (9)
Rh(1)-C(5)	2.217 (9)
Rh(1)-C(6)	2.234 (9)
Intramolecular Angles (deg)	
P(1)-Rh(1)-P(2)	95.16 (9)
P(1)-Rh(1)-C(1)	94.2 (2)
P(1)-Rh(1)-C(2)	88.9 (2)
P(2)-Rh(1)-C(5)	96.8 (2)
P(2)-Rh(1)-C(6)	89.7 (2)

The bis(phospholano)phosphine (*S,S*)-**6** was reacted with [(COD)RhCl]$_2$ to afford the square-planar rhodium complex [((*S,S*)-**6**)RhCl]. The tridentate coordination of the PP$_2$ ligand was confirmed by X-ray crystallography and the molecular structure is shown in Figure 2. Selected interatomic bond distances and angles are shown in Table II. Coordination of the three phosphorus atoms leads to a *trans*-disposition between the chiral phospholane moieties, and the rhodium center is essentially surrounded by the asymmetric environment. Geometric constraints imposed by the ligand create a significant distortion of the square-planar geometry at Rh as indicated by the *trans* P-Rh-P angle of 162.8°.

Reaction between [(COD)$_2$Rh]$^+$SbF$_6^-$ and bis(phospholano)amine (*S,S*)-**7** provided the five-coordinate rhodium complex [(COD)Rh((*S,S*)-**7**)]$^+$SbF$_6^-$. Structural confirmation of the tridentate nature of the HNP$_2$ ligand was obtained by X-ray crystallography and the ORTEP diagram is shown in Figure 3. Selected interatomic bond distances and angles are given in Table III.

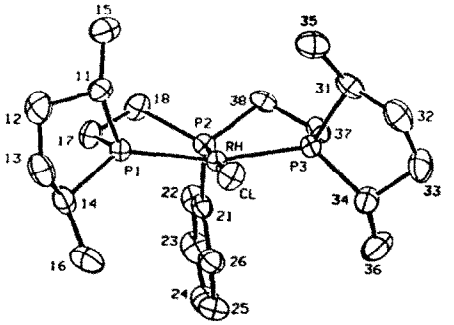


Figure 2. ORTEP diagram of [((*S,S*)-6)RhCl]

Table II. Selected Interatomic Distances (Å) and Intramolecular Angles (deg) for [((*S,S*)-6)RhCl]

Interatomic Distances (Å)	
Rh(1)-P(1)	2.2658 (9)
Rh(1)-P(2)	2.1453 (8)
Rh(1)-P(3)	2.2730 (9)
Rh(1)-Cl(1)	2.4018 (8)
Intramolecular Angles (deg)	
P(1)-Rh(1)-P(2)	84.81 (3)
P(1)-Rh(1)-P(3)	162.83 (3)
P(2)-Rh(1)-P(3)	84.16 (3)
Cl(1)-Rh(1)-P(1)	95.60 (3)
Cl(1)-Rh(1)-P(2)	178.3 (2)
Cl(1)-Rh(1)-P(3)	95.05 (3)

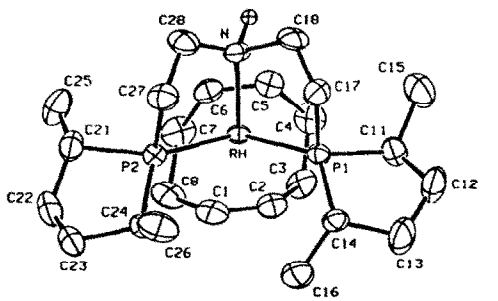


Figure 3. ORTEP diagram of [(COD)Rh((*S,S*)-7)]$^+SbF_6^-$

Table III. Selected Interatomic Distances (Å) and Intramolecular Angles (deg) for [(COD)Rh((*S,S*)-7)]$^+SbF_6^-$

Interatomic Distances (Å)	
Rh(1)-P(1)	2.331 (2)
Rh(1)-P(2)	2.377 (2)
Rh(1)-N(1)	2.131 (6)
Rh(1)-C(1)	2.189 (8)
Rh(1)-C(2)	2.195 (9)
Rh(1)-C(5)	2.181 (9)
Rh(1)-C(6)	2.144 (8)
Intramolecular Angles (deg)	
P(1)-Rh(1)-P(2)	105.43 (8)
P(1)-Rh(1)-N(1)	84.2 (2)
P(2)-Rh(1)-N(1)	82.7 (2)

Asymmetric Hydrogenations

In order to calibrate the catalytic efficiency and enantioselectivity of complexes containing our new phosphine ligands (both relative to each other as well as relative to known chiral phosphines), we have examined asymmetric hydrogenation reactions involving several unsaturated substrates.

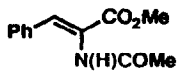
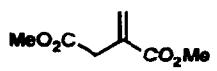
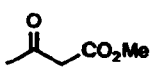
Olefins. Rhodium complexes $[(COD)Rh(P)_n]^+SbF_6^-$ (n = 2, 3) containing the new phosphines **1**, **4**, **5**, and **9** were found to behave as efficient catalysts for asymmetric hydrogenation reactions involving the standard olefinic substrate methyl acetamidocinnamate (MAC). We observed rapid hydrogenation to the phenylalanine derivative and the results are shown in Table IV. While unoptimized, the best conditions found in terms of rates and selectivity were: 20-25°C, 1000/1 substrate/catalyst (S/C) ratio, 30 psi H_2, and MeOH solvent. Qualitatively,

lower rates and slightly lower ee's were observed in THF solvent. The iridium analogs were inactive for these hydrogenations. The highest enantioselectivity with bis(phosphine) catalysts was associated with the ethano-bridged diphospholane **4a** where 85% ee observed. In all cases examined, the *R,R* ligands afforded products of *R* absolute stereochemistry while *S,S* ligands provided the *S* product. Moving to the propano-bridged diphospholane (*R,R*)-**5a** we observed a decrease to 60% ee. The lower selectivity seen with (*R,R*)-**5a** is probably a result of the greater flexibility of the propane backbone relative to the ethane bridge of **4a**. Only a slight improvement to 64% ee was observed with (*R,R*)-**5b** which has ethyl substituents on the phospholane moieties. Apparently, the placement of *iso*-propyl groups on the phospholanes provides a sterically encumbered environment, as very low conversions (5%) were observed over extended reaction times using the rhodium complex [(COD)Rh((*R,R*)-**5c**)]$^+SbF_6^-$. The enantioselectivity dropped again to 60% ee when the monodentate phospholane (*R,R*)-**1a** was used. The importance of both phosphine chelation and ligand rigidity in the attainment of high enantioselectivities is evident here, and has been well-documented for other catalyst systems.[3]

We were pleased to find that the C_3-symmetric phosphine (*S,S*)-**9** afforded 89% ee which was the highest selectivity observed for these systems with this substrate. Importantly, however, in contrast to the bis(phosphine) catalysts, reasonable rates were not obtained without heating the reaction to 50°C at which long reaction times (72 h) were still required for complete conversion to product. Attempts to increase the rate of the hydrogenation further with higher reaction temperatures (65°C) were successful, but led to a dramatic decrease in the selectivity (40% ee). While activation of the catalyst [(COD)Rh((*S,S*)-**9**)]$^+SbF_6^-$ through hydrogenation of the COD ligand was shown to occur at 25°C, virtually no substrate hydrogenation was observed at this temperature. The temperature requirement suggests that a stable five-coordinate (18-electron) intermediate [(MAC)Rh((*S,S*)-**9**)]$^+SbF_6^-$ is formed under the reaction conditions. Dissociation of one arm of the chelating substrate or the tris(phospholane) ligand would be necessary for further reaction with hydrogen. In light of the catalytic competence found for the tris(phospholane) complex, we were surprised to find that use of the bis(phospholano)amine complex [(COD)Rh((*S,S*)-**7**)]$^+SbF_6^-$ afforded virtually no MAC reduction product, even at temperatures as high as 65°C. Apparently dissociation of one arm of (S,S)-**7** is less favored, and the intermediate complex [(MAC)Rh((*S,S*)-**7**)]$^+SbF_6^-$ is too stable for reaction with hydrogen. This result is consistent with the need for ligand dissociation in catalysis involving the tris(phospholane) complex [(COD)Rh((*S,S*)-**9**)]$^+SbF_6^-$.

The asymmetric hydrogenation of dimethyl itaconate using the above catalyst systems also was investigated and the results are shown in Table IV. Of the more efficient diphospholane catalysts, ethano-bridged **4a** afforded the highest enantiomeric excess (90%). With the propano-bridged systems **5** and monodentate phosphine **1a**, the same trends as noted above were observed. Again, the C_3-symmetric phosphine (*S,S*)-**9** provided the highest ee (94%), but required a higher temperature (50°C) and longer reaction time (20 h).

Table IV. Catalytic Asymmetric Hydrogenations[a]

Substrate	Ligand	Time (h)[b]	% ee[c] (confign)[d]
	(*R*,*R*)-**4a**	3	85 (*R*)
	(*S*,*S*)-**4a**	3	85 (*S*)
	(*R*,*R*)-**5a**	3	60 (*R*)
	(*R*,*R*)-**5b**	3	64 (*R*)
	(*R*,*R*)-**1a**	3	60 (*R*)
	(*S*,*S*)-**9**	72	89 (*S*)
	(*S*,*S*)-**9**	48	40 (*S*)
	(*R*,*R*)-**4a**	2	90 (*R*)
	(*S*,*S*)-**4a**	2	90 (*S*)
	(*R*,*R*)-**5a**	2	78 (*R*)
	(*R*,*R*)-**1a**	2	65 (*R*)
	(*S*,*S*)-**9**	20	94 (*S*)
	(*R*,*R*)-**5a**	48	6 (*R*)
	(*S*,*S*)-**5b**	48	18 (*S*)
	(*R*,*R*)-**5c**	60	9 (*R*)
	(*R*,*R*)-**5a**	48	20 (*R*)
	(*S*,*S*)-**5b**	48	22 (*S*)
	(*R*,*R*)-**5c**	60	27 (*R*)

[a] Reactions were carried out in Fisher-Porter tubes at 20-25°C and an initial H_2 pressure of 30 psi (2 atm) in 0.25-0.35 M methanol solutions of substrate with 0.1 mol % (S/C = 1000/1) catalyst $[(COD)Rh(P)_n]^+SbF_6^-$ (n = 2,3). [b] Time required for 100% conversion of substrate. [c] Enantiomeric excesses were determined as described in the experimental section. [d] Absolute configurations were determined by optical rotation measurements.

Carbonyl Reductions. Electron-rich phosphines are known to greatly enhance the rate of ketone reductions by rhodium complexes.[6a,b] We, therefore, have investigated the reduction of acetophenone and methyl acetoacetate with rhodium complexes bearing several of our new phosphine ligands. We were particularly interested in the reaction involving methyl acetoacetate since a highly enantioselective reduction would provide the β-hydroxy ester required for the synthesis of our phospholane ligands. This would lead to the self-generation of our phosphines, effectively resulting in a ligand breeder cycle.[14] The results of these studies are listed in Table IV. While reasonable reduction rates were observed, as can be seen, relatively low enantioselectivites were obtained. A key observation is that rhodium catalysts containing either the monodentate phospholanes **1** or the 1,2-bis(phospholane) **4a** were found ineffective for carbonyl hydrogenations. As was indicated by the studies of Tani and coworkers,[6a] ligand backbone flexibilty appears to be important for the catalysis to proceed in these reactions; to our knowledge, no catalyst containing 1,2-diphosphine ligands has yet been found for the efficient reduction of carbonyl groups. For high absolute stereocontrol, however, such ligand flexibilty is

known to be detrimental, as is borne out in our experiments where we were restricted to use of the propano-bridged diphospholane derivatives **5**.

Summary. We have outlined the preparation of a new series of electron-rich chiral phospholane ligands as well as a convenient three-step synthesis of the important enantiomerically pure 1,4-diols **3**. We currently are examining the use of our new chiral phosphine ligands in other transition metal-catalyzed reactions.

Experimental Section.

General Procedures. All reactions and manipulations were performed in a nitrogen-filled Vacuum Atmospheres Dri-Lab glovebox or using standard Schlenk techniques. Benzene, toluene, diethyl ether (Et_2O), tetrahydrofuran (THF), glyme, hexane, and pentane were distilled from sodium-benzophenone ketyl under nitrogen. Acetonitrile (CH_3CN) and methylene chloride (CH_2Cl_2) were distilled from CaH_2. Methanol (MeOH) was distilled from $Mg(OMe)_2$.

Melting points were determined using a Mel-Temp apparatus in capillaries sealed under nitrogen and are uncorrected. HPLC analyses were performed using a Hewlett Packard Model HP 1090 LC interfaced to a HP 9000 Series 300 computer workstation. Optical rotations were obtained using a Perkin Elmer Model 241 MC Polarimeter. NMR spectra were obtained on Nicolet NT-360 wide-bore (360 MHz ^1H, 146 MHz ^{31}P), Nicolet NMC-300 wide-bore (300 MHz ^1H, 120.5 MHz ^{31}P, 75.5 MHz ^{13}C) and Nicolet QM-300 narrow-bore (300 MHz ^1H) spectrometers. ^{13}C and ^{31}P NMR chemical shifts are positive downfield (and negative upfield) from external Me_4Si and 85% H_3PO_4, respectively. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY, or Pascher Mikroanalytisches Labor, Remagen-Bandorf (FRG).

Preparation of chiral β-hydroxy esters. Preparations of the chiral β-hydroxy esters used in the diol syntheses were carried out as described by Noyori and coworkers[12] who have described the asymmetric reduction of β-keto esters using a ruthenium catalyst bearing the chiral diphosphine ligand BINAP (both (*R*)-(+)- and (*S*)-(-)-enantiomers commercially available from Strem Chemicals). All keto ester reductions were conducted on a 300 g scale in Hasteloy steel autoclave vessels using a MeOH/CH_2Cl_2 (300 mL/300mL) solvent mixture. The reactions were allowed to proceed at constant H_2 pressure (1500 psi) for 48 h at 25°C. Complete conversion of the β-keto ester substrates was observed in all cases and the products were simply distilled from the crude reaction mixture. Consistent with the results of Noyori et al.,[12] all products were determined to be >99% enantiomerically pure.

Preparation of chiral β-hydroxy acids. The hydrolysis of chiral β-hydroxy esters to the corresponding acids previously has been reported by Noyori[12] and Seebach,[13c] but in several instances no procedures were provided. We have developed a general protocol for the isolation of large quantities of the acids of interest. An example follows: A mixture of (3*R*)-methyl 3-hydroxypentanoate (290 g, 2.2 mol) in water (200 mL) and ethanol (200 mL) was cooled to 0°C. To this cold solution was added a solution of KOH (185 g, 3.3 mol) in water (1 L). The reaction was then allowed to stir at 25°C for 48 h. The resulting solution was concentrated to ca. 500 mL and acidified (conc. HCl) until pH = 1 was reached. The precipitated salts were filtered and the filtrate was subjected to continuous liquid/liquid extraction with diethyl ether (1 L) for 24 h. The diethyl ether was removed on a rotovap to afford the product (3*R*)-3-hydroxypentanoic acid as a colorless oil (250 g, 97%): $[\alpha]^{25}_D = -37.2 \pm 0.5$ (*c* 1, $CHCl_3$). The crude products thus obtained were sufficiently pure to use in the next step (Kolbe-coupling).

(2*R*,5*R*)-2,5-hexanediol ((*R*,*R*)-2a). A 1000 mL jacketed reaction vessel was charged with (3*R*)-3-hydroxybutyric acid (52.0 g, 0.5 mol), methanol (390 mL) and sodium methoxide (110 mL of a 0.5 N solution in methanol, 0.055 mol), and the mixture (pH = 5.38) was cooled to 0°C with a circulating bath. The electrode configuration used consists of a Pt foil anode (20 cm^2) wrapped around the outside bottom of a small jointed tube which fits inside a larger jointed tube with a Pt foil cathode (30 cm^2) lining the inside (avg electrode gap = 2.5 mm). Using a 30 amp DC power supply (Hewlett Packard Model No. 6269B), a constant current (current density 0.25 A/cm^2) of 5 amp was applied until 56,000 coulombs (1.2 F/mol) were passed at which point complete conversion of hydroxy acid was indicated by gas chromatography. The reaction and gas evolution (H_2 and CO_2) proceed normally until ca. 1.0 F/mol current were passed, after which the resistance and solution pH were observed to increase. The colorless reaction mixture was then concentrated on a rotovap, and the resulting solid residue was extracted with EtOAc (500 mL). After filtering, the obtained solids were stirred with EtOAc (100 mL) for 10 h, filtered, and the combined EtOAc extracts (600 mL) were concentrated to a colorless solid. The solids were dissolved in a minimum amount of warm Et_2O, quickly filtered through a coarse frit (if necessary), and the filtrate cooled to -78°C. After two hours, the colorless crystals were filtered, washed with cold pentane, and dried in vacuo (Yield 14.4 g, 48%). mp 53-54°C; $[\alpha]^{25}_D$ = -39.6 ± 0.5 (*c* 1, $CHCl_3$) [lit.[27] mp 53.0-53.3°C, $[\alpha]^{20}_D$ = +35.1 (*c* 9.49, $CHCl_3$) for *S,S* isomer]; ^1H NMR (CD_2Cl_2) δ 1.15 (d, J_{HH} = 6.2 Hz, 6H, CH_3), 1.50 (m, 4H, CH_2), 2.95 (br, 2H, OH), 3.75 (m, 2H, CH); ^{13}C NMR (CD_2Cl_2) δ 23.6, 35.9, 68.1. Anal. Calcd for $C_6H_{14}O_2$: C, 60.98; H, 11.94. Found: C, 61.12; H, 11.64.

(2*S*,5*S*)-2,5-hexanediol ((*S*,*S*)-2a). Prepared as described above except that (3*S*)-3-hydroxybutyric acid was used as substrate. $[\alpha]^{25}_D$ = +39.4 ± 0.5 (*c* 1, $CHCl_3$). Other spectroscopic properties were identical to those given for (*R*,*R*)-**2a**.

(3*R*,6*R*)-3,6-octanediol ((*R*,*R*)-2b). The procedure given above for (*R*,*R*)-**2a** was followed except that (3*R*)-3-hydroxypentanoic acid (50.0 g, 0.42 mol), methanol (380 mL) and sodium methoxide (120 mL of a 0.5 N solution in methanol, 0.06 mol) were used. Recrystallization from cold (-78°C) Et_2O afforded the product as a colorless crystalline solid (11.0 g, 36%). mp 51-52°C; $[\alpha]^{25}_D$ = -22.8 ± 0.5 (*c* 1, $CHCl_3$); ^1H NMR δ 0.9 (t, J_{HH} = 7.4 Hz, 6H, CH_3), 1.45 (m, 6H, CH_2), 1.60 (m, 2H, CH_2), 2.55 (br, 2H, OH), 3.46 (m, 2H, CH); ^{13}C NMR (CD_2Cl_2) δ 10.2, 31.0, 34.1, 74.0. Anal. Calcd for $C_8H_{18}O_2$: C, 65.71; H, 12.41. Found: C, 65.61; H, 12.21.

(3*S*,6*S*)-3,6-octanediol ((*S*,*S*)-2b). Prepared as above except that (3*S*)-3-hydroxypentanoic acid was used as substrate. $[\alpha]^{25}_D$ = +22.8 ± 0.5 (*c* 1, $CHCl_3$). Other spectroscopic properties were identical to those given for (*R*,*R*)-**2b**.

(3*S*,6*S*)-3,6-dihydroxy-2,7-dimethyloctane ((*S*,*S*)-2c). The procedure given above for (*R*,*R*)-**2a** was followed except that (3*S*)-3-hydroxy-4-methylpentanoic acid (66.0 g, 0.5 mol), methanol (395 mL) and sodium methoxide (105 mL of a 0.5 N solution in methanol, 0.053 mol) were used. Recrystallization from cold (-78°C) Et_2O afforded the colorless product as a fluffy crystalline solid (21.8 g, 50%). mp 99-101°C; $[\alpha]^{25}_D$ = -35.2 ± 0.5 (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.89 (d, J_{HH} = 6.8 Hz, 12H CH_3), 1.45 (m, 2H CH_2), 1.62 (m, 4H, CH_2), 3.0 (br, 2H, OH), 3.35 (m, 2H, CH); ^{13}C NMR ($CDCl_3$) δ 17.4, 18.7, 31.1, 34.0, 77.2. Anal. Calcd for $C_{10}H_{22}O_2$: C, 68.92; H, 12.72. Found: C, 69.24; H, 12.39.

(2*R*,5*R*)-2,5-hexanediol bis(methanesulfonate). To a solution of (2*R*,5*R*)-2,5-hexanediol (8.9 g, 0.075 mol) in CH_2Cl_2 (200 mL) was added triethylamine (26.2 mL, 0.188 mol). The solution was cooled to 0°C, and methanesulfonyl chloride (12.82 mL, 0.166 mol) in CH_2Cl_2 (30 mL) was added dropwise over 30 min. Upon complete addition, the mixture containing precipitated salts was allowed to stir at 0°C for 30 min, and then at 25°C for 30 min. The mixture was then poured

into 1N HCl (250 mL) at 0°C. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed successively with 1N HCl (50 mL), saturated $NaHCO_3$, and brine. After drying ($MgSO_4$), the solution was concentrated on a rotovap to a pale yellow oil (18.2 g, 88%). The crude product thus obtained was sufficiently pure to be used in further reactions. ^{1}H NMR ($CDCl_3$) δ 1.41 (d, J_{HH} = 6.3 Hz, 6H, CH_3), 1.78 (m, 4H, CH_2), 3.0 (s, 6H, CH_3), 4.85 (m, 2H, CH). The same general procedure was followed to prepare the other bis(methanesulfonates) used in this study.

(2*R*,5*R*)-2,5-dimethyl-1-phenylphospholane ((*R*,*R*)-1a). To a slurry of $Li_2PPh{\cdot}THF$[28] (20.3 g, 0.105 mol) in THF (300 mL) at -78°C was added dropwise a solution of (2*S*,5*S*)-2,5-hexanediol bis(methanesulfonate) (26.0 g, 0.095 mol) in THF (50 mL). Upon complete addition, the orange mixture was allowed to stir at -78°C for 1h. The reaction was then slowly warmed to 25°C and, after transferring to a glovebox, stirring was continued for 16 h. The resulting pale yellow mixture was filtered through a coarse frit, and concentrated to a semi-solid. Extraction with pentane (100 mL) and filtration, followed by concentration *in vacuo* yielded a pale yellow oil. Distillation afforded the product as a colorless oil (13.9 g, 76%): bp 61-64°C (0.2 torr); $[\alpha]^{25}_D$ = -51.0 ± 1 (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 0.70 (dd, J_{HH} = 7.2 Hz, J_{PH} = 10.6 Hz, 3H, CH_3), 1.1-1.3 (m, 2H, CH_2), 1.20 (dd, J_{HH} = 7.2 Hz, J_{PH} = 18.8 Hz, 3H, CH_3), 1.65 (m, 1H, CH), 2.0 (m, 2H, CH_2), 2.45 (m, 1H, CH); **^{31}P NMR** (C_6D_6) δ 10.0; **^{13}C NMR** (C_6D_6) δ 15.43 (CH_3), 21.23 (d, J_{PC} = 34.2 Hz, CH_3), 32.25 (d, $^2J_{PC}$ = 10.0 Hz, CH_2), 35.62 (d, $^2J_{PC}$ = 13.1 Hz, CH_2), 37.17 (CH), 37.24 (d, J_{PC} = 3.6 Hz, CH), 128.11, 128.30, 134.51 (d, J_{PC} = 19.0 Hz, *ortho*), 137.67 (d, J_{PC} = 28.1 Hz, *ipso* Ph); **HRMS** (EI, direct insert): *m/z* 192.1068 (M^+, exact mass calcd for $C_{12}H_{17}P$: 192.1068), 177.0839 (M-CH_3), 150.0559 (M-C_3H_6), 135.0367 (M-C_4H_9), 108.0127 (C_6H_5P fragment).

(2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane ((*S*,*S*)-1a). Prepared as above from (2*R*,5*R*)-2,5-hexanediol bis(methanesulfonate): $[\alpha]^{25}_D$ = +51.6 ± 1 (*c* 1, hexane). Other spectroscopic properties identical to (*R*,*R*)-**2a**.

(2*S*,5*S*)-2,5-diethyl-1-phenylphospholane ((*S*,*S*)-1b). To a slurry of $Li_2PPh{\cdot}THF$[28] (33.4 g, 0.17 mol) in THF (300 mL) at -78°C was added dropwise a solution of (3*R*,6*R*)-3,6-octanediol bis(methanesulfonate) (49.5 g, 0.16 mol) in THF (75 mL). The procedure followed was identical to that described for (*R*,*R*)-**1a**. Distillation afforded the product as a colorless oil (18.6 g, 51%): bp 83-86°C (0.15 torr); $[\alpha]^{25}_D$ = -53.0 ± 1 (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 0.81 (t, J_{HH} = 7.0 Hz, 3H, CH_3), 0.94 (t, J_{HH} = 7.3 Hz, 3H, CH_3), 0.8-1.40 (m, 4H, CH_2), 1.60 (m, 2H, CH_2), 1.80 (m, 2H, CH), 2.05 (m, 1H, CH), 2.30 (m, 1H, CH), 7.05 (m, 3H, Ph), 7.45 (m, 2H, Ph); **^{31}P NMR** (C_6D_6) δ +1.8; **^{13}C NMR** (C_6D_6) δ 14.46 (d, J_{PC} = 12.5 Hz, CH_3), 14.60 (d, J_{PC} = 6.8 Hz, CH_3), 24.15, 29.29, 34.55, 43.82 (d, J_{PC} = 12.3 Hz, CH_2), 43.99 (d, J_{PC} = 13.3 Hz, CH_2), 128.03, 128.13, 128.69, 135.03 (d, J_{PC} = 19.8 Hz, *ortho*), 138.34 (d, J_{PC} = 28.8 Hz, *ipso* Ph).

(2*R*,5*R*)-2,5-diethyl-1-phenylphospholane ((*R*,*R*)-1b). Prepared as above from (3*S*,6*S*)-3,6-octanediol bis(methanesulfonate). $[\alpha]^{25}_D$ = +55.4 ± 1 (*c* 1, hexane). Other spectroscopic properties identical to (*S*,*S*)-**1b**.

(2*R*,5*R*)-2,5-diisopropyl-1-phenylphospholane ((*R*,*R*)-1c). To a slurry of $Li_2PPh{\cdot}THF$[28] (9.30 g, 0.048 mol) in THF (300 mL) at -78°C was added dropwise a solution of (3*S*,6*S*)-3,6-dihydroxy-2,7-dimethyloctane bis(methanesulfonate) (15.12 g, 0.046 mol) in THF (50 mL). The procedure followed was identical to that described for (*R*,*R*)-**1a**. Distillation afforded the product as a colorless oil (8.65 g, 73%): bp 78-80°C (0.07 torr); $[\alpha]^{25}_D$ = -92.6 ± 1 (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 0.83 (d, J_{HH} = 6.5 Hz, 3H, CH_3), 1.00 (m, 1H, CH), 1.02 (d, J_{HH} = 6.6 Hz, 3H, CH_3), 1.05 (d, J_{HH} = 6.4 Hz, 3H, CH_3), 1.11 (d, J_{HH} = 6.6 Hz, 3H, CH_3), 1.28 (m, 1H, CH_2), 1.60 (m, 1H, CH_2), 1.70 (m, 1H, CH_2), 1.85 (m, 1H, CH), 2.00 (m, 1H, CH), 2.15 (m, 1H, CH_2), 2.30 (m, 1H, CH); **^{31}P**

NMR (C_6D_6) δ -3.2; **^{13}C NMR** (CD_2Cl_2) δ 22.17 (d, $^2J_{PC}$ = 10.5 Hz, CH), 22.51 (CH_3), 22.69 (CH_3), 24.05 (d, $^2J_{PC}$ = 6.7 Hz, CH), 29.83 (CH_3), 32.57 (CH_3), 33.45 (d, $^2J_{PC}$ = 26.2 Hz, CH_2), 33.95 (d, $^2J_{PC}$ = 3.2 Hz, CH_2), 51.46 (d, J_{PC} = 13.4 Hz, CH), 52.06 (d, J_{PC} = 12.4 Hz, CH), 128.20, 128.84, 135.77 (d, $^2J_{PC}$ = 20.4 Hz, *ortho*), 139.10 (d, J_{PC} = 28.7 Hz, *ipso* Ph); **HRMS** (EI, direct insert): *m/z* 248.1688 (M^+, exact mass calcd for $C_{16}H_{25}P$: 248.1694), 233.1458 (M-CH_3), 205.1147 (M-C_3H_7), 164.0756 (M-C_6H_{12}), 151.0661 (M-C_7H_{13}), 136.0439 (M-C_8H_{16}).

1,2-Bis((2*R*,5*R*)-2,5-dimethylphospholano)ethane ((*R*,*R*)-4a). To phospholane (*R*,*R*)-**1a** (6.0 g, 0.031 mol) in THF (200 mL) at 25°C under Ar was added clean Li ribbon (0.54 g, 0.078 mol), and the reaction was allowed to stir for 10 h. To the resulting brown mixture was added dropwise a solution of ethylene glycol di-*p*-tosylate (6.90 g, 0.018 mol) in THF (100 mL). After stirring for 1 h, MeOH (3 mL) was added and the mixture turned pale yellow. The reaction was allowed to stir for 30 min and then was filtered. The filtrate was concentrated to dryness in vacuo, and the resulting solids were extracted with pentane (200 mL) and filtered. The pentane filtrate was concentrated to a yellow oil which was fractionally distilled *in vacuo* to afford the product as a colorless oil (2.10 g, 52%): bp 64-67°C (0.06 torr); $[\alpha]^{25}_D$ = +263 ± 3 (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 0.98 (dd, J_{HH} = 7.2 Hz, J_{PH} = 9.1 Hz, 6H, CH_3), 1.0-1.35 (m, 5H, CH_2), 1.22 (dd, J_{HH} = 7.2 Hz, J_{PH} = 17.3 Hz, 6H, CH_3), 1.55 (m, 2H, CH, CH_2), 1.70 (m, 5H, CH, CH_2), 1.90 (m, 4H, CH, CH_2); **^{31}P NMR** (C_6D_6) δ 3.2; **^{13}C NMR** (C_6D_6) δ 14.6 (CH_3), 20.71 (d, J_{PC} = 6.0 Hz, CH_3), 21.48 (dd, J_{PC} = 15.5 Hz, bridge CH_2), 34.44 (dd, J_{PC} = 5.8, 5.9 Hz, ring CH), 37.02 (ring CH_2), 37.42 (ring CH_2), 38.32 (dd, J_{PC} = 5.5 Hz, ring CH); **HRMS** (EI, direct insert): *m/z* 258.1670 (M^+, exact mass calcd for $C_{14}H_{28}P_2$: 258.1667), 230.1344 (M-C_2H_4), 175.0785 (M-C_6H_{11}), 144.1072 (M-$C_6H_{11}P$), 116.0748 (M-$C_8H_{15}P$).

1,3-Bis((2*R*,5*R*)-2,5-dimethylphospholano)propane ((*R*,*R*)-5a). To phospholane (*R*,*R*)-**1a** (6.0 g, 0.031 mol) in THF (200 mL) at 25°C under Ar was added clean Li ribbon (0.54 g, 0.078 mol), and the reaction was allowed to stir for 10 h. To the resulting brown mixture was added dropwise a solution of 1,3-dichloropropane (2.11 g, 0.018 mol) in THF (25 mL). The reaction decolorized toward the end of the addition, and after stirring for 30 min, MeOH (3 mL) was added. This mixture was allowed to stir 10 min, then was filtered, and the filtrate concentrated *in vacuo*. The resulting oil was extracted with pentane (125 mL), filtered, and the pentane layer was concentrated to a yellow oil. Distillation afforded the product as a colorless oil (3.2 g, 75%): bp 98-101°C (0.08 torr); $[\alpha]^{25}_D$ = +279 ± 3° (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 1.0 (dd, J_{HH} = 7.1 Hz, J_{PH} = 9.6 Hz, 6H, CH_3), 1.05 (m, 2H, CH_2), 1.20 (dd, J_{HH} = 7.1 Hz, J_{PH} = 17.5 Hz, 6H, CH_3), 1.20 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.55 (m, 4H, CH_2), 1.70 (m, 4H, CH, CH_2), 1.90 (m, 4H, CH, CH_2); **^{31}P NMR** (C_6D_6) δ -2.85; **^{13}C NMR** (C_6D_6) δ 14.60 (CH_3), 21.45 (d, J_{PC} = 30.8 Hz, CH_3), 24.34 (t, J_{PC} = 18.9 Hz, bridge central CH_2), 25.70 (dd, J_{PC} = 11.3, 22.3 Hz, bridge CH_2), 34.05 (d, J_{PC} = 12.1 Hz, ring CH), 37.10 (d, J_{PC} = 3.6 Hz, ring CH_2), 37.51 (ring CH_2), 38.30 (d, J_{PC} = 11.5 Hz, ring CH); **HRMS** (EI, direct insert): *m/z* 272.1816 (M^+ exact mass calcd for $C_{15}H_{30}P_2$: 272.1823), 229.1283 (M-C_3H_7), 188.0831 (M-C_6H_{12}), 157.1139 (M-$C_6H_{12}P$), 130.0900 (M-$C_8H_{15}P$), 116.0742 ($C_6H_{13}P$ fragment).

1,3-Bis((2*S*,5*S*)-2,5-diethylphospholano)propane ((*S*,*S*)-5b). Prepared as described above for (*R*,*R*)-**5a** except that (*S*,*S*)-**1b** (6.0 g, 0.027 mol) was used in place of (*R*,*R*)-**1a**. Distillation afforded the product as a colorless oil (2.68 g, 52%): bp 125-130°C (0.05 torr); $[\alpha]^{25}_D$ = +256 ± 3 (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 0.94 (t, J_{HH} = 7.3 Hz, 6H, CH_3), 1.00 (t, J_{HH} = 7.1 Hz, 6H, CH_3), 1.00-1.70 (m, 22H, CH_2), 1.80 (m, 2H, CH), 1.95 (m, 2H, CH); **^{31}P NMR** (C_6D_6) δ -11.1; **^{13}C NMR** (C_6D_6) δ 14.60 (d, J_{PC} = 12.9 Hz, CH_3), 15.00 (d, J_{PC} = 7.0 Hz, CH_3), 23.46, 23.82 (t, J_{PC} = 19.3 Hz, bridge central CH_2), 25.29 (dd, J_{PC} = 11.4, 22.2 Hz, bridge CH_2), 29.57 (d, J_{PC} = 27.9 Hz, ring CH), 34.20 (d, J_{PC} = 4.7 Hz, ring CH_2), 34.93 (ring CH_2), 42.64 (d, J_{PC} = 12.3 Hz, ring CH), 45.66 (d, J_{PC} = 13.3 Hz, ring CH); **HRMS** (EI, direct insert): *m/z* 328.2415 (M^+ exact mass

calcd for $C_{19}H_{38}P_2$: 328.2449), 286.1894 (M-C_3H_6), 216.1197 (M-C_8H_{16}), 185.1441 (M-$C_8H_{16}P$), 144.1068 ($C_8H_{17}P$ fragment).

1,3-Bis((2*R*,5*R*)-2,5-diisopropylphospholano)propane ((*R*,*R*)-5c). Prepared as described above for (*R*,*R*)-**5a** except that (*R*,*R*)-**1c** (4.0 g, 0.016 mol) was used in place of (*R*,*R*)-**1a**. Distillation afforded the products as a colorless oil (1.58 g, 51% of a 4:1 isomeric mixture): **^{31}P NMR** (C_6D_6) δ -17.0 (2P), -16.95 (1P), -9.6 (1P); **HRMS** (EI, direct insert): *m/z* 384.3061 (M^+ exact mass calcd for $C_{23}H_{46}P_2$: 384.3047), 369.2804 (M-CH_3), 245.1629 (M-$C_{10}H_{19}$), 213.1732 (M-$C_{10}H_{20}P$), 172.1406 ($C_{10}H_{21}P$ fragment), 130.0912 ($C_7H_{15}P$ fragment).

Bis(2-((2*S*,5*S*)-2,5-dimethylphospholanoethyl))phenylphosphine ((*S*,*S*)-6). To (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (6.0 g, 0.031 mol) in THF (100 mL) at 25°C under Ar was added clean Li ribbon (0.55 g, 0.079 mol), and the reaction was allowed to stir for 12 h. To the resulting brown/orange mixture was added MeOH (1.64 mL, 0.04 mol, 1.3 equiv.) dropwise upon which the reaction warmed and a gelatinous precipitate (LiOMe) formed. After stirring for 10 min, a THF solution (10 mL) of divinylphenylphosphine (2.27 g, 0.14 mol) was added dropwise via pipet. The reaction remained warm, and after stirring for 30 min, MeOH (6 mL) was slowly added to the brown mixture to produce a pale yellow slurry. After 10 min, the reaction was filtered through a large (600 mL) medium porosity frit and the filtrate concentrated to a pale yellow oil. The resulting oil was dissolved in pentane (100 mL) and filtered. Concentration of the filtrate afforded a pale yellow oil which was distilled in vacuo to yield the product as a colorless oil (3.05 g, 55%): bp 73-75°C (0.025 torr); $[\alpha]^{25}_D$ = -137 ± 2 (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 0.83 (dd, J_{HH} = 7.17 Hz, J_{PH} = 9.7 Hz, 3H, CH_3), 0.92 (dd, J_{HH} = 7.15 Hz, J_{PH} = 9.7 Hz, 3H, CH_3), 1.15 (dd, J_{HH} = 7.10 Hz, J_{PH} = 11.6 Hz, 3H, CH_3), 0.9-1.40 (m, 5H, CH_2), 1.21 (dd, J_{HH} = 7.17 Hz, J_{PH} = 11.6 Hz, 3H, CH_3), 1.50-1.80 (m, 2H, CH, CH_2), 1.80-2.10 (m, 5H, CH, CH_2), 7.10 (m, 3H, Ph), 7.55 (m, 2H, Ph); **^{31}P NMR** (C_6D_6) δ -16.15 (dd, J_{PP} = 24.0 Hz, 1P, PPh), 3.29 (d, J_{PP} = 24.0 Hz, 1P), 3.48 (d, J_{PP} = 24.0 Hz, 1P); **^{13}C NMR** ($CDCl_3$) δ 14.23 (CH_3), 14.28 (CH_3), 19.05 (dd (overlapping), 2C, bridge CH_2), 21.03 (d, J_{PC} = 29.5 Hz, CH_3), 21.06 (d, J_{PC} = 28.8 Hz, CH_3), 24.47 (d, J_{PC} = 15.5 Hz, CH_2), 24.67 (d, J_{PC} = 15.7 Hz, CH_2), 34.02, 34.15, 36.65 (dd, J_{PC} = 3.8 Hz), 36.99 (ring CH_2), 37.55 (d, J_{PC} = 8.81 Hz, ring CH), 37.67 (d, J_{PC} = 8.71 Hz, ring CH), 128.29, 128.38, 128.88, 132.39 (d, J_{PC} = 18.5 Hz, *ipso*-Ph); **HRMS** (EI, direct insert): *m/z* 394.2107 (M^+, exact mass calcd for $C_{22}H_{37}P_3$: 394.2108), 279.1402 (M-$C_6H_{12}P$), 251.1110 (M-$C_8H_{16}P$).

Bis(2-((2*S*,5*S*)-2,5-dimethylphospholanoethyl))amine ((*S*,*S*)-7). To (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (5.0 g, 0.026 mol) in THF (100 mL) at 25°C under Ar was added clean Li ribbon (0.463 g, 0.067 mol), and the reaction was allowed to stir for 12 h. To the resulting brown/orange mixture was added bis(2-chloroethyl)trimethylsilylamine[20] (2.62 g, 0.012 mol, 0.47 equiv.) in THF (5 mL) dropwise and the reaction was allowed to stir for 2 h. To the resulting mixture was then added MeOH (5 mL), and after 10 min, the colorless reaction was filtered through a large (600 mL) medium porosity frit and the filtrate concentrated to a pale yellow oil. The resulting oil was dissolved in pentane (100 mL) and filtered. Concentration of the filtrate afforded a pale yellow oil (2.91 g). To the resulting oil was added THF (25 mL), followed by n-Bu_4NF (9.4 mL of a 1 M solution in THF), and the reaction was allowed to stir for 5 h. Concentration of the mixture afforded an orange residue which was extracted with pentane (50 mL) and filtered through a celite pad. Concentration of the filtrate provided the product as a pale yellow oil (2.23 g, 57%): $[\alpha]^{25}_D$ = -157.6 ± 2 (*c* 1, hexane); **^{1}H NMR** ($CDCl_3$) δ 1.06 (dd, J_{HH} = 7.16 Hz, J_{PH} = 9.8 Hz, 6H, CH_3), 1.29 (dd, J_{HH} = 7.16 Hz, J_{PH} = 17.75 Hz, 6H, CH_3), 0.90-1.40 (m, 7H, CH_2), 1.65 (m, 2H, CH, CH_2), 1.80 (m, 4H, CH, CH_2), 2.00 (m, 4H, CH, CH_2), 2.80 (m, 4H, CH, CH_2); **^{31}P NMR** (C_6D_6) δ -5.3; **^{13}C NMR** (C_6D_6) δ 14.57 (CH_3), 21.39 (d, J_{PC} = 31.0 Hz, CH_3), 25.05 (d, J_{PC} = 22.0 Hz, bridge CH_2), 33.87 (d, J_{PC} = 11.6 Hz, ring CH), 37.11 (d, J_{PC} = 4.5 Hz, ring CH_2), 37.47 (ring CH_2), 38.40 (d, J_{PC} = 10.9 Hz, ring CH), 48.04 (d, J_{PC} = 22.0 Hz, bridge CH_2).

Bis(2-((2*S*,5*S*)-2,5-dimethylphospholanoethyl))ether ((*S*,*S*)-8). To (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (3.0 g, 0.016 mol) in THF (100 mL) at 25°C under Ar was added clean Li ribbon (0.280 g, 0.040 mol), and the reaction was allowed to stir for 12 h. To the resulting brown/orange mixture was added a THF solution (5 mL) of bis(2-chloroethyl)ether (1.07 g, 7.5 mmol). After stirring for 1 h, MeOH (3 mL) was slowly added to the brown mixture to produce a colorless slurry. After 10 min, the reaction was filtered through a large (125 mL) medium porosity frit and the filtrate was concentrated to a pale yellow oil. The resulting oil was dissolved in pentane (100 mL) and filtered. Concentration of the filtrate afforded a pale yellow oil which was distilled in vacuo to yield the product as a colorless oil (0.53 g, 22%): bp 62-63°C (0.06 torr); $[\alpha]^{25}_D$ = -132.0 ± 2 (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 0.91 (dd, J_{HH} = 7.12 Hz, J_{PH} = 10.0 Hz, 3H, CH_3), 1.13 (dd, J_{HH} = 7.15 Hz, J_{PH} = 18.0 Hz, 6H, CH_3), 0.97 (m, 2H, CH_2), 1.15 (m, 2H, CH_2), 1.33 (m, 2H, CH_2), 1.55 (m, 2H, CH_2), 1.70 (m, 3H, CH, CH_2), 1.85 (m, 3H, CH, CH_2), 2.05 (br, 2H, CH_2), 3.60 (m, 4H, CH_2O); **^{31}P NMR** (C_6D_6) δ -8.3; **^{13}C NMR** (C_6D_6) δ 14.53 (CH_3), 21.15 (d, J_{PC} = 30.9 Hz, CH_3), 27.99 (d, J_{PC} = 22.0 Hz, CH_2), 33.61 (d, J_{PC} = 10.7 Hz, CH_3), 37.08 (d, J_{PC} = 4.6 Hz, CH), 37.39, 38.31 (d, J_{PC} = 9.9 Hz, CH_2), 60.98 (d, J_{PC} = 25.6 Hz, CH_2O); **HRMS** (EI, direct insert): *m/z* 302.1900 (M^+, exact mass calcd for $C_{16}H_{32}OP_2$: 302.1929), 187.1232 (M-$C_6H_{12}P$), 160.0947 (M-$C_8H_{15}P$).

Tris(((2*S*,5*S*)-2,5-dimethylphospholano)methyl)methane ((*S*,*S*)-9). To (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (6.07 g, 0.032 mol) in THF (200 mL) at 25°C under Ar was added clean Li ribbon (0.55 g, 0.079 mol), and the reaction was allowed to stir for 15 h. To the resulting brown/orange mixture was added dropwise a solution of 1,3-dichloro-2-(chloromethyl)propane[25] (1.70 g, 10.5 mmol) in THF (15 mL) at 25°C. The reaction remained brown throughout the addition, and after stirring for 30 min, MeOH (3 mL) was added. The resulting colorless mixture was allowed to stir 15 min, then was filtered through a celite pad, and the filtrate concentrated *in vacuo*. The resulting solids were extracted with pentane (125 mL), filtered, and the pentane layer was concentrated to ca. 15 mL. Rapid filtration afforded the product as a colorless crystalline solid (1.0 g). The filtrate was then concentrated to a pale yellow solid which was dissolved in a minimum amount of Et_2O (3 mL). To this solution was added MeOH (15 mL) and the mixture was cooled to -20°C for 12 h. The resulting colorless crystals were filtered, washed with cold MeOH and dried in vacuo (1.65 g). Combined yield 2.65 g (63%): $[\alpha]^{25}_D$ = -329 ± 4 (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 1.0-1.2 (m, 3H, CH, CH_2), 1.07 (dd, J_{HH} = 7.2 Hz, J_{PH} = 9.8 Hz, 9H, CH_3), 1.29 (dd, J_{HH} = 7.0 Hz, J_{PH} = 17.6 Hz, 9H, CH_3), 1.40 (m, 3H, CH, CH_2), 1.60 (m, 3H, CH_2), 1.80 (m, 3H, CH, CH_2), 1.9-2.2 (m, 13H, CH, CH_2); **^{31}P NMR** (C_6D_6) δ -8.0; **^{13}C NMR** (C_6D_6) δ 14.89 (CH_3), 21.51 (d, J_{PC} = 30.7 Hz, CH_3), 31.85 (dt, J_{PC} = 8.3, 22.1 Hz, bridge P-CH_2), 32.67 (q, J_{PC} = 14.9 Hz, bridge CH), 34.12 (d, J_{PC} = 11.6 Hz, ring CH), 37.30 (d, J_{PC} = 3.8 Hz, ring CH_2), 37.47 (ring CH_2), 38.49 (d, J_{PC} = 11.3 Hz, ring CH); **HRMS** (EI, direct insert): *m/z* 400.2583 (M^+ exact mass calcd for $C_{22}H_{43}P_3$: 400.2578), 357.2021 (M-C_3H_7), 315.1557 (M-C_6H_{13}), 285.1896 (M-$C_6H_{12}P$), 273.1104 (M-C_9H_{19}), 232.0678 (M-$C_{12}H_{24}$), 201.0955 (M-$C_{12}H_{24}P$).

Tris(2-((2*S*,5*S*)-2,5-dimethylphospholano)ethyl)amine ((*S*,*S*)-10). To (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (3.0 g, 15.6 mmol) in THF (100 mL) at 25°C under Ar was added clean Li ribbon (0.27 g, 39.0 mmol), and the reaction was allowed to stir for 15 h. To the resulting brown/orange mixture was added dropwise a solution of tris(2-chloroethyl)amine (1.06 g, 5.2 mmol) in THF (15 mL) at 25°C. The reaction remained brown throughout the addition, and after stirring for 30 min, MeOH (3 mL) was added. The resulting colorless mixture was allowed to stir 15 min, then was filtered through a celite pad, and the filtrate concentrated *in vacuo*. The resulting solids were extracted with pentane (125 mL), filtered, and the pentane layer was concentrated to ca. 15 mL. Rapid filtration afforded the product as a colorless crystalline solid (0.6 g). The filtrate was then concentrated to a pale yellow solid which was dissolved in a minimum amount of warm MeOH (3-4 mL) and the mixture was cooled to -20°C for 12 h. The resulting colorless crystals were filtered, washed with cold MeOH and dried in vacuo (1.20 g). Combined yield 1.80 g (76%): $[\alpha]^{25}_D$ = -167 ± 3 (*c* 1, hexane); **^{1}H NMR** (C_6D_6) δ 1.0-1.2 (m, 3H, CH, CH_2), 1.11 (dd, J_{HH} = 7.2

Hz, J_{PH} = 9.8 Hz, 9H, CH_3), 1.32 (dd, J_{HH} = 7.0 Hz, J_{PH} = 17.7 Hz, 9H, CH_3), 1.30-1.45 (m, 3H, CH, CH_2), 1.55 (m, 3H, CH_2), 1.70-2.15 (m, 15H, CH, CH_2), 2.80 (m, 6H, NCH_2); **^{31}P NMR** (C_6D_6) δ -3.4; **^{13}C NMR** (C_6D_6) δ 14.66 (CH_3), 21.34 (d, J_{PC} = 31.0 Hz, CH_3), 22.02 (d, J_{PC} = 22.8 Hz, bridge P-CH_2), 33.97 (d, J_{PC} = 12.0 Hz, ring CH), 37.12 (d, J_{PC} = 3.6 Hz, ring CH_2), 37.41 (ring CH_2), 38.41 (d, J_{PC} = 11.3 Hz, ring CH), 51.73 (d, J_{PC} = 25.6 Hz, bridge N-CH_2); **HRMS** (EI, direct insert): *m/z* 443.3035 (M^+ exact mass calcd for $C_{24}H_{48}NP_3$: 443.3000), 328.2315 (M-$C_6H_{12}P$), 314.2146 (M-$C_7H_{14}P$), 242.1216 (M-$C_{12}H_{26}P$).

Optical Purity of Phosphines. The phosphines **1**, **4a**, **5a**, and **5b** were ascertained to be optically pure (within the limits of detection) by reacting each with (*R*)-[(dimethyl-(α-methylbenzyl)-aminato-C,N]palladium(II) chloride dimer[15] and monitoring the ^{31}P NMR spectrum. Comparisons were made with the spectrum of the opposite phosphine enantiomer.

Rhodium Complexes: General Procedure. All cationic rhodium complexes containing COD (COD = 1,5-cyclooctadiene) were prepared by the reaction of $[(COD)_2Rh]^+X^-$ (X = SbF_6, PF_6, OTf) with the appropriate quantity of phosphine ligand.

[(COD)Rh((*R,R*)-1a)$_2$]$^+$SbF$_6^-$. ^{1}H NMR (CD_2Cl_2) δ 0.70 (dd, J_{HH} = 6.9 Hz, J_{PH} = 13.8 Hz, 6H, CH_3), 1.00 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.62 (dd, J_{HH} = 7.2 Hz, J_{PH} = 18.6 Hz, 6H, CH_3), 1.90 (m, 2H, CH_2, CH), 2.20 (m, 6H, CH_2, CH), 2.40 (M, 8H, COD-CH_2), 4.90 (br, 2H, COD-CH), 5.34 (br, 2H, COD-CH), 7.0 (m, 4H, Ph), 7.30 (m, 4H, Ph), 7.40 (m, 2H, Ph); **^{31}P NMR** (CD_2Cl_2) δ 43.8 (d, J_{RhP} = 143.4 Hz); Anal. Calcd for $C_{32}H_{46}P_2F_6SbRh$: C, 46.23; H, 5.58; P, 7.45. Found: C, 46.26; H, 5.47; P, 7.43.

[(COD)Rh((*R,R*)-4a)]$^+$SbF$_6^-$. ^{1}H NMR (CD_2Cl_2) δ 1.20 (dd, J_{HH} = 6.9 Hz, J_{PH} = 14.4 Hz, 6H, CH_3), 1.40 (dd, J_{HH} = 7.1 Hz, J_{PH} = 17.7 Hz, 6H, CH_3), 1.3-1.6 (m, 6H, CH_2), 1.95 (m, 2H, CH, CH_2), 2.10-2.60 (m, 10H, CH_2, CH), 4.95 (br, 2H, COD-CH), 5.40 (br, 2H, COD-CH); **^{31}P NMR** (CD_2Cl_2) δ 76.7 (d, J_{RhP} = 146.3 Hz); Anal. Calcd for $C_{22}H_{40}F_6P_2SbRh$: C, 37.47; H, 5.72. Found: C, 37.64; H, 5.37.

[(COD)Rh((*R,R*)-5a)]$^+$PF$_6^-$. ^{1}H NMR (CD_2Cl_2) δ 1.15 (dd, J_{HH} = 6.9 Hz, J_{PH} = 14.8 Hz, 6H, CH_3), 1.50 (dd, J_{HH} = 7.2 Hz, J_{PH} = 18.7 Hz, 6H, CH_3), 1.3-1.6 (m, 6H, CH_2), 1.80 (m, 2H, CH, CH_2), 2.10 (m, 4H, CH, CH_2), 2.20-2.60 (m, 12H, CH_2, CH), 4.80 (m (br), 2H, COD-CH), 5.15 (m (br), 2H, COD-CH); **^{31}P NMR** (CD_2Cl_2) δ 27.7 (d, J_{RhP} = 139.6 Hz), -145 (sept., PF_6); Anal. Calcd for $C_{23}H_{42}F_6P_3Rh$: C, 43.96; H, 6.74. Found: C, 44.19; H, 6.43.

[(COD)Rh((*R,R*)-5c)]$^+$SbF$_6^-$. ^{1}H NMR (CD_2Cl_2) δ 0.98 (d, J_{HH} = 6.6 Hz, 6H, CH_3), 1.08 (d, J_{HH} = 6.7 Hz, 6H, CH_3), 1.14 (d, J_{HH} = 6.5 Hz, 6H, CH_3), 1.53 (d, J_{HH} = 6.6 Hz, 6H, CH_3), 1.25 (m, 2H), 1.40-1.65 (m, 6H), 1.90 (m, 8H), 2.20 (m, 8H), 2.40 (m, 6H), 4.22 (br, 2H, COD-CH), 5.40 (br, 2H, COD-CH); **^{31}P NMR** (CD_2Cl_2) δ 15.0 (d, J_{RhP} = 138.3 Hz). Anal. Calcd for $C_{31}H_{58}F_6P_2RhSb$: C, 44.78; H, 7.03; P, 7.45. Found: C, 44.73; H, 6.99; P, 7.54.

[(COD)Rh((*S,S*)-7)]$^+$SbF$_6^-$. ^{1}H NMR (CD_2Cl_2) δ 0.92 (dd, J_{HH} = 7.5 Hz, J_{PH} = 17.5 Hz, 3H, CH_3), 1.10 (dd, J_{HH} = 6.9 Hz, J_{PH} = 12.7 Hz, 3H, CH_3), 1.48 (dd, J_{HH} = 7.2 Hz, J_{PH} = 13.6 Hz, 3H, CH_3), 1.59 (dd, J_{HH} = 7.3 Hz, J_{PH} = 16.1 Hz, 6H, CH_3),1.25-1.70 (m, 4H), 1.7-2.0 (m, 4H), 2.0-2.5 (m, 12H), 2.55-2.8 (m, 4H), 2.8-3.0 (m, 4H), 3.42 (br, 1H, NH), 3.60 (br, 4H, COD-CH); **^{31}P NMR** (CD_2Cl_2) δ 50.63 (dd, J_{RhP} = 106.2 Hz, J_{PP} = 29.9 Hz), 62.74 (dd, J_{RhP} = 113.9 Hz, J_{PP} = 29.9 Hz); Anal. Calcd for $C_{24}H_{45}F_6NP_2RhSb$: C, 38.53; H, 6.06; P, 8.28. Found: C, 38.52; H, 6.01; P, 8.54.

[(COD)Rh((*S,S*)-9)]$^+$SbF$_6^-$. ^{1}H NMR (CD_2Cl_2) δ 1.16 (dd, J_{HH} = 7.4 Hz, J_{PH} = 10.9 Hz, 9H, CH_3), 1.27 (dd, J_{HH} = 7.0 Hz, J_{PH} = 15.1 Hz, 9H, CH_3), 1.6-1.8 (m, 12H, CH_2), 2.0-2.2 (m, 11H, CH,

COD-CH_2), 2.30 (m, 3H, CH), 2.65 (m, 6H, PCH_2), 3.15 (q(br), 1H, CH), 3.85 (br, 2H, COD-CH), 4.20 (br, 2H, COD-CH); **^{31}P NMR** (CD_2Cl_2) δ 22.0 (d, J_{RhP} = 99 Hz); Anal. Calcd for $C_{30}H_{55}F_6P_3RhSb$: C, 42.52; H, 6.44; P, 10.97. Found: C, 41.94; H, 6.32; P, 10.90.

[Rh((*S,S*)-6)Cl]. To [(COD)RhCl]$_2$ (0.062 g, 0.126 mmol) in THF (5 mL) was added a THF solution of (*S,S*)-**6** (0.1 g, 0.252 mol). The solution turned yellow and homogeneous upon addition. After stirring for 30 min, the solution was concentrated to 3 mL and hexanes added to precipitate a pale yellow microcrystalline solid. Recrystallization from THF/hexane afforded the pale yellow crystalline product (0.110 g, 81%): **^{1}H NMR** (THF-d_8) δ 1.0 (m, 6H, CH_3), 1.15 (m, 6H, CH_3),1.2-1.4 (m, 8H), 1.55 (m, 4H), 1.7-2.2 (m, 4H), 2.4 (m, 2H), 2.75 (m, 2H), 1.73 (m, 2H, Ph), 8.0 (m, 3H, Ph); **^{31}P NMR** (THF-d_8) δ 67.35 (ddd, J_{RhP} = 139.8 Hz, J_{PP} = 26.3 Hz, J_{PP} = 29.3 Hz, 2P coincidental overlap), 115.70 (ddd, J_{RhP} = 167.9 Hz, J_{PP} = 29.3 Hz, J_{PP} = 29.3 Hz, 1P--central P). Anal. Calcd for $C_{22}H_{37}ClP_3Rh$: C, 49.59; H, 7.00; P, 17.44. Found: C, 49.72; H, 7.07; P, 17.30.

Asymmetric Hydrogenations: General Procedure. In a dry box, a 100 mL Fisher-Porter tube was charged with substrate (1.26 mmol), anhydrous, degassed MeOH or THF (20 mL), and catalyst (0.1 mol %). After four vaccum/H_2 cycles, the tube was pressurized to an initial pressure of 30 psig H_2 (Matheson, 99.998%). The reactions were allowed to stir at 20°C until no further hydrogen uptake was observed. Complete conversion to product was indicated by GC and ^{1}H NMR analyses, unless otherwise noted. Reactions were concentrated, and the residue passed through a short SiO_2 column (Et_2O/pentane, 50/50) to afford the pure products. Enantiomeric excesses were determined as follows: methyl acetamidophenylalanine (HPLC, Chiralcel OB, 1.0 mL/min 5% IPA/Hexane, t_1 17.2 min; t_2 20.6 min); dimethyl methylsuccinate (500 MHz ^{1}H NMR, chiral shift reagent (+)-Eu(hfc)$_3$), baseline resolution of ester methoxyl resonance at δ 3.69 observed at Δδ 0.25; *sec*-phenyl alcohol (HPLC, Chiralcel OB, 0.5 mL/min 10% IPA/Hexane, t_1 9.9 min; t_2 12.9 min); methyl 3-hydroxy butyrate (^{1}H NMR analysis of the MPTA ester and optical rotation based on $[\alpha]^{25}_D$ = -48.5 ± 0.5 (*c* 1, $CHCl_3$) for optically pure methyl (*R*)-3-hydroxybutyrate).

Acknowledgement. We thank L. Lardear, and W. Marshall for expert technical assistance in the structure determinations and J. Lazar for obtaining HRMS data.

Supplementary Material. X-ray diffraction data including a data summary table, tables of final positional and isotropic thermal parameters, anisotropic thermal parameters, hydrogen fixed atom coordinates, complete interatomic bond distances, complete intramolecular bond angles, additional ORTEP plots, and tables of observed and calculated structure factors for [(COD)Rh((*R,R*)-**5c**)]$^+$$SbF_6^-$, [((*S,S*)-**6**)RhCl], and [(COD)Rh((*S,S*)-**7**)]$^+$$SbF_6^-$.

References and Notes

(1) (a) Chaloner, P.A. *Handbook of Coordination Catalysis in Organic Chemistry*, Butterworth and Co.: London, 1986. (b) Parshall, G.W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980. (c) Alyea, E.C.; Meek, D.W., Eds., *Catalytic Aspects of Metal Phosphine Complexes*, Advances in Chem. Ser., American Chemical Society: Washington, D.C., 1982.
(2) (a) Kagan, H.B. In *Asymmetric Synthesis*: Morrison, J.D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 1. (b) Valentine, D., Jr. In *Asymmetric Synthesis*: Morrison, J.D., Ed.; Academic Press: New York, 1984; Vol. 4, Chapter 3.
(3) (a) Bosnich, B. (Ed.): *Asymmetric Catalysis*; Martinus Nijhoff Publishers, Dordrecht 1986. (b) Knowles, W.S. *Acc. Chem. Res.*, **1983**, *16*, 106. (c) Halpern, J. In *Asymmetric Synthesis*: Morrison, J.D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 2. (d) Koenig, K. E. In *Asymmetric Synthesis*: Morrison, J.D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 3. (e) Brunner, H. *J. Organometal. Chem.*, **1986**, *300*, 39. (f) Nagel, U.; Rieger, B. *Organometallics*, **1989**, *8*, 1534.

(4) (a) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.*, **1980**, *53*, 1138. (b) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.*, **1986**, *108*, 6405. (c) Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.*, **1988**, *110*, 8153. (d) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.*, **1989**, *111*, 6301.
(5) (a) Burk, M.J.; Feaster, J.E.; Harlow, R.L. *Organometallics*, **1990**, *10*, 2653. (b) Burk, M.J.; Harlow, R.L. *Angew. Chemie, Int. Ed. Engl.*, **1990**, *29*, 1462.
(6) For recent reports dealing with electron-rich asymmetric phosphines: (a) Tani, K.; Suwa, K.; Tanigawa, E.; Ise, T.; Yamagata, T.; Tatsuno, Y.; Otsuka, S. *J. Organometal. Chem.*, **1989**, *370*, 203. (b) Miyashita, A.; Karino, H.; Shimamura, J.; Chiba, T.; Nagano, K.; Nohira, H.; Takaya, H. *Chem. Lett.*, **1989**, 1849. (c) Brunner, H.; Sievi, R. *J. Organomet. Chem.*, **1987**, *328*, 71.
(7) For recent examples of monodentate phosphines possessing C_3 symmetry, see: (a) Bolm, C; Davis, W.M; Halterman, R.L.; Sharpless, K.B. *Angew. Chem. Int. Ed. Engl. 27* (1988) 835. (b) Bolm, C.; Sharpless, K.B. *Tetrahedron Lett. 29* (1988) 5101. (c) Bogdanovic, B.; Henc, B.; Meister, B.; Pauling, H.; Wilke, G. *Angew. Chem. Int. Ed. Engl. 11* (1972) 1023.
(8) For a recent review, see: Whitesell, J.K. *Chem. Rev.*, **1989**, *89*, 1581, and references therein.
(9) Lieser, J.K. *Synth. Commun.*, **1983**, *13(a)*, 765.
(10) Short, R.P.; Kennedy, R.M.; Masamune, S. *J. Org. Chem.*, **1989**, *54*, 1755.
(11) (a) Servi, S. *Synthesis*, **1990**, 1. (b) Jones, J.B. In *Asymmetric Synthesis*; Morrison, J.D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter 9. (c) Simon, H.; Bader, J.; Gunther, H.; Neumann, S.; Thanos, J. *Angew. Chem. Int. Ed. Engl.*, **1985**, *24*, 539.
(12) (a) Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.*, **1987**, *109*, 5856. (b) Kitamura, M.; Ohkuma, T.; Inoue, S.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ohta, T.; Takaya, H.; Noyori, R. *J. Am. Chem. Soc.*, **1988**, *110*, 629. (c) Kawano, H.; Ikariya, T.; Ishii, Y.; Sauri, M.; Yoshikawa, S.; Uchida, Y.; Kumobayashi, H. *J. Chem. Soc. Perkin Trans. I*, **1989**, 1571.
(13) a) Ross, S.D.; Finkelstein, M.; Rudd, E.J. *Anodic Oxidation*; Academic Press: New York, 1975. (b) Schafer, H.J. *Angew. Chem. Int. Ed. Engl.*, **1981**, *20*, 911. (c) Seebach, D.; Renaud, P. *Helv. Chim. Acta*, **1985**, *68*, 2342. (d) Haufe, J.; Beck, F. *Chemie-Ing.-Techn.*, **1970**, *42*, 170.
(14) For a similar example of a chiral phosphine breeder cycle, see: Fryzuk, M.D.; Bosnich, B. *J. Am. Chem. Soc.*, **1978**, *100*, 5491.
(15) (a) Otsuka, S.; Nakamura, A.; Kano, G.; Tani, K. *J. Am. Chem. Soc.*, **1971**, *93*, 4301. (b) Tani, K.; Brown, L.D.; Ahmed, T.; Ibers, J.A.; Yokota, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.*, **1977**, *99*, 7876.
(16) (a) Kosolapoff, W.; Maier, L. *Organic Phosphorus Compounds*; Wiley-Interscience: New York, 1972; Vol 1, Chapter 2. (b) Toth, I.; Hanson, B.E.; Davis, M.E. *Organometallics*, **1990**, *9*, 675.
(17) (a) Issleib, K.; Muller, D.-W. *Chem. Ber.*, **1959**, *92*, 3175. (b) Issleib, K.; Doll, G. *Chem. Ber.*, **1961**, *94*, 2664.
(18) (a) MacAuliffe, C.A.; Levason, W. *Phosphine, Arsine, and Stibene Complexes of the Transition Elements*; Elsevier: Amsterdam, 1979. (b) Sacconi, L.; Mani, F. In *Transition Metal Chemistry*; Melson, G.A.; Figgis, B.N. (Eds.); Marcel Dekker: New York, 1982; Vol. 8, Chapter 2. (c) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; Vol. 1, p. 146. (d) Bianchini, C. *Comments Inorg. Chem.*, **1988**, *8*, 27. (e) Fryzuk, M.D.; MacNeil, P.A.; Rettig, S.J.; Secco, A.S.; Trotter, J. *Organometallics*, **1982**, *1*, 918.
(19) (a) Bianchini, C.; Meli, A.; Peruzinni, M.; Vizza, F. *Organometallics*, **1990**, *9*, 226, and references therein. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics*, **1990**, *9*, 2283, and references therein.
(20) Danopoulos, A.A.; Wills, A.R.; Edwards, P.G. *Polyhedron*, **1990**, *9*, 2413.
(21) King, R.B.; Kapoor, P.N. *J. Am. Chem. Soc.*, **1971**, *93*, 4158.
(22) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics*, **1991**, *10*, 500.
(23) (a) Pfaltz, A. in *Modern Synthetic Methods*; R. Scheffold (Ed.); Springer-Verlag: Berlin 1989, Vol. 5, p. 199.
(24) (a) Brown, J.M.; Chaloner, P.A. *J. Chem. Soc. Chem. Commun.*, **1980**, 344. (b) Chan, A.S.C.; Pluth, J.J.; Halpern, J. *J. Am. Chem. Soc.*, **1980**, *102*, 5952. (c) Landis, C.R.; Halpern, J. *J.*

Am. Chem. Soc., **1987**, *109*, 1746. (d) McCulloch, B.; Halpern, J.; Thompson, M.R.; Landis, C.R. *Organometallics*, **1990**, *9*, 1392.
(25) (a) Collman, J.P.; Hegedus, L.S.; Norton, J.R.; Finke, R.G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books, Mill Valley, CA 1987. (b) Kochi, J.K. *Organometallic Mechanisms and Catalysis*; Academic Press, New York 1978.
(26) S. Latour, J. D. Wuest, *Synthesis* **1987**, 742.
(27) Serk-Hanssen, K.; Stallberg-Stenhagen, S.; Stenhagen, E. *Arkiv. Kemi.*, **1953**, *5*, 203.
(28) Issleib, K.; Hausler, S. *Chem. Ber.*, **1961**, *94*, 113.