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Bis(phospholane) Ligands Containing Chiral Backbones. Matching and Mismatching Effects in Enantioselective Hydrogenation of α-Keto Esters

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The preparation of a series of new bis(phospholane) ligands is described. A convenient procedure that allows the synthesis of secondary 2,5-dialkylphospholanes and their borane adducts has been developed. Use of the borane adducts to prepare diastereomeric bis(phospholane) ligands possessing chiral 2,4-pentane backbones also is described. Stereochemical matching and mismatching effects within these ligands are assessed in rhodium-catalyzed asymmetric hydrogenation reactions. In the hydrogenation of α-keto esters, substantially higher enantioselectivities (up to 78% ee) are observed with catalysts derived from the matched ligand relative to the analogous mismatched ligand and the ligand possessing an achiral 1,3-propane backbone. Two diastereomeric rhodium catalyst precursors have been characterized by X-ray crystallography, and the results have been analyzed in an effort to correlate the hydrogenation data with specific structural features of the catalysts.

Introduction

Transition-metal-catalyzed enantioselective hydrogenation of ketones potentially represents one of the most efficient and economically attractive methods for the preparation of many valuable chiral alcohols.[1] The most notable achievements in this area of research are based upon ruthenium catalysts derived from atropisomeric biaryl−diphosphine ligands (e.g., BINAP, BIPHEP, etc.).[2,3] This class of catalysts has been found to allow asymmetric hydrogenation of a wide range of functionalized ketones, including *β*-keto esters[4] and more recently arylalkyl ketones,[5] with very high levels of enantioselectivity (>98% ee) and extraordinary catalytic efficiencies (S/C up to 2.4 × 10^6).

In contrast, the asymmetric homogeneous hydrogenation of α-keto acid derivatives remains a formidable challenge.[6] Several α-keto esters have been hydrogenated with moderate to high enantioselectivity using Ru−BINAP and analogous catalysts.[7] Quite often, however, these catalyst systems were inefficient and required the addition of a strongly acidic cocatalyst, long reaction times, and high hydrogen pressures. Cationic rhodium complexes have been demonstrated to hydrogenate selected α-keto esters with moderate to high selectivities.[8] However, these processes are not general and each substrate demands a different chiral ligand. Again, low reaction rates, even at high hydrogen pressures and high catalyst loading, remain a prevalent affliction that greatly restricts the use of these cationic

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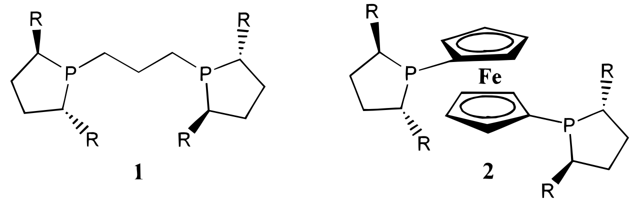

1 **2**

Figure 1. Bis(phospholane) ligands **1** and **2** possessing flexible ligand backbones.

catalyst systems for enantioselective α-keto ester hydrogenation.

Overall, no broadly effective catalyst has been developed for the asymmetric homogeneous hydrogenation of α-keto acid derivatives, and achievement of both high hydrogenation rates and high enantioselectivities appears particularly exacting. In terms of hydrogenation rates, perusal of the literature indicates that a certain degree of backbone flexibility (larger available bite angle) within a diphosphine ligand is necessary to achieve good catalytic activity in keto group hydrogenation reactions. Thus, a three- or four-carbon diphosphine backbone tends to afford much more active catalysts relative to two-carbon-bridged systems.[9] Also, the electronic character of the ligand appears important; more electron-rich (e.g., more highly alkylated) phosphines evoke higher rates in Rh-catalyzed hydrogenation of carbonyl groups.[9,10] On the basis of these two concepts, we recently developed rhodium catalysts based upon the achiral ligand 1,1′-bis(diisopropylphosphino)ferrocene (DiPFc).[9a] These catalysts have displayed exceedingly high rates in hydrogenation reactions and are quite effective for ketone and aldehyde reductions.

The achievement of high rates using the DiPFc-Rh catalysts inspired us to examine analogous chiral ligands that may afford superior catalysts for asymmetric ketone hydrogenations. Our studies involving *trans*-2,5-disubstituted phospholanes[11] led us to design conformationally flexible ligand systems bearing electron-rich phospholane groups. Two of the ligands that we have prepared are 1,3-bis(phospholano)propane (**1**)[12] and 1,1′-bis(phospholano)ferrocene (**2**),[13] shown in Figure 1. Rhodium catalysts bearing ligands **1** and **2** were found to be very efficient for hydrogenation of various types of carbonyl groups. Unfortunately, these catalysts afforded alcohol products with only low to moderate enantioselectivities. Apparently, the flexible backbones of electron-rich chiral ligands such as **1** and **2**, while important for high rates, are too conformationally dynamic for the achievement of high enantioselectivities in asymmetric hydrogenation reactions.[10,14]

Control of conformational properties is believed to be an important element in the design of effective asymmetric ligands that efficiently transfer their chirality. Detailed structural analysis of a range of rhodium complexes containing phospholane ligands has revealed that the backbone unit connecting the phospholanes can dramatically influence the chiral environment imposed by the ligand system and the selectivities achieved in hydrogenation reactions.[11b,12] In an effort to systematically control the conformation of the backbone structure, while maintaining a degree of flexibility such that different ligand bite angles may be accessed,[15] we have endeavored to design ligands that contain stereogenic centers in a three-carbon bridging unit of a bis(phospholane). In this manner, we hoped to maintain high catalytic activity associated with the large bite angle of a flexible electron-rich diphosphine yet optimize enantioselectivity through enforcement of a dominant backbone conformation. Moreover, the presence of stereogenic centers within a backbone linking two chiral phospholane moieties offers the opportunity to prepare diastereomeric ligands that could display the effects of *matching* and *mismatching* caused by interactions between the different stereochemical elements within each ligand.[16,17]

In this paper, we outline development of a convenient synthetic route that provides access to a series of bis(phospholane) ligands possessing a chiral 2,4-pentane backbone structure. Use of antipodal backbones has allowed the preparation of diastereomeric ligands. These ligands have been examined for utility in asymmetric hydrogenation reactions. X-ray crystallographic analyses of diastereomeric catalyst precursors were performed, and attempted correlation between the hydrogenation results and catalyst structural features will be discussed below.

Results and Discussion

The new series of bis(phospholane) ligands that we sought to prepare are shown in Figure 2. In particular, we planned to prepare both distereoisomeric forms of ligands of type **3** and **4** in order to examine the effects

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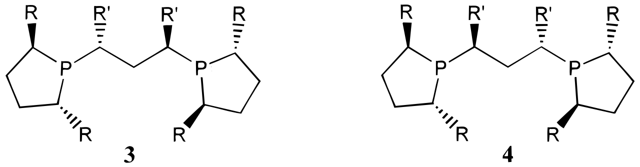
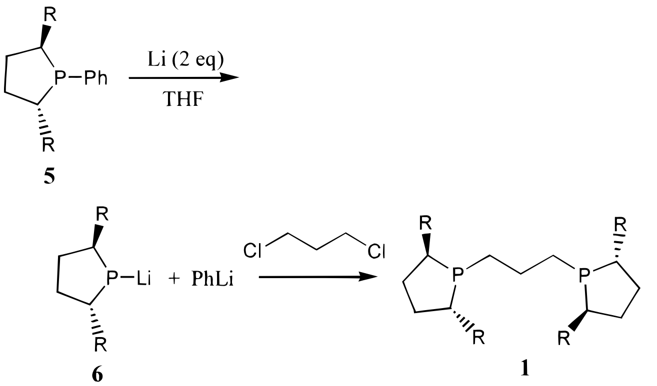


3 **4**

Figure 2. New bis(phospholane) ligands **3** and **4** possessing a chiral backbone tether.

Scheme 1. Original Reductive Cleavage Method for in Situ Preparation of Phospholides 6



5

6 **1**

of stereochemical *matching* and *mismatching* interactions upon the structural and catalytic properties of the corresponding rhodium complexes.

We reasoned that introduction of the requisite chiral backbone could occur through reaction between the phosphide anion of a secondary phospholane and an appropriate 1,3-diol equivalent. Since no convenient procedure had been developed for the synthesis and purification of chiral secondary phospholanes, we set out to establish a viable route to these compounds.

Chiral Secondary Phospholanes and Borane Adducts. Previously, we have reported the in situ preparation of solutions of chiral secondary 2,5-disubstituted phospholide anions through reaction between enantiomerically pure 1-phenylphospholanes **5** and lithium metal (Scheme 1). Treatment of **5** with lithium in THF led to selective reductive cleavage of the P−Ph bond to afford the phosphide **6** in solution, along with 1 equiv of phenyllithium. In the case of 2,5-dimethylphospholanes (**5**; R = Me), P−Ph cleavage occurred smoothly to afford the desired phosphide **6** (R = Me), and subsequent reaction between the in situ generated phosphide **6** and a wide range of electrophilic species was shown to afford a new class of bis(phospholane) and tris(phospholane) ligands.[12,18] However, upon reaction with certain electrophiles, such as 1,3-dichloropropane, the expected products (e.g. **1**) were isolated in only low to moderate yields after tedious purification procedures.

It was believed that the phenyllithium formed in the cleavage process may be responsible for some of the observed side reactions, and thus, attempts were made to isolate and purify the corresponding secondary phosphines. Unfortunately, the secondary phospholane derived from **6** (R = Me) was found to be quite volatile and was difficult to obtain in high yield and pure form. Moreover, it was discovered that reductive cleavage of the P−Ph bond of phospholanes bearing larger substituents (e.g., **5**; R = Et, *i*-Pr) was not as efficient and was subject to stereoisomerism at the 2,5-positions,[12] thus making this method impractical for the preparation of a series of chiral secondary phospholanes and derivatives thereof. Finally, electron-rich dialkylphosphides analogous to **6** are notorious for their propensity to engage in single-electron-transfer processes, which are another likely source of the low yields observed in substitution reactions involving **6**.[12]

We now have found that the requisite chiral secondary phospholanes **11** and their borane adducts **12** may be prepared cleanly and conveniently by the route shown in Scheme 2. The borane adducts **12** were particularly desirable, since such compounds are known to be easier to handle than the air-sensitive secondary phosphines and also the corresponding anions (i.e., see **13** in Scheme 3 below) are less basic, softer nucleophiles.[19]

Initial experiments were performed with the cyclic sulfate **7a** derived from enantiomerically pure (*S*,*S*)-2,5-hexanediol. Treatment of **7a** with 1 equiv of the nucleophile lithium bis(trimethylsilyl)phosphide ($(TMS)_2PLi$), prepared through addition of 1 equiv of MeLi to tris(trimethylsilyl)phosphine,[20] led cleanly to the corresponding ring-opened species **8a**. Progress of this reaction was readily monitored by proton-decoupled ^{31}P NMR spectroscopy, whereby the chemical shift of the product **8a** appeared at δ −137.3 ppm relative to starting $LiP(TMS)_2$, which appeared at δ −302.4 ppm.

The $Me_3Si{-}P$ bond is well-documented to be a convenient phosphide equivalent through simple nucleophile-induced cleavage of the phosphorus−silicon bond.[21] Accordingly, reaction between **8a** and MeLi was examined and found to afford the trimethylsilyl-substituted monophospholane **9a** as the only species formed, other than tetramethylsilane and lithium sulfate. Unfortunately, further attempts to use **9a** as a source of the phosphide anion **6a** were unsuccessful, as the P−TMS bond of **9a** proved unexpectedly resistant to nucleophilic cleavage. For instance, little reaction was observed between **9a** and hard nucleophiles such as BuLi and MeLi. Simple hydrolysis of **9a** with excess MeOH did afford the corresponding secondary phosphine (i.e. **11**); however, purification of the secondary phosphine again was difficult and was hampered by the presence of MeOH, which was troublesome to remove completely.

An alternative path involving hydrolytic cleavage of the intermediate **8a** proved more successful. Thus, treating a diethyl ether solution of preformed **8a** with excess MeOH over 24 h afforded the unique primary phosphine sulfate salt **10a** as a colorless solid in good overall yield (95%). Again, the progress of this transformation was readily assessed by ^{31}P NMR spectroscopy. The product salt **10a** displayed a ^{31}P resonance at δ −112.8 ppm, and the proton-coupled spectrum appeared as a triplet with P−H coupling constant J_{PH} = 203 Hz. Prior to reaction completion, the inter-

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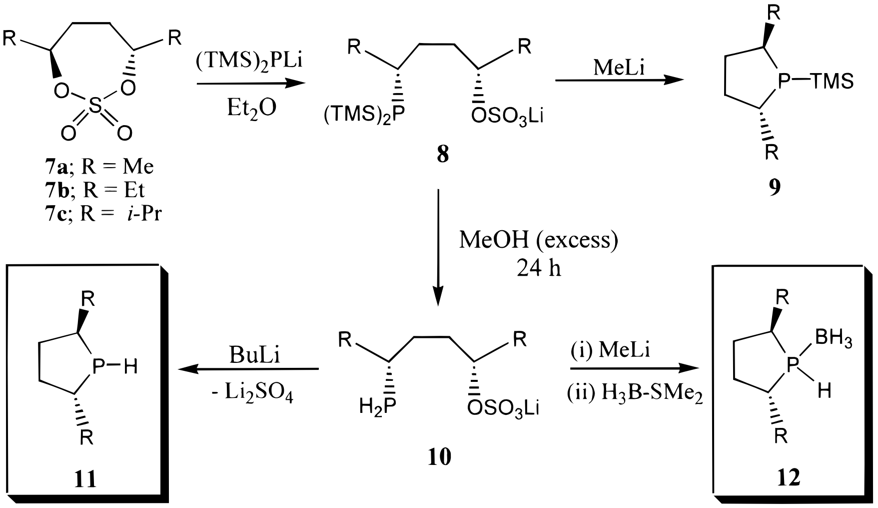
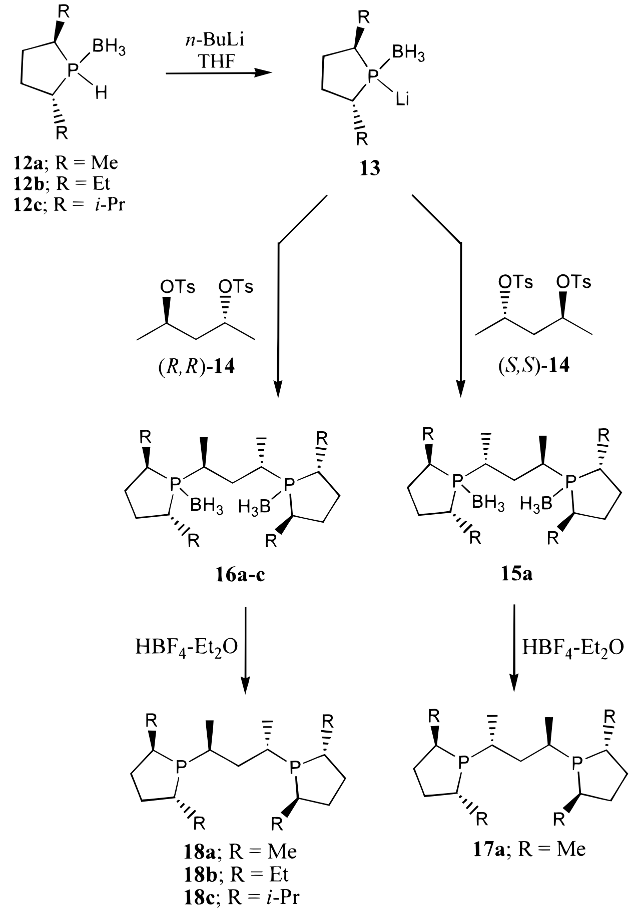
Scheme 2. Preparation of Chiral Secondary Phospholanes 11 and Borane Adducts 12



Scheme 3. Preparation of Diastereomeric Bis(phospholane) Ligands 17 and 18



mediate species possessing a $-P(H)(SiMe_3)$ unit could be detected as a pair of diastereoisomers exhibiting ^{31}P resonances at δ −120.5 ppm and δ −129.7 ppm. The proton-coupled spectrum of this intermediate species showed the expected pair of doublets with P−H coupling constants of J_{PH} = 185 and 169 Hz, respectively.

With the intermediate **10a** in hand, we next realized a straightforward route to the desired secondary phospholane **11a** through simple treatment of the salt **10a** with 1 equiv of *n*-BuLi or MeLi in diethyl ether. This versatile reaction was found to furnish **11a** ($^{31}P\{^1H\}$ NMR (C_6D_6) δ −29.8 ppm (J_{PH} = 190 Hz)) cleanly in high yield with only lithium sulfate as a byproduct. As the secondary phosphines of type **11** previously were found tedious to isolate due to high volatility and sensitivity to oxygen, we preferred to convert **11a** to the stable borane adduct **12a**, which was readily prepared through addition of $H_3B{\cdot}SMe_2$ to a solution of **11a**. Importantly, at no point in the sequence was loss of stereochemical purity apparent, and the borane adduct **12a** was isolated in enantiomerically pure form.

Once the route detailed in Scheme 2 was established as viable for the synthesis of **11a** and **12a**, we next attempted to prepare a series of borane adducts **12**. Moreover, in contrast to the stepwise procedure that was originally employed, a convenient one-pot sequence was introduced which required no isolation or purification of intermediates **8**, **10**, or **11**. Hence, reaction between $(TMS)_3P$ with MeLi rendered the requisite phosphide $(TMS)_2PLi$, which upon addition of cyclic sulfates **7** yielded **8**. Subsequent addition of excess methanol to the solution of **8** provided **10**. Following evaporation of volatiles and reintroduction of diethyl ether solvent, the phosphine **10** was reacted sequentially with 1 equiv of MeLi and then borane−dimethyl sulfide, to provide the desired borane adducts **12** in good overall isolated yields. The enantiomerically pure phospholanoborane adducts **12** thus obtained were found stable to air and were easily isolated and fully characterized.

Chiral Backbone Ligands. Preparation of the desired bis(phospholane) ligands containing a chiral 2,4-pentane backbone structure required reaction between a suitable phospholane-based nucleophile and an enantiomerically pure bis-electrophile. The choice of electrophile was straightforward, and the bis(tosylate) derivative of commercially available (*S*,*S*)-2,4-pentanediol was utilized for this purpose. In terms of phospholane nucleophiles, we initially attempted to react (*S*,*S*)-2,4-pentanediol ditosylate ((*S*,*S*)-**14**) with the phosphide **6** formed by deprotonation of the secondary phospholane **11** using *n*-BuLi. Unfortunately, only intractable mixtures were formed in this reaction and no conditions could be found which cleanly provided the desired bis(phospholane) ligands. As previously alluded to, dialkylphosphides are rather basic nucleophiles and, in addition to engaging in nucleophilic displacement reactions, are well-documented to undergo a range of undesirable reactions with electrophiles, including elimination, metal−halogen exchange, and electron-transfer reactions.[22] On the basis of these results, we sought to use the less reactive borane−phospholide nucleophiles.

Borane adducts of phosphides, and particularly dialkylphosphides, recently have found wide application as highly nucleophilic species that display substantially reduced basicity.[19] Upon examination of the phospholane borane adducts **12** in the above reaction, we found far superior results (Scheme 3). Thus, deprotonation of **12a** (R = Me) in THF with 1 equiv of *n*-BuLi afforded a solution of the boronated lithium phosphide **13a**. Subsequent addition of a THF solution of the ditosylate (*R*,*R*)-**14** to **13a** provided after 48 h the desired 2,4-bis(phospholano)pentane ligand as the bis(borane) adduct **16a** (R = Me) in good isolated yield (75%). The bis(borane) adducts **16b** (R = Et) and **16c** (R = *i*-Pr) were obtained by the same procedure through condensation between (*R*,*R*)-**14** and the corresponding borano-phospholides **13b** and **13c**. Analogously, the diastereomeric form of the bis(boronated) ligand **15a** was prepared through reaction between **13a** and the antipodal electrophile (*S*,*S*)-**14.**

Liberation of free phosphines by removal of borane from phosphine−borane adducts previously has been reported using both basic (e.g., NEt_2H) and acidic (e.g., CF_3SO_3H, HBF_4) conditions.[19] We have found that the 2,4-bis(phospholano)pentane ligands **17** and **18** could be obtained directly in a high state of purity through treatment with tetrafluoroboric acid−diethyl etherate in dichloromethane,[19d,e] followed by neutralization with sodium bicarbonate (Scheme 3).

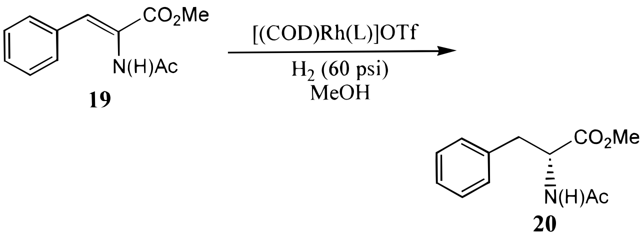
The availability of diastereomeric bis(phospholane) ligands **17** and **18** raised several interesting questions. For instance, we wondered how the different diastereomers would perform comparatively in catalysis. Would we see significant matching and mismatching effects associated with the reactivity and selectivity of catalysts bearing the diastereomeric ligands? Would the most reactive diastereomeric catalyst also correspond to the most selective catalyst, or would these two properties be independent? And finally, if different selectivity or reactivity was observed, could we relate the disparate chemical properties to specific structural aspects of the two diastereomeric catalyst systems?

Catalytic Hydrogenation Studies. Our initial studies involving the ligands **17** and **18** focused upon asymmetric catalytic hydrogenation reactions. Accordingly, we have prepared a range of rhodium complexes through standard procedures involving reaction between each of the available diastereomeric bis(phospholane) ligands and the precursor complex $[(COD)_2Rh]OTf$ in tetrahydrofuran.[11b] The complexes of general structure [(COD)Rh(bis-phospholane)]OTf were isolated in high yield as orange crystalline solids. As shown below, these complexes serve as efficient hydrogenation catalyst precursors.

α-Enamides. To compare the competence of the two diastereomeric catalyst systems bearing ligands of type **17** and **18**, we first examined asymmetric hydrogenation of the model enamide substrate α-*N*-(acetylamino)cinnamic acid methyl ester (**19**).

Table 1. Asymmetric Hydrogenation of α-*N*-Acetylcinnamic Acid Methyl Ester 19

entry	ligand	% ee	abs confign
1	**17a**	71	*R*
2	**18a**	82	*R*
3	**1a**	60	*R*



The two diastereomeric catalyst precursors that we scrutinized for efficacy in the hydrogenation of **19** were the cationic complexes [(COD)Rh(**17a**)]OTf (**17a**-Rh) and [(COD)Rh(**18a**)]OTf (**18a**-Rh). Both catalysts were found effective for this hydrogenation in methanol, allowing complete conversion to **20** over 12 h at S/C = 500. The enantioselectivities achieved in these reactions are shown in Table 1. The catalyst containing ligand **18a** was found to afford the product **20** with higher enantioselectivity (82% ee), suggesting that this ligand represents the desired matched combination of stereochemical elements. Interestingly, the analogous catalyst bearing the parent bis(phospholano)propane ligand (*R*,*R*)-**1a** (R = Me, unsubstituted backbone) performed relatively poorly in this reaction (60% ee, entry 3). Another important finding was that in each case the same enantiomer of product was formed, regardless of the overall backbone stereochemistry. Each of the ligands **17a**, **18a**, and **1a** contain 2,5-dimethylphospholane moieties with *R* absolute configuration at the 2,5-positions. That the catalyst bearing the parent ligand (*R*,*R*)-**1a** afforded (*R*)-**20** reconfirms the previously observed inherent *R* stereocontrol of (*R*,*R*)-phospholanes in the hydrogenation of enamides.[11] It may be deduced that the phospholane chirality determines the absolute stereochemistry observed in hydrogenations when using ligands **17** and **18** and that the phospholane chirality overrides any bias imposed by the backbone chirality in these ligands.

We also have performed a comparative examination of the cationic catalysts **17a**-Rh and **18a**-Rh in the hydrogenation of *β*,*β*-disubstituted enamide **21**. Hydrogenation of *β*,*β*-disubstituted enamides is known to be challenging in terms of both reaction rates and enantioselectivities. Only recently have catalysts appeared that furnish relatively high enantioselectivities.[11c,23] Rates, however, remain low in these reactions, thus severely limiting the practical utility of known catalysts. The development of catalysts that offer both high rates and high selectivities would represent a significant practical advance.

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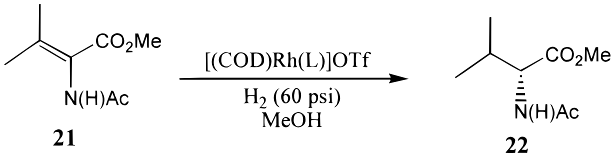
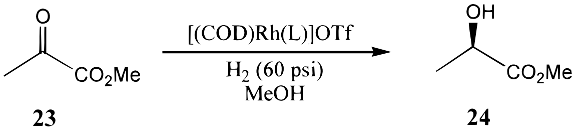
[23] (a) Sawamura, M.; Kuwano, R.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9602. (b) Imamoto, T.; Watanabe, J.; Wada, Y.; Masuda, H.; Yamada, H.; Tsuruta, H.; Matsukawa, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 1635. (c) Yamanoi, Y.; Imamoto, T. *J. Org. Chem.* **1999**, *64*, 2988.

Scheme 4. Matching and Mismatching Effects in Hydrogenation of Enamide 21



Entry	Ligand	% ee	Abs. Conf.
1	**17a**	25	*R*
2	**18a**	78	*R*

Table 2. Asymmetric Hydrogenation of Methyl Pyruvate 23[a]



entry	ligand	solvent	% ee	abs confign
1	**17a**	MeOH	19	*R*
2	**17a**	THF	43	*R*
3	**18a**	MeOH	24	*R*
4	**18a**	DME	76	*R*
5	**18a**	THF	75	*R*
6	**18b**	THF	78	*R*
7	**18c**	THF	54	*S*
8	**1a**	THF	5	*R*

[a] Reactions were carried out at room temperature under an initial H_2 pressure of 60 psig and 0.2 M solutions of substrate using the catalyst precursors $[(COD)Rh(P_2)]OTf$ (0.2 mol %) for 12 h. Enantiomeric excesses were determined by chiral GC (Macherey Nagel FS-Lipodex A, 60 °C).

As shown in Scheme 4, hydrogenation of enamide **21** proceeded readily over 12 h under mild conditions (20 °C, S/C = 500, 60 psi of H_2) to afford the *N*-acetylvaline methyl ester **22** in quantitative yield. Substantially greater matching and mismatching effects were observed in asymmetric hydrogenation of β,β-disubstituted enamide **21**, relative to enamide **19**. The catalyst containing ligand **17a** was found to be far inferior to the diastereomeric catalyst **18a**-Rh, which provided the reduced product **22** in 78% ee. These results, combined with those listed in Table 1, suggested that the desired matched ligand system was **18a** comprised of (*R*,*R*)-phospholane units tethered with an (*S*,*S*)-2,4-pentane bridge.

The stereochemical elements within ligand **18a** appear to cooperate most effectively to provide the highest selectivities. To further explore and optimize these systems, we examined a homochiral series of ligands **18** that possessed different alkyl substitutents attached to the 2,5-positions of the phospholanes (see Scheme 3).

α-Keto Esters. Our main objective in this program was to develop catalysts that may allow both efficient and enantioselective hydrogenation of α-keto esters. Toward this end, we next examined the asymmetric hydrogenation of methyl pyruvate **23** to methyl lactate **24** using a range of cationic rhodium catalysts bearing the ligands **17** and **18**. Results of these studies are shown in Table 2.

These hydrogenations proceeded smoothly to completion within 12 h under very mild conditions (20 °C, S/C = 500, 60 psi of H_2). As can be seen from the first four entries, the effect of solvent was found to be dramatic in these reactions. Relatively poor selectivities were observed in protic alcohols, whereas the highest enantioselectivities were achieved in polar ethereal solvents such as DME and THF. As we observed in the hydrogenation of enamides **19** and **21**, the superior (matched) ligand system for this reaction was found to be **18**. In fact, the catalyst **18a**-Rh afforded the reduced product **24** in up to 76% ee. Again, the phospholane stereochemistry dominated over the backbone chirality, as both catalysts **17a**-Rh and **18a**-Rh afforded methyl lactate **24** with the same *R* absolute configuration.

In the DuPHOS and BPE ligand series, we have found that ee's and rates may be optimized simply by varying the phospholane R substituents, thereby matching the sterics of the ligand to the steric demands of the substrates under scrutiny.[24] Hence, we next assessed the influence of increasing the size of the 2,5-alkyl substituents attached to the phospholane rings of the matched ligand **18**. As can be seen, increasing the size of the phospholane substituents of **18** from Me to Et led to a slight increase in the selectivity (78% ee), while moving to the more sterically encumbering *i*-Pr groups resulted in a diminution of stereocontrol (entry 7; 54% ee). Importantly, however, in all cases the ee's achieved in hydrogenation of methyl pyruvate using the new catalysts **17**-Rh and **18**-Rh were much higher than the selectivity observed upon use of the parent catalyst derived from unsubstituted propano-bridged ligand **1** (entry 8; 5% ee).

The enantioselectivities achieved in hydrogenation of methyl pyruvate using the cationic catalysts **18a**-Rh and **18b**-Rh are considerably higher than other cationic Rh catalysts attempted to date. Neutral ruthenium[7] and rhodium[8] catalysts previously have allowed higher ee's to be achieved, but only at very low rates (2−3 days) under rather harsh conditions (20−30 atm of hydrogen pressure).

X-ray Crystallography. We sought to obtain structural information regarding the asymmetric environments imposed by the diastereomeric ligands **17** and **18**. We were interested in gaining insight concerning the differences that may exist between the diastereomeric ligands and how they coordinate to transition metals. We also hoped that certain solid-state structural features may be correlated with the results achieved in hydrogenation reactions. It is important to note that such a correlation is not a mechanistic proposal. Ultimately, we anticipated that such studies may qualitatively facilitate and guide our efforts to design improved catalysts that exhibit both high rates and high selectivities in α-keto ester hydrogenations.

Cationic rhodium complexes bearing the two ligands **17a** and **18a** were prepared and recrystallized from a mixture of dichloromethane and diethyl ether to afford crystals suitable for X-ray diffraction studies. The complexes [(COD)Rh(**17a**)]OTf (**17a**-Rh) and [(COD)Rh(**18a**)]OTf (**18a**-Rh) were characterized by X-ray crystal-

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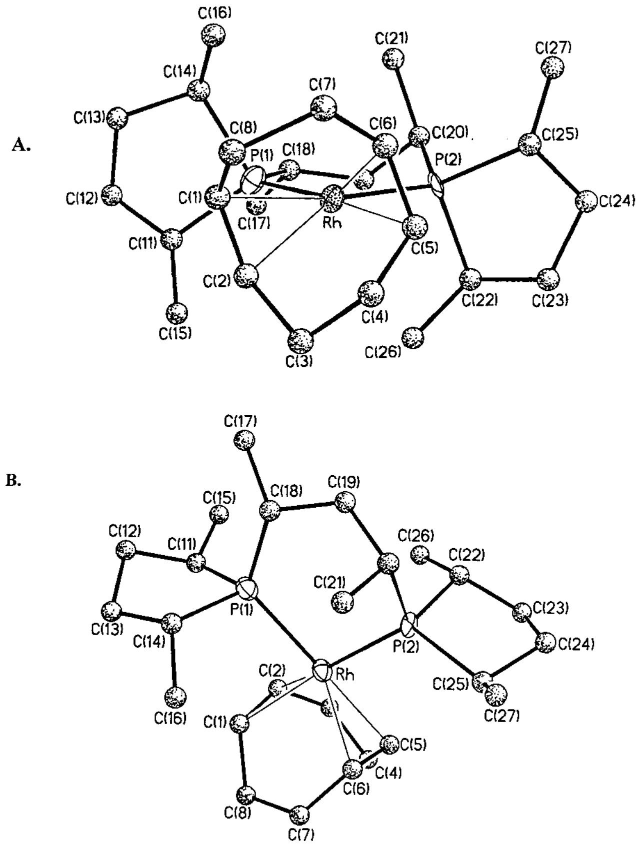

Figure 3. ORTEP diagram (30% probability thermal ellipsoids) of the catalyst precursor [(COD)Rh(**17a**)]OTf (**17a**-Rh): (A) front view, showing orientation of phospholane groups and backbone conformation; (B) top view, showing distortion of phospholane groups. The triflate counterion and hydrogen atoms have been omitted for clarity.

lography, and the ORTEP diagrams are displayed in Figures 3 and 4, respectively. Selected interatomic distances and intramolecular angles are provided in Tables 3 and 4. Crystallographic data for complexes **17a**-Rh and **18a**-Rh are provided in Table 5.

The environment around rhodium for both **17a**-Rh and **18a**-Rh is a distorted square plane. Both complexes were found to pack without significant inter-ion contacts in the same chiral space group ($P2_12_12_1$), and both complexes are therefore resolved in the solid state. For **17a**-Rh, the asymmetric unit contains three independent, but chemically equivalent, ion pairs, and this complex packs slightly more efficiently ($\rho = 1.489$ g cm^{-3} at 218 K) than **18a**-Rh ($\rho = 1.474$ g cm^{-3} at 218 K), which has two independent, but chemically equivalent, ion pairs in the asymmetric unit. The three independent ion pairs of **17a**-Rh are arranged along the *c* axis in nearly identical orientations, giving rise to the appearance of a superlattice-like packing (see the packing diagram in the Supporting Information). A consequence of a superlattice is that the average I/σ value for the reflection data is very low (1.6) and the bond metric parameters have higher than normal esd's. The overall weakness derives from the fact that two-thirds of the reflections are inherently weak because the only contributors to them are the minor differences between the members of the asymmetric unit. In contrast, the independent molecules of **18a**-Rh show no apparent relationship and, therefore, do not give rise to superlattice-like behavior.

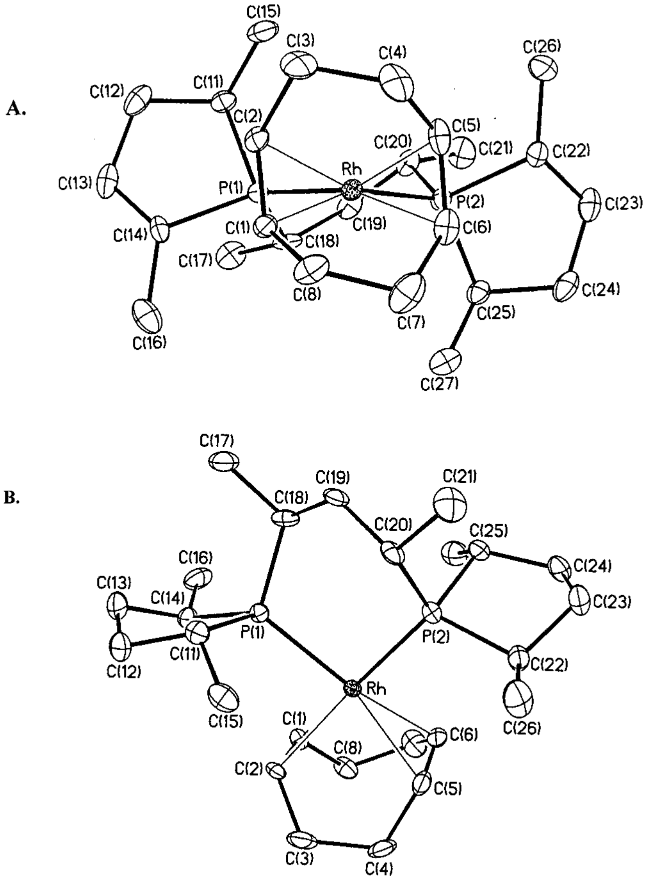

Figure 4. ORTEP diagram (30% probability thermal ellipsoids) of the catalyst precursor [(COD)Rh(**18a**)]OTf (**18a**-Rh): (A) front view, showing the orientation of phospholane groups and backbone conformation; (B) top view, showing the twisting of the phosphoane group. The triflate counterion and hydrogen atoms have been omitted for clarity.

Table 3. Selected Interatomic Distances (Å) and Intramolecular Angles (deg) for [(COD)Rh(17a)]OTf

	Interatomic Distances		
Rh(1)−P(1)	2.362(8)	Rh(1)−C(5)	2.27(2)
Rh(1)−P(2)	2.274(7)	Rh(1)−C(6)	2.13(2)
Rh(1)−C(1)	2.31(2)	C(1)−C(2)	1.42(3)
Rh(1)−C(2)	2.20(3)	C(5)−C(6)	1.40(3)
	Intramolecular Angles		
P(1)−Rh−P(2)	93.2(3)	C(2)−Rh−C(5)	81.5(10)
C(1)−Rh−C(5)	89.8(9)	C(2)−Rh−C(6)	93.9(10)
C(1)−Rh−C(6)	79.3(8)		

Table 4. Selected Interatomic Distances (Å) and Intramolecular Angles (deg) for [(COD)Rh(18a)]OTf

	Interatomic Distances		
Rh(1)−P(1)	2.319(2)	Rh(1)−C(5)	2.245(7)
Rh(1)−P(2)	2.299(2)	Rh(1)−C(6)	2.218(7)
Rh(1)−C(1)	2.235(7)	C(1)−C(2)	1.371(9)
Rh(1)−C(2)	2.234(7)	C(5)−C(6)	1.399(10)
	Intramolecular Angles		
P(1)−Rh−P(2)	89.71(7)	C(2)−Rh−C(5)	79.7(3)
C(1)−Rh−C(5)	85.6(3)	C(2)−Rh−C(6)	95.0(3)
C(1)−Rh−C(6)	79.1(3)		

The hydrogenation results presented above have led us to suggest that ligand **17** possesses a *mismatched*

Table 5. Crystallographic Data for [(COD)Rh(17a)]OTf (17a-Rh) and [(COD)Rh(18a)]OTf (18a-Rh)

	17a-Rh	**18a**-Rh
formula	$C_{26}H_{46}F_3O_3P_2RhS$	$C_{26}H_{46}F_3O_3P_2RhS$
fw	660.54	660.54
space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	11.4184(2)	15.9738(6)
b, Å	26.6953(4)	18.1865(6)
c, Å	28.9991(7)	20.4938(8)
V, Å^3	8839.4(4)	5953.6(4)
Z	12	8
cryst color, habit	orange block	orange blade
D(calcd), g cm^3	1.489	1.474
μ(Mo Kα), cm^{-1}	8.04	7.96
temp, K	218(2)	218(2)
diffractometer	Siemens P4/CCD	
radiation	Mo Kα (λ = 0.710 73 Å)	
R(*F*), %^{a}	7.63	6.25
$R_w(F^2)$, %^{a}	17.38	8.74

^{a} Quantity minimized = $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$. $R = \sum\Delta/\sum(F_o)$. $\Delta = |(F_o - F_c)|$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = [2F_c^2 + \mathrm{Max}(F_o, 0)]/3$.

arrangement of stereochemical elements, while **18** is the *matched* ligand. Structural characterization of rhodium complexes containing diastereomeric ligands **17a** and **18a** reveals that the two different ligands display dissimilar backbone conformations in the solid state. In both cases, the configuration of the phospholane units remains constant and, therefore, the ligand backbone conformation apprently depends on the relative stereochemistries and the associated steric interactions that exist between the backbone and phospholane stereogenic centers.

When a 1,3-bis(phosphino)propane type ligand (P−C−C−C−P) coordinates to a metal center, the ligand−metal fragment may adopt two limiting conformations, namely skew and chair.[25] The two conformations influence the orientation of the remaining groups attached to phosphorus (i.e., the phenyl groups in BDPP or the phospholane groups in **1**). Below we examine various differences that exist between the two diastereomeric structures **17a**-Rh and **18a**-Rh.

As can be seen in Figure 3, the bis(phospholane)−metal fragment of mismatched complex **17a**-Rh adopts a distorted chair conformation with the backbone methyl groups occupying axial and equatorial positions, in a fashion similar to that observed in the cationic complex [(NBD)Rh(BDPP)]$^+$.[26] The chair conformation of **17a**-Rh effectively precludes the C_2 symmetry element that may have been expected for this complex. From the front view shown in Figure 3A, one can observe that the chair conformation produces an angular disposition of the two phospholane groups about rhodium. This angular disposition is at variance with the parallel orientation of phospholanes usually observed in the analogous bidentate BPE-Rh and DuPHOS-Rh complexes.[11b] Such an angular disposition of phospholane units leads to a slight displacement of the methyl groups of one phospholane moiety away from the metal center. In contrast, the rhodium complex bearing phosphine **18a** (Figure 4) adopts a skew conformation with both methyl groups of the backbone tether in the more favorable equatorial position, analogous to the complex [(COD)Rh(BDPP)]$^+$.[25] As can be seen from the front view (Figure 4A), the matched complex **18a**-Rh is ostensibly C_2-symmetric with the two phospholane units oriented roughly parallel to each other, analogous to the BPE-Rh and DuPHOS-Rh complexes.

A second notable structural difference is associated with the dihedral angle between the planes defined by the chelating bis(phospholane) ligand (P−Rh−P) and the midpoints of the COD ligand (cent(1,2)−Rh−cent(5,6)). Previously, attempts have been made to correlate this dihedral angle and the sense of twist of the COD ligand with effectiveness and the stereochemical course to be expected in asymmetric hydrogenation reactions.[27] The dihedral angles for the three independent cations of the mismatched complex **17a**-Rh are 18.4, 17.7, and 21.9° for Rh, Rh′, and Rh″, respectively. The rather large twisting of the ligand planes in **17a**-Rh appears to be caused by intramolecular steric forces focused on the C(1)−C(16) interaction between ligands (the average distance for three independent cations is 3.5 Å). The dihedral angle of **17a**-Rh is comparable to those previously observed in the structurally characterized complexes [(COD)Rh((*R*,*R*)-Me-BPE)]$^+$ (24.2°)[12a] and [(COD)-Rh((*R*,*R*)-*i*-Pr−BPP)]$^+$ (24.6°).[12b] Interestingly, and in contrast, the independent cations of the matched complex **18a**-Rh, which packs as multiples of 2, displays small dihedral angles of 2.3 and 2.9° for Rh and Rh′, respectively. These values are closer to that observed for the structurally rigid complex [(COD)Rh((*S*,*S*)-Me-DuPHOS)]$^+$SbF$_6^-$ (dihedral angle 5.9°).[11b] Taken together, the data collected thus far for bis(phospholane)-rhodium complexes ostensibly suggest that cationic precursor complexes of the type [(COD)Rh(bis-phospholane)]X displaying small dihedral angles (<8°) are superior catalysts for asymmetric catalytic hydrogenation.

Another marked feature is the relative angle of twisting between the two phospholane moieties of the matched structure **18a**-Rh (Figure 4B, top view). The relative twist of the two phospholane groups of **17a**-Rh is less acute, as can be seen in Figure 3B. Such a twisting phenomenon could be associated with the divergent enantioselectivities observed for these catalyst systems. The great degree of twisting observed between the phospholane groups of **18a**-Rh may be attributed to severe steric interactions that occur, for instance, between the backbone methyl group C(21) and the phospholane methyl group C(26). This analysis suggests that increasing the size of the backbone substituents of ligand **18** may lead to a greater degree of phospholane twisting and possibly higher selectivities in catalysis.

The final structural aspect for comparison is the bite angle exhibited by the phosphines in the two complexes. As previously mentioned, recent reports have highlighted the important role that ligand bite angles may play in determining selectivity and reactivity in catalysis.[15] In the present complexes, we find that the mismatched complex **17a**-Rh exhibits a distorted chair-

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(26) Bakos, J.; Toth, I.; Heil, B.; Szalontai, G.; Parkanyi, L.; Fulop, V. *J. Organomet. Chem.* **1989**, *370*, 263.

(27) (a) Kyba, E. P.; Davis, R. E.; Juri, P. N.; Shirley, K. R. *Inorg. Chem.* **1981**, *20*, 3616. (b) Armstrong, S. K.; Brown, J. M.; Burk, M. J. *Tetrahedron Lett.* **1993**, *34*, 879.

type conformation with a ligand bite angle of 93.2°, while the matched complex **18a**-Rh displays a skew conformation with a ligand bite angle of 89.7°. To avoid confusion, these values are limited to one of the independent cations for both **17a**-Rh and **18a**-Rh because of the variation in the bond metric parameters for **17a**-Rh. It is interesting to compare these bite angle values with that observed in the analogous Rh complex possessing the ligand 1,3-bis(2,5-diisopropylphospholano)propane (**1**, R = *i*-Pr; bite angle 95.2°).[12b] These structural observations are consistent with those seen with the cationic complexes [(skewphos)Rh(diolefin)]$^+$ (skewphos = 1,3-bis(diphenylphosphino)butane; diolefin = NBD, 1,5-COD), where skew conformations often presented smaller bite angles.[28] The best results in the enantioselective hydrogenations above appear to derive from the matched ligands **18**, which also exhibit a skew conformation and the smallest bite angles.

Summary and Conclusions. The overall objective of the present study was to develop an efficacious catalyst system that allows the hydrogenation of α-keto acid derivatives with both high catalytic rates and high enantioselectivities. The strategy was based upon previous results indicating that electron-rich, flexible ligands are useful for rhodium-catalyzed ketone hydrogenation processes. Toward this end, we have prepared a range of new bis(phospholane) ligands **17** and **18** that are tethered by a chiral 2,4-pentane backbone structure. Cationic rhodium catalysts bearing the two diastereomeric ligand systems were examined for effectiveness in hydrogenation reactions. Substantially higher enantioselectivities were achieved using these new ligands, relative to the analogous bis(phospholane) ligands, such as **1** and **2**, bearing achiral backbones. Moreover, the selectivity data revealed significant matching and mismatching effects between the different stereochemical elements within the diastereomeric ligands **17** and **18**. The *matched* ligand system was found to be **18**, which afforded much higher enantioselectivities in hydrogenation of enamides and methyl pyruvate.

The cationic catalysts reported herein (**18**-Rh) are promising from a practical standpoint, due to the relatively high catalytic activity these systems display. The selectivity results also suggest that we may be moving in a rational fashion toward our goal. The crystal structures of diastereomeric complexes **17a**-Rh and **18a**-Rh were analyzed, and the catalytic data were correlated with specific structural features associated with the two different catalyst systems. In an effort to further optimize these catalysts, we plan to further reduce the conformational mobility of the ligand through introduction of bulkier substituents into the ligand backbone structure.

Experimental Section

General Procedures. All reactions and manipulations were performed under nitrogen either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques. Benzene, diethyl ether (Et$_2$O), tetrahydrofuran (THF), hexanes, and pentane were distilled from sodium−benzophenone ketyl under nitrogen. Methylene chloride (CH$_2$Cl$_2$) was distilled from CaH$_2$ and methanol (MeOH) from Mg(OMe)$_2$. Hydrogen gas (99.99%) was purchased from National Welders, Inc. (Raleigh, NC), and used as received. All reagents were purchased from commercial suppliers and used as received.

GC analyses were performed by using Hewlett-Packard Model HP 5890 Series II GC. HPLC analyses were performed using a Hewlett-Packard Model HP 1090 Series II LC interfaced to a HP Vectra 486/66U computer workstation. HRMS data was obtained using a JEOL JMS-SX 102A mass spectrometer. NMR spectra were obtained on a Varian XL-400 (400 MHz, ^{1}H; 161 MHz, ^{31}P; 100 MHz, ^{13}C) spectrometer with chemical shifts reported in ppm (δ) relative to Me$_4$Si or residual protons in the solvent. Elemental analyses were performed by Atlantic Microlab, Norcross, GA, or by the Analytical Service of the Instituto de Investigaciones Químicas-CSIC.

2,5-Dialkylphospholane−Boranes 12. All these compounds were prepared in a one-pot reaction from P(TMS)$_3$ and the appropriate cyclic sulfate following a similar procedure. Preparation of (*R,R*)-2,5-diethylphospholane−borane is exemplified below. To a solution of 6.0 mmol (1.5 g) of P(TMS)$_3$ in 200 mL of THF was added 6.3 mmol of MeLi (4.5 mL, 1.4 M solution in diethyl ether). The solution was stirred for 12 h, and the volatiles were removed. The white solid residue was redissolved in diethyl ether (ca. 200 mL), giving a yellow solution, and 1.25 g (6.0 mmol) of (*S,S*)-3,6-octanediol cyclic sulfate was added slowly, decolorizing the solution. The mixture was stirred for 2 h, and subsequently 5 mL of methanol was added slowly. After the mixture was stirred for 24 h, careful removal of volatiles yielded the corresponding phosphine−sulfate **10b** (1.4 g, 95%) as a white solid. The resulting product was suspended in 200 mL of diethyl ether, a stoichiometric amount of MeLi (4.1 mL, 1.4 M Et$_2$O solution) was added, and the resulting mixture was stirred for 2 h. Then, the suspension was cooled at 0 °C and 4 equiv of BH$_3$·SMe$_2$ added. The reaction mixture was warmed to room temperature and stirred for 12 h. Volatiles were removed under vacuum, and the resulting residue was extracted in hexanes and the extract filtered through a short pad of silica. Evaporation of the solvent yielded (*R,R*)-2,5-diethylphospholaneborane **12b** as a colorless oil (0.6 g, 63%). All yields are based upon starting P(SiMe$_3$)$_3$.

(*R,R*)-2,5-Dimethylphospholane−Borane (12a). Yield: 60%. $[\alpha_D^{20}] = 3.3$ ($c = 0.15$, CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ 0.1−1.0 (br q, 3H), 1.24 (dd, $J_{HP} = 17.2$ Hz, $J_{HH} = 6.8$ Hz, 3H), 1.32 (dd, $J_{HP} = 15.8$ Hz, $J_{HH} = 7.0$ Hz, 3H), 1.40 (m, 2H), 2.15 (m, 3H), 2.50 (m, 1H), 4.33 (dq, $J_{HP} = 348$ Hz, $J_{HH} = 7.2$ Hz, 1H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 25.8 (q, $J_{PB} = 44$ Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 15.1 (d, $J_{CP} = 4$ Hz), 16.8 (s), 27.0 (d, $J_{CP} = 34$ Hz), 32.3 (d, $J_{CP} = 36$ Hz), 35.6 (s), 35.7 (d, $J_{CP} = 3$ Hz). HRMS (EI, direct insert): *m/z* 129.1009, (M − H)$^+$ (exact mass calculated for C$_6$H$_{15}$PB 129.1004).

(*R,R*)-2,5-Diethylphospholane−Borane (12b). Yield: 63%. $[\alpha_D^{20}] = 30.9$ ($c = 0.6$, CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ 0.1−1.0 (br q, 3H), 1.01 (t, $J_{HH} = 7.6$ Hz, 3H), 1.05 (t, $J_{HH} = 7.6$ Hz, 3H), 1.37 (m, 2H), 1.57 (m, 2H), 1.78 (m, 2H), 1.98 (m, 1H), 2.42 (m, 3H), 4.43 (dq, $J_{HP} = 348$ Hz, $J_{HH} = 6.8$ Hz, 1H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 16.9 (q, $J_{PB} = 45$ Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 13.6 (d, $J_{CP} = 8$ Hz), 13.7 (d, $J_{CP} = 8$ Hz), 23.2 (d, $J_{CP} = 15$ Hz), 26.2 (d, $J_{CP} = 10$ Hz), 33.1 (d, $J_{CP} = 3$ Hz), 33.2 (s), 35.0 (d, $J_{CP} = 34$ Hz), 39.7 (d, $J_{CP} = 36$ Hz). HRMS (EI, direct insert): *m/z* 144.1067, (M − BH$_3$)$^+$ (exact mass calculated for C$_8$H$_{17}$P 144.1067).

(*R,R*)-2,5-Diisopropylphospholane−Borane (12c). A somewhat modified procedure was used in this case. The (*S,S*)-2,5-diisopropylphospholane **11c** produced after MeLi-induced cyclization was purified from the reaction media by trap-to-trap distillation. Subsequent treatment of **11c** with BH$_3$·SMe$_2$ as described above followed by column chromatography using a EtOAc−hexanes (15:1) mixture as eluent afforded the corresponding phospholane−borane **12c** (25%). $[\alpha_D^{20}] = -81.2$

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[28] Bakos, J.; Toth, I.; Szalontai, G.; Fulop, V.; Heil, B. *J. Organomet. Chem.* **1989**, *371*, 101.

(c = 0.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.1−0.7 (br q, 3H), 1.06 (d, J_{HH} = 6.0 Hz, 3H), 1.00 (d, J_{HH} = 6.4 Hz, 3H), 1.06 (d, J_{HH} = 6.8 Hz, 3H), 1.08 (d, J_{HH} = 6.8 Hz, 3H), 1.25−1.51 (m, 3H), 1.72−1.83 (m, 1H), 1.88−2.28 (m, 4H), 4.60 (dq, J_{HP} = 348 Hz, J_{HH} = 6.0 Hz 1H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 7.2 (q, J_{PB} = 50 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.4 (s), 21.5 (d, J_{CP} = 3 Hz), 22.7 (d, J_{CP} = 4 Hz), 23.7 (d, J_{CP} = 4 Hz), 28.3 (d, J_{CP} = 4 Hz), 31.1 (d, J_{CP} = 6 Hz), 31.9 (s), 32.2 (d, J_{CP} = 3 Hz), 42.4 (d, J_{CP} = 34 Hz), 45.8 (d, J_{CP} = 37 Hz). HRMS (EI, direct insert): m/z 172.1380, $(M - BH_3)^+$ (exact mass calculated for $C_{10}H_{21}P$ 172.1381).

Preparation of Bis(phospholane−boranes) 15 and 16. These compounds were prepared by deprotonation of the 2,5-dialkylphospholane−boranes **12** and condensation of the resulting phosphide−borane (**13**) with the appropriate ditosylate of 2,5-pentanediol. Preparation of (S,S)-2,4-bis[(R,R)-2,5-diethylphospholane−borane]pentane (**16b**) is exemplified below. (R,R)-2,5-diethyl-phospholaneborane **12b** (190 mg, 1.2 mmol) was dissolved in 20 mL of THF, and 1.05 equiv of BuLi (0.75 mL, 1.6 M solution in hexanes) were added. The mixture was stirred for 1 h at room temperature, and 235 mg (0.57 mmol) of (R,R)-2,4-pentanediol ditosylate ((R,R)-**14**) was added. The reaction mixture was stirred for 2 days, and the solvent was then evaporated in vacuo. The residue is redissolved in 10 mL of diethyl ether and filtered through a short pad of silica. Solvent removal followed by recrystallization from a 1:1 diethyl ether−hexanes mixture yielded 164 mg of 2,4-(S,S)-bis[(R,R)-2,5-diethylphospholane−borane]pentane (**12b**) in 75% yield.

(R,R)-2,4-Bis[(R,R)-2,5-dimethylphospholane−borane]pentane (15a). Yield: 70%. $[\alpha_D{}^{20}]$ = 44.0 (c = 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ −0.1−0.8 (br q, 6H), 1.16 (dd, J_{HP} = 15.2 Hz, J_{HH} = 6.8 Hz, 6H), 1.26 (dd, J_{HP} = 15.2 Hz, J_{HH} = 6.5 Hz, 6H), 1.28 (dd, J_{HP} = 13.0 Hz, J_{HH} = 7.8 Hz, 6H), 1.36 (m, 6H), 1.62 (m, 2H), 2.10 (m, 8H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 48.0 (br m). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.3 (s), 14.4 (s), 15.7 (s), 22.8 (dd, J_{CP} = 43, 18 Hz), 30.9 (s), 31.5 (d, J_{CP} = 33 Hz), 34.2 (d, J_{CP} = 3 Hz), 34.7 (d, J_{CP} = 33 Hz), 35.1 (s). HRMS (EI, direct insert): m/z 327.2707, $(M - H)^+$ (exact mass calculated for $C_{17}H_{39}P_2B_2$ 327.2713).

(S,S)-2,4-Bis[(R,R)-2,5-dimethylphospholane−borane]pentane (16a). Yield: 75%. $[\alpha_D{}^{20}]$ = −39.3 (c = 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ −0.1−0.9 (br q, 6H), 1.13 (dd, J_{HP} = 13.6 Hz, J_{HH} = 6.8 Hz, 6H), 1.24 (dd, J_{HP} = 12.4 Hz, J_{HH} = 6.8 Hz, 6H), 1.29 (dd, J_{HP} = 13.0 Hz, J_{HH} = 7.8 Hz, 6H), 1.36 (br m, 4H), 1.83 (br m, 2H), 1.96 (br m, 2H), 2.11 (br m, 8H); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 47.5 (br m). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 12.8 (s), 14.2 (s), 15.6 (d, J_{CP} = 4 Hz), 23.6 (dd, J_{CP} = 26, 12 Hz), 30.0 (d, J_{CP} = 38 Hz), 32.2 (s), 34.3 (d, J_{CP} = 3 Hz), 34.9 (d, J_{CP} = 34 Hz), 35.2 (s). HRMS (EI, direct insert): m/z 327.2713, $(M - H)^+$ (exact mass calculated for $C_{17}H_{39}P_2B_2$ 327.2719).

(S,S)-2,4-Bis[(R,R)-2,5-diethylphospholane−borane]pentane (16b). Yield: 63%. $[\alpha_D{}^{20}]$ = −12.1 (c = 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ −0.1−1.0 (br q, 6H), 0.99 (t, J_{HH} = 7.6 Hz, 6H), 1.04 (t, J_{HH} = 7.2 Hz, 6H), 1.12 (dd, J_{HP} = 13.2 Hz, J_{HH} = 6.8 Hz, 6H), 1.19 (m, 2H), 1.20 (m, 4H), 1.26 (m, 4H), 1.47 (m, 2H), 1.55 (m, 2H), 1.71 (m, 2H), 1.89 (m, 8H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 46.1 (br d). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.9 (d, J_{CP} = 9 Hz), 14.2 (d, J_{CP} = 9 Hz), 14.3 (d, J_{CP} = 9 Hz), 22.0 (s), 24.3 (dd, J_{CP} = 28, 11 Hz), 24.4 (s), 32.3 (s), 32.5 (s), 33.0 (s), 35.7 (d, J_{CP} = 30 Hz), 43.1 (d, J_{CP} = 34 Hz). HRMS (EI, direct insert): m/z 383.3347, $(M - H)^+$ (exact mass calculated for $C_{21}H_{47}P_2B_2$ 383.3339).

(R,R)-2,4-Bis[(R,R)-2,5-diisopropylphospholane−borane]pentane (16c). Yield: 48%. $[\alpha_D{}^{20}]$ = −32.4 (c = 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.1−0.8 (br q, 6H), 0.97 (d, J_{HH} = 6.0 Hz, 6H), 1.02 (d, J_{HH} = 5.6 Hz, 6H), 1.08 (d, J_{HH} = 6.4 Hz, 6H), 1.16 (d, J_{HH} = 6.0 Hz, 6H), 1.19 (dd, J_{HP} = 11.6, J_{HH} = 6.4 Hz, 6H), 1.24−1.41 (m, 4H), 1.75−1.86 (m, 4H), 1.87−2.02 (m, 8H), 2.02−2.08 (m, 4H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 43.9 (br d). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.4 (d, J_{CP} = 6 Hz), 21.3 (d, J_{CP} = 9 Hz), 22.9 (d, J_{CP} = 10 Hz), 23.9 (s), 24.2 (d, J_{CP} = 3 Hz), 24.4 (t, J_{CP} = 12 Hz), 28.4 (s), 28.7 (d, J_{CP} = 5 Hz), 30.3 (s), 32.3 (s), 33.9 8s), 40.9 (d, J_{CP} = 27 Hz), 49.6 (d, J_{CP} = 32 Hz). HRMS (EI, direct insert): m/z 439.3952, $(M - H)^+$ (exact mass calculated for $C_{25}H_{55}P_2B_2$ 439.3955).

Synthesis of (2,4-Bis(dialkylphospholano)pentanes 17 and 18. Ligands **17** and **18** were liberated by deprotection of the phosphine−borane adducts **15** and **16** through treatment with HBF_4 as described previously by Livinghouse and coworkers.[19d,e] Preparation of (R,R)-2,4-bis[(R,R)-2,5-dimethylphospholane]pentane (**17a**) is exemplified. To 165 mg (0.5 mmol) of (R,R)-2,4-bis[(R,R)-2,5-dimethylphospholane−borane]pentane (**15a**) in CH_2Cl_2 (10 mL) at 0 °C was added an excess of $HBF_4{\cdot}OEt_2$ adduct (1.25 mL, 85% solution in diethyl ether). The mixture was stirred at room temperature for 12 h. The mixture was then sequentially hydrolyzed with degassed aqueous $NaHCO_3$ (10 mL, saturated solution) and diluted with 20 mL of CH_2Cl_2, the organic layer was separated, and the aqueous phase was reextracted with additional portions of CH_2Cl_2. Organic fractions were combined, washed with degassed brine, and dried over $MgSO_4$. The volatiles were evaporated in vacuo, and the resulting oily residue was dissolved in hexane. After the solution was passed through a short pad of neutral alumina, the solvent was evaporated to produce 140 mg of the diphosphine as a colorless oil (93% yield).

(R,R)-2,4-Bis[(R,R)-2,5-dimethylphospholano]pentane (17a). Yield: 93%. $[\alpha_D{}^{20}]$ = 109 (c = 0.5, $CHCl_3$). ^{1}H NMR ($CHCl_3$): δ 1.10 (m, 2H), 1.12 (dd, J_{HP} = 16.0 Hz, J_{HH} = 7.2 Hz, 6H), 1.13 (dd, J_{HP} = 6.8 Hz, J_{HH} = 6.8 Hz, 6H), 1.27 (dd, J_{HP} = 16.8 Hz, J_{HH} = 6.8 Hz, 6H), 1.28 (m, 2H), 1.45 (m, 2H), 1.84 (m, 6H), 1.96 (m, 2H), 2.09 (m, 2H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 16.3 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.8 (s), 18.2 (d, J_{CP} = 22 Hz), 21.7 (d, J_{CP} = 31 Hz), 23.7 (dd, J_{CP} = 22, 8 Hz), 35.0 (d, J_{CP} = 16 Hz), 35.6 (d, J_{CP} = 13 Hz), 36.6 (s), 36.8 (d, J_{CP} = 22 Hz), 37.8 (d, J_{CP} = 3 Hz). HRMS (EI, direct insert): m/z 300.2139, M^+ (exact mass calculated for $C_{17}H_{34}P_2$ 300.2136).

(S,S)-2,4-Bis[(R,R)-2,5-dimethylphospholano]pentane (18a). Yield: 98%. $[\alpha_D{}^{20}]$ = −10.5 (c = 0.2, $CHCl_3$). ^{1}H NMR (C_6D_6): δ 0.98 (dd, J_{HP} = 11.6 Hz, J_{HH} = 6.8 Hz, 6H), 1.06 (m, 2H), 1.13 (dd, J_{HP} = 7.8 Hz, J_{HH} = 7.8 Hz, 6H), 1.21 (m, 2H), 1.28 (dd, J_{HP} = 17.2 Hz, J_{HH} = 6.8 Hz, 6H), 1.75 (m, 2H), 1.89 (m, 8H), 2.06 (m, 2H). ^{31}P{^{1}H} NMR (C_6D_6): δ 15.1 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.5 (d, J_{CP} = 11 Hz), 15.9 (s), 21.6 (d, J_{CP} = 31 Hz), 24.2 (dd, J_{CP} = 21, 13 Hz), 34.7 (d, J_{CP} = 13 Hz), 35.0 (d, J_{CP} = 16 Hz), 36.5 (s), 37.7 (d, J_{CP} = 3 Hz), 41.9 (t, J_{CP} = 24 Hz). HRMS (EI, direct insert): m/z 300.2139, M^+ (exact mass calculated for $C_{17}H_{34}P_2$ 300.2136).

(S,S)-2,4-Bis[(R,R)-2,5-diethylphospholano]pentane (18b). Yield: 90%. $[\alpha_D{}^{20}]$ = 82.4 (c = 0.8, hexanes). ^{1}H NMR (C_6D_6): δ 1.01 (t, J_{HH} = 8.2 Hz, 6H), 1.03 (dd, J_{HP} = 10.4 Hz, J_{HH} = 6.0 Hz, 6H), 1.05 (t, J_{HH} = 7.6 Hz, 6H), 1.28 (m, 3H), 1.43 (m, 3H), 1.61 (m, 5H), 1.90 (m, 6H), 1.95 (m, 7H). ^{31}P{^{1}H} NMR (C_6D_6): δ 8.7 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 14.4 (d, J_{CP} = 14 Hz), 15.2 (d, J_{CP} = 6 Hz), 16.6 (d, J_{CP} = 9 Hz), 23.9 (s), 24.5 (dd, J_{CP} = 25, 13 Hz), 29.7 (d, J_{CP} = 29 Hz), 34.1 (s), 34.7 (d, J_{CP} = 3 Hz), 40.7 (d, J_{CP} = 16 Hz), 42.2 (s), 43.8 (d, J_{CP} = 16 Hz). HRMS (EI, direct insert): m/z 356.2759, M^+ (exact mass calculated for $C_{21}H_{42}P_2$ 356.2762).

(R,R)-2,4-Bis[(R,R)-2,5-diisopropylphospholano]pentane (18c). Yield: 83%. $[\alpha_D{}^{20}]$ = −142 (c = 0.8, hexanes). ^{1}H NMR (C_6D_6): δ 0.94 (d, J_{HH} = 6.0 Hz, 6H), 1.03 (d, J_{HH} = 6.0 Hz, 6H), 1.06 (dd, J_{HP} = 6.8 Hz, J_{HH} = 6.8 Hz, 6H), 1.14 (d, J_{HH} = 6.8 Hz, 6H), 1.30 (d, J_{HH} = 6.0 Hz, 6H), 1.38 (m, 2H), 1.51 (m, 4H), 1.67 (m, 4H), 1.83 (m, 2H), 1.92 (m, 4H), 2.00 (m, 2H), 2.20 (m, 2H). ^{31}P{^{1}H} NMR (C_6D_6): δ 1.9 (s). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.2 (s), 22.1 (d, J_{CP} = 10 Hz), 23.0 (d, J_{CP} = 13 Hz), 23.4 (d, J_{CP} = 5 Hz), 24.7 (dd, J_{CP} = 26, 14 Hz), 25.2 (d, J_{CP} = 7 Hz), 29.6 (s), 32.6 (s), 33.3 (d, J_{CP} = 25 Hz), 34.3 (d, J_{CP} = 4 Hz), 42.4 (t, J_{CP} = 21 Hz), 45.0 (d, J_{CP} = 18 Hz), 51.1 (d, J_{CP} = 16 Hz). HRMS (EI, direct insert): m/z 412.3385, M^+ (exact mass calculated for $C_{25}H_{50}P_2$ 412.3388).

Synthesis of [(COD)Rh(P−P)]OTf Complexes. All rhodium complexes were prepared from the precursor complex [(COD)$_2$Rh]OTf through treatment with 1 equiv of the corresponding diphosphine as described previously.[11b,12b]

[(COD)Rh((*R*,*R*)-2,4-bis[(*R*,*R*)-2,5-dimethylphospholano]pentane)]OTf. Yield: 61%. ^{1}H NMR (CDCl$_3$): δ 1.08 (m, 14H), 1.36 (m, 8H), 1.77 (m, 4H), 1.97 (m, 10H), 2.21 (m, 6H), 4.38 (m, 2H), 5.01 (m, 2H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 34.2 (d, $J_{RhP} = 140$ Hz). Anal. Calcd for $C_{26}H_{46}P_2RhSO_3F_3$: C, 47.3; H, 7.0. Found: C, 47.1; H, 7.0.

[(COD)Rh((*S*,*S*)-2,4-bis[(*R*,*R*)-2,5-dimethylphospholano]pentane)]OTf. Yield: 64%. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.21 (dd, $J_{HP} = 11.0$ Hz, $J_{HH} = 6.9$ Hz, 6H), 1.2−1.5 (m, 2H), 1.28 (dd, $J_{HP} = 13.2$ Hz, $J_{HH} = 7.0$ Hz, 6H, 2 Me), 1.58 (dd, $J_{HP} = 17.3$ Hz, $J_{HH} = 7.1$ Hz, 6H), 1.5−1.7 (m, 2H), 1.80 (m, 2H), 2.10 (m, 6H), 2.45 (m, 10H), 2.60 (m, 2H), 4.59 (m, 2H), 5.13 (m, 2H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 40.4 (d, $J_{RhP} = 142$ Hz). Anal. Calcd for $C_{26}H_{46}P_2RhSO_3F_3$: C, 47.3; H, 7.0. Found: C, 47.2; H, 7.1.

[(COD)Rh((*S*,*S*)-2,4-bis[(*R*,*R*)-2,5-diethylphospholano]pentane)]OTf. Yield: 55%. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.06 (t, $J_{HH} = 6.8$ Hz, 6H), 1.19 (m, 12H), 1.29 (m, 2H), 1.44 (m, 2H), 1.61 (m, 4H), 1.78 (m, 4H), 1.92 (m, 2H), 2.00 (m, 4H), 2.27 (m, 6H), 2.42 (m, 8H), 4.41 (m, 2H), 5.14 (m, 2H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 37.1 (d, $J_{RhP} = 141$ Hz). Anal. Calcd for $C_{30}H_{54}P_2RhSO_3F_3$: C, 50.3; H, 7.6. Found: C, 49.8; H, 7.4.

[(COD)Rh((*R*,*R*)-2,4-bis[(*R*,*R*)-2,5-diisopropylphospholano]pentane)]OTf. Yield: 43%. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.99 (d, $J_{HH} = 6.8$ Hz, 6H), 1.09 (d, $J_{HH} = 6.8$ Hz, 6H), 1.18 (d, $J_{HH} = 6.4$ Hz, 6H), 1.22 (dd, $J_{HP} = 11.4$ Hz, $J_{HH} = 7.0$ Hz, 6H), 1.35 (m, 2H), 1.53 (d, $J_{HH} = 6.8$ Hz, 6H), 1.58 (m, 4H), 1.6−2.6 (m, 22H), 4.08 (m, 2H), 5.37 (m, 2H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 28.2 (d, $J_{RhP} = 140$ Hz). Anal. Calcd for $C_{34}H_{62}P_2RhSO_3F_3$: C, 52.8; H, 8.1. Found: C, 52.6; H, 7.8.

Asymmetric Hydrogenations. Catalytic hydrogenation reactions were performed as described previously.[11] Enantiomeric excesses were determined using the following analytical methods and conditions. *N*-Acetylphenylalanine methyl ester (**20**): capillary GC, Chrompack Chirasil-L-Val, 180 °C isothermal, 15 psi of He; (*R*) $t_1 = 3.54$ min, (*S*) $t_2 = 3.70$ min. *N*-Acetylvaline methyl ester (**22**): capillary GC, Chrompack Chirasil-L-Val, 135 °C isothermal, 15 psi of He; (*R*) $t_1 = 2.85$ min, (*S*) $t_2 = 3.14$ min. Methyl lactate (**24**): capillary GC, Macherey-Nagel Lipodex A, 60 °C, isothermal, 10 psi of He; (*S*) $t_1 = 4.35$ min, (*R*) $t_2 = 5.03$ min.

Crystallographic Studies. Crystal, data collection, and refinement parameters are provided in Table 5. Suitable crystals of [(COD)Rh(**17a**)]OTf (**17a**-Rh) and [(COD)Rh(**18a**)]OTf (**18a**-Rh) were selected and mounted in thin-walled, nitrogen-flushed glass capillaries and flame-sealed. The data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector.

The systematic absences in the diffraction data for **17a**-Rh and **18a**-Rh are uniquely consistent for orthorhombic space group $P2_12_12_1$. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures. There are three independent, but chemically equivalent, ion pairs in the asymmetric unit of **17a**-Rh ($Z' = 3$) and two independent, but chemically equivalent, ion pairs in the asymmetric unit of **18a**-Rh ($Z' = 2$). The rhodium, sulfur, and phosphorus atoms in **17a**-Rh and all non-hydrogen atoms in **18a**-Rh were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The absolute configuration of each compound was determined and confirmed: Flack parameters were 0.06(5) for **17a**-Rh and −0.04(3) for **17a**-Rh.

All software and sources of the scattering factors are contained in the SHELXTL (versions 5.03 and 5.10) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

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Supporting Information Available: X-ray diffraction data, including listings of crystal data and structure refinement parameters, atomic coordinates and equivalent isotropic displacement parameters, interatomic bond distances, intromolecular bond angles, anisotropic displacement coefficients, and hydrogen atom coordinates, ORTEP plots for each independent cation and anion (30% probability thermal ellipsoids) of the complexes [(COD)Rh(**17a**)]OTf and [(COD)Rh(**18a**)]OTf, and a packing diagram for [(COD)Rh(**17a**)]OTf. This material is available free of charge via the Internet at http://pubs.acs.org.

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