Stereochemically Matched (and Mismatched) Bisphosphine Ligands: DIOP-DIPAMP Hybrids

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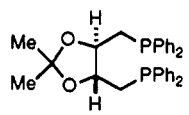
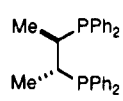
The three diastereomers of (*R*,*R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis([2-methoxyphenyl]-phenylphosphino)butane (**1**) and of (*R*,*R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis([2-(dimethyl-amino)phenyl]phenylphosphino)butane (**2**) have been prepared and isolated. Advanced intermediates in the preparation and isolation of diastereomers of (*R*,*R*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis([2,6-dimethoxyphenyl]phenylphosphino)butane (**3**) are also described. Absolute configurations of four of the chiral phosphine ligands were determined via single-crystal X-ray diffraction studies of molybdenum tetracarbonyl derivatives ((*R*P,*R*P)-**6**, (*R*P,*R*P)-**7**, (*R*P,*R*P)-**8**, and (*S*P,*S*P)-**8**); this facilitated assignments of absolute configurations for all the isomers of ligands **1**–**3**. These bisphosphine ligands are rare insofar as they have chiral phosphorus centers supported on an asymmetric carbon framework. Several reactions were performed to test for "cooperativity" between chiral centers in these ligands with respect to asymmetric induction in transition-metal-catalyzed processes. Matching and mismatching effects were observed, but there are some irregular trends in the data. The enantioselectivities obtained were moderate but greater than that for the parent ligand DIOP in some cases. The *o*-dimethylamino functionality of ligands **2** may play an active role in the coordination of these isomeric bisphosphine ligands. Trends and factors influencing the performance of ligands **1**–**3** in asymmetric catalysis are discussed. Crystal data for the compounds analyzed via X-ray diffraction are as follows. (*R*P,*R*P)-**6**: monoclinic, space group $P2_1$ (No. 4), a = 11.621 (3) Å, b = 10.676 (2) Å, c = 14.850 (2) Å, β = 101.59 (2)°, V = 1804.8 (6) Å^3, Z = 2, R = 0.029. (*R*P,*R*P)-**7**·0.5CH_2Cl_2: monoclinic, space group $P21$ (No. 4), a = 11.013 (6) Å, b = 21.134 (5) Å, c = 18.555 (6) Å, β = 101.32 (3)°, V = 4235 (2) Å^3, Z = 4, R = 0.111. (*R*P,*R*P)-**8**: triclinic, space group $P1$ (No. 1), a = 11.64 (1) Å, b = 16.05 (1) Å, c = 10.760 (7) Å, α = 94.06 (6)°, β = 97.05 (6)°, γ = 97.10 (7)°, V = 1973 (5) Å^3, Z = 2, R = 0.098. (*S*P,*S*P)-**8**: orthorhombic, space group $P2_12_12_1$ (No. 19), a = 14.007 (3) Å, b = 27.419 (8) Å, c = 10.394 (3) Å, V = 3992 (2) Å^3, Z = 4, R = 0.052.

Introduction

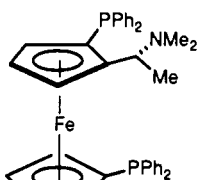
Optically active bisphosphines[1] such as DIOP,[2] BINAP,[3] CHIRAPHOS,[4] BPPFA,[5,6] and DIPAMP[7] are useful for asymmetric catalysis of industrial- and laboratory-scale reactions.[8-13] Four of these ligands have asymmetric "backbones" which link achiral phosphorus atoms. The bisphosphine DIPAMP is fundamentally different; it has asymmetric phosphorus centers connected via achiral molecular fragments.



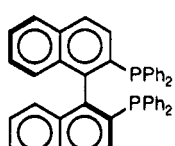
(*R*,*R*)-DIOP



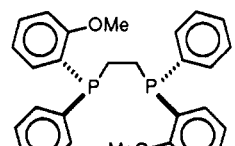
(*R*,*R*)-CHIRAPHOS



(*S*,*R*)-BPPFA

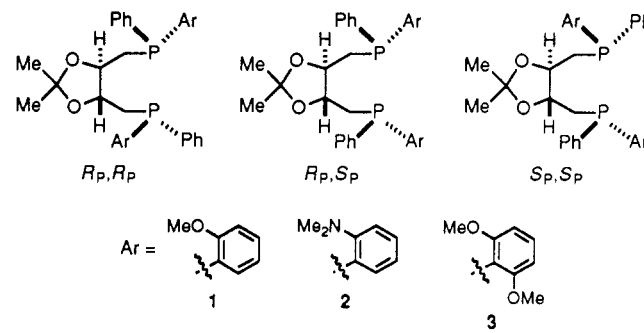


(*S*)-BINAP



(*S*,*S*)-DIPAMP

This paper described syntheses and reactions of the DIPAMP/DIOP hybrid ligands **1** and similar systems with different aryl substituents **2**. Advanced intermediates in a procedure to obtain diastereomerically pure samples of ligands **3** are also described. Syntheses of these materials have facilitated a preliminary study of matching and mismatching effects[14] relating backbone- and phosphorus-based chirality with the performance of these ligands in asymmetric catalysis. Several reaction types have been



*R*P and *S*P refer to *R* and *S* configurations at phosphorus

investigated to establish the stereochemically dominant features in ligand design and to find clues for the rational design of more effective ligands for asymmetric induction.

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Table I. Chemoselectivity in the Reductive Cleavage of Simple Triarylphosphines

$$PPhAr^1Ar^2 \xrightarrow[\text{(ii) MeI}]{\text{(i) Na/K, dioxane, 25 °C}} MePPhAr^1$$

entry no.	Ar^1	Ar^2	redn time, h	predominant product	isolated yield, %
1	Ph	2-$MeOC_6H_4$	2	$MePPh_2$	*a*
2	2-$MeOC_6H_4$	2-$MeOC_6H_4$	2	$MePPh(2\text{-}MeOC_6H_4)$	56
3	Ph	4-$MeOC_6H_4$	4	$MePPh(4\text{-}MeOC_6H_4)$	48
4	2-$Me_2NC_6H_4$	2-$Me_2NC_6H_4$	1	$MeP(S)Ph(2\text{-}Me_2NC_6H_4)$[b]	38
5	Ph	2-$Me_2NC_6H_4$	2	$MeP(O)Ph_2$[c]	39

[a] Not determined. [b] After oxidation with S_8. [c] After oxidation with hydrogen peroxide.

To the best of our knowledge, there have been only two previous investigations of cooperativity between chiral inducing factors in phosphine ligands. Those studies focused upon ferrocenyl bisphosphines with an element of planar chirality and a chiral amine substituent[15-21] and upon hydrogenations of dehydroamino acids with aryldialkylphosphines which are chiral at the backbone and at the phosphorus atoms.[22-24]

Results and Discussion

Three major challenges were encountered in this work: (i) development of convenient preparations of the ligands as mixtures of diastereomers, (ii) separations of stereochemically distinct, but chemically similar, compounds, and (iii) stereochemical assignments. In this event we were fortunate to discover directed reductive cleavages of aryl–phosphorus bonds which greatly facilitate the preparation of diastereomeric mixtures of the ligands (issue i).

Directed Reductive Cleavage of Aryl–Phosphorus Bonds. Formation of chiral phosphines via alkylation requires a convenient route to phosphide anions with different substituents, in this work given as $[PPhAr]^-$ (where Ar = aryl ≠ Ph). Literature procedures for the formation of such anions involve the preparation and reduction of chiral phosphine chlorides (eq 1) or synthesis and deprotonation of chiral secondary phosphines (eq 2).[25]

$$Cl_2PPh \xrightarrow{MAr} ClPArPh \xrightarrow{\text{reduction}} [PArPh]^- \quad (1)$$

$$Cl_2PPh \xrightarrow{MAr} ClPArPh \xrightarrow{H^-} HPArPh \xrightarrow{\text{deprotonation}} [PArPh]^- \quad (2)$$

Controlled additions of organometallics to dichlorophenylphosphine and purifications via distillation are required for both routes.[26-33] Consequently, reactions of this type are inconvenient for several reasons: (i) heavy-metal reagents are usually required since organolithium and organomagnesium reagents are too reactive for selective monosubstitution from a phosphine dichloride, (ii) the starting materials and products are toxic, somewhat volatile, air sensitive, and water sensitive, and (iii) isolated yields are generally less than 50%. An improved methodology for the production of arylphenylphosphide anions is clearly desirable.

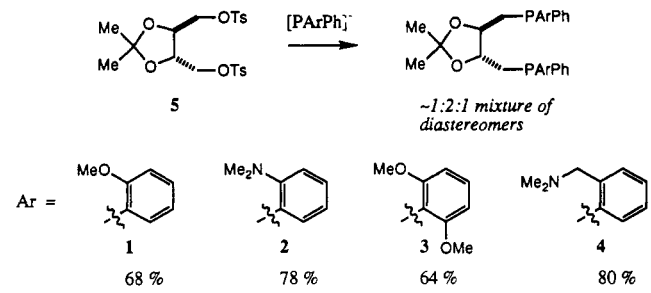

Figure 1. Syntheses of diastereomeric mixtures of phosphines 1–4.

Diarylphenylphosphines are easily prepared via reaction of dichlorophenylphosphine with aryllithium or aryl Grignard reagents; they are nonvolatile, air- and water-stable compounds, which, in many cases, can be purified via recrystallization. Further, many diarylphenylphosphines with ortho hetero substituents can be prepared via directed metalation of the corresponding aromatic fragments.[34,35] A series of probe reactions were performed to explore the reduction of such compounds with sodium/potassium alloy, followed by alkylation with methyl iodide. Data from these experiments (Table I) indicate *aryl groups with coordinating ortho substituents can be cleaved chemoselectively* (entries 1, 2, 4, and 5). If no such substituent exists, the reaction is slower and the least electron-rich aryl substituent is cleaved (e.g. Ph in preference to 4-$MeOC_6H_4$, entry 3). Others have observed reductive cleavage of phenyl groups from alkyldiphenylphosphines (sodium/sonication),[36,37] and reduction rates of triarylphosphines (PAr_3, all Ar groups the same) vary with the aryl substituents.[38,39] However, to the best of our knowledge, this is the first example of chemoselective cleavage of C–P bonds in a triarylphosphine of the type

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PAr_2Ar'.[65] It provides a convenient method for forming and alkylating diarylphosphide ions. Such chemoselective cleavages of phosphorus–aryl substituents were invaluable in this work (vide infra), and they may be useful for syntheses of many other organophosphorus compounds.

The methodology outlined above was used to prepare diastereomeric mixtures of the target phosphine compounds **1–4**; in this case (−)-*trans*-4,5-bis[(tosyloxy)methyl]-2,2-dimethyl-1,3-dioxolane (**5**) was the electrophile used.[38] No carbon-to-phosphorus induction was observed in any of the examples studied; i.e., a near-statistical mixture (1:2:1) of R_P,R_P, R_P,S_P, and S_P,S_P stereoisomers was obtained in each case. Figure 1 illustrates these reactions and shows the yield information.

Separation of Diastereomers of Phosphines 1–3. Epimers of each bisphosphine **1–4** have clearly resolved ^{31}P NMR signals at 101 MHz; this provides a convenient technique for assessing their diastereomeric purity. Those isomers with like chirality at phosphorus (R_P,R_P and S_P,S_P) are C_2 symmetric; thus, they each give one ^{31}P NMR signal. Phosphorus atoms of the R_P,S_P epimers, however, are inequivalent, and the corresponding ^{31}P NMR signals occur at different chemical shifts. Five-bond ^{31}P–^{31}P coupling could be resolved in spectra of the R_P,S_P isomers of compounds **2–4**. The ^{31}P spectrum of a stereoisomeric mixture of bisphosphine **2** is typical and is shown in Figure 2.

Careful recrystallization of the stereoisomeric mixture of bisphosphines **3** from ethanol precipitated (R_P,R_P)-**3** and (S_P,S_P)-**3** as a ~1:1 mixture. Repeated recrystallization of the material recovered from the mother liquors gave a 30:1 mixture of (R_P,S_P)-**3**: {(R_P,R_P)-**3** + (S_P,S_P)-**3**}, but the C_2-symmetric isomers could not be separated by recrystallization. Chromatographic separation (TLC or HPLC) of epimers of bisphosphines **1** or of **2** was not feasible. Consequently, other derivatives were examined and, after considerable experimentation, molybdenum carbonyl complexes of the ligands were selected for further investigations.

Ethanolic solutions of molybdenum hexacarbonyl were refluxed with each of the diastereomeric mixtures in the presence of sodium borohydride.[40] This procedure cleanly (^{31}P NMR) gave the molybdenum tetracarbonyl adducts **6–9** (Figure 3). For each set of complexes, two stereoisomers (R_P,R_P and S_P,S_P) are C_2 symmetric and their ^{31}P NMR spectra consist of single peaks.[41] Two ^{31}P signals are observed for each of the four R_P,S_P adducts, and the relatively large two-bond ^{31}P–^{31}P couplings through the metal are clearly resolved. Spectra for the diastereomeric complexes of **6** are typical and are shown in Figure 4.

Complexes **6–9** are air-stable crystalline solids, but in solution they begin to decompose after a few hours if left in contact with the air; compounds **6** and **7** are particularly sensitive in this regard.

Selective precipitation of (R_P,S_P)-**7** from an ethanolic solution was observed, but the overall separation was unsatisfactory. Fractional crystallizations of the other stereoisomeric mixtures were also attempted, without success. Fortunately, *all three isomers of complexes* **6** *and* **7** *are separable by flash chromatography*[42] (ethyl acetate/hexane or diethyl ether/hexane eluant), although for the complexes **6** the R_f difference between the R_P,S_P and S_P,S_P isomers is very small.[43] Similarly, the R_P,R_P and S_P,S_P

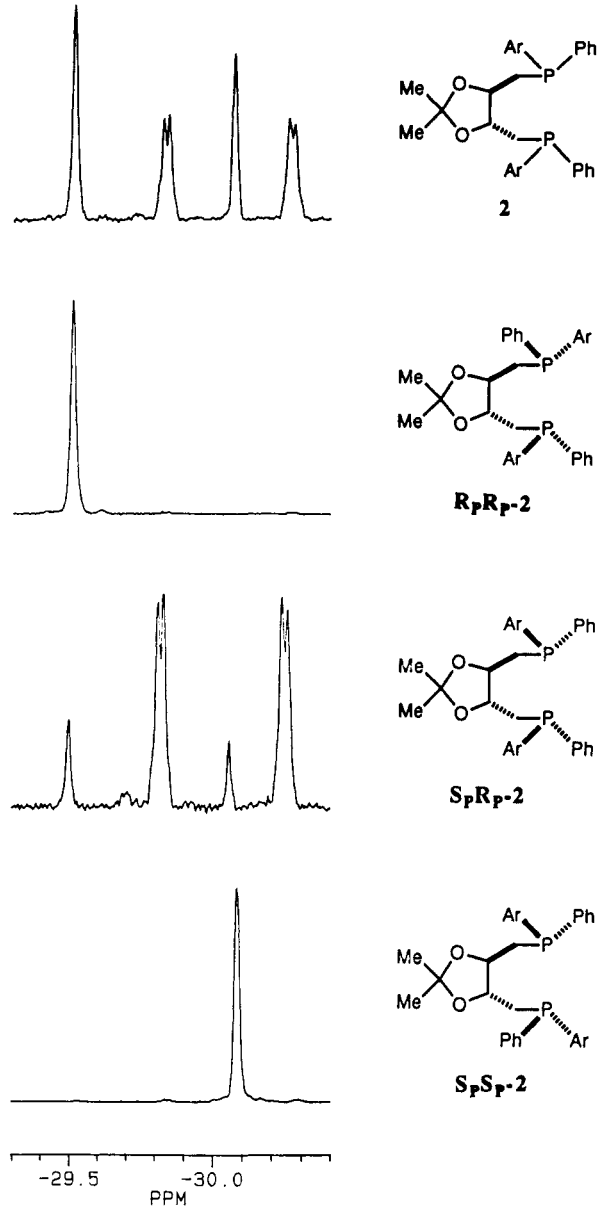

Figure 2. ^{31}P NMR data for diastereomers of ligand **2** (Ar = 2-$Me_2NC_6H_4$).

complexes of **8** (the R_P,S_P phosphine having previously been largely removed by fractional crystallization, vide supra) can be separated cleanly on silica by eluting with ethyl acetate/hexane mixtures. Several hundreds of milligrams of diastereomerically pure complexes can be separated via this procedure, and approximately 50–60% of the material loaded onto the column is recovered. Unfortunately, we have not yet developed a method to separate diastereomers of ligand **4** or complexes of these.

After chromatography, the isolated R_P,S_P complexes are easily identified (^{31}P and ^1H NMR), but the R_P,R_P and S_P,S_P complexes are indistinguishable. Eventually, stereochemical assignments were made on the basis of single-crystal X-ray diffraction studies (vide infra); hence, spectral correlations like those shown in Figure 4 were possible.

The next challenge in this project was to remove the phosphine ligands from the metal[44] without epimerization, preferably via conditions that give free phosphines directly,

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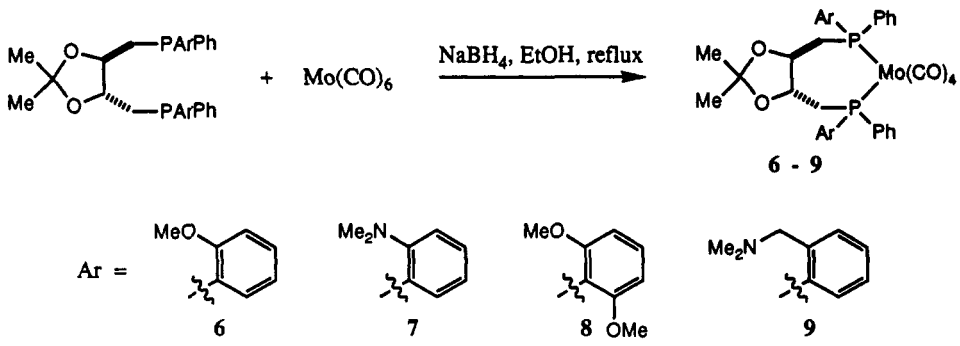

Figure 3. Syntheses of diastereomeric mixtures of $MoP_2(CO)_4$ complexes **6–9**.

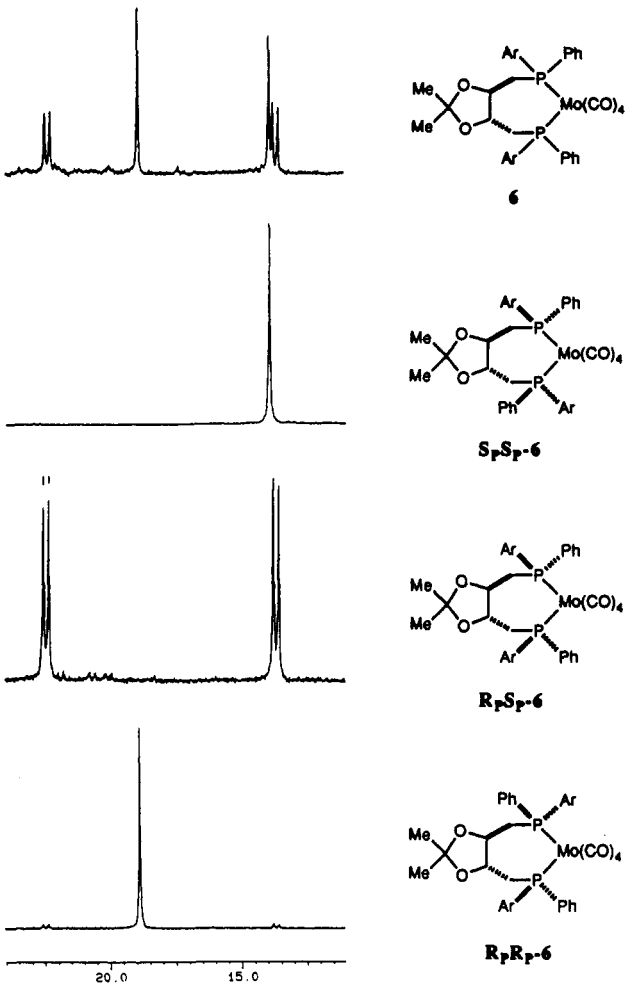

Figure 4. ^{31}P NMR data for diastereomeric complexes **6** (Ar = 2-$MeOC_6H_4$).

rather than derivatives such as the corresponding oxides. Preliminary experiments with ligand exchange, and with oxidative degradation,[45] were not encouraging. Reduction of $Mo(CO)_4$(TMEDA) in sodium/liquid ammonia has been reported,[46] presumably with expulsion of the TMEDA ligand. Following this lead, we developed a procedure whereby the molybdenum complexes are reduced by sodium naphthalenide at −78 °C. Ionic byproducts are precipitated by addition of deoxygenated anhydrous ether, and then the solution is filtered through Celite under an inert atmosphere; the filtrate is a solution of the free bisphosphine. This procedure affords the three stereoisomers of bisphosphine **1** (Ar = 2-$MeOC_6H_4$) in yields of around 30% *without epimerization of the phosphine chiral centers*. Reductive decomplexation to give the ligands **2** (Ar = 2-$Me_2NC_6H_4$) is more efficient; the protocol consistently gives yields of around 60%. However, only a 16% yield of (S_P,S_P)-**3** (Ar = 2,6-$(MeO)_2C_6H_3$) was obtained via this method, and none of the (R_P,R_P)-**3** isomer was produced. Apparently, some phosphines, especially those bearing a 2,5-dimethoxyphenyl group, are particularly vulnerable to reductive cleavages of aryl–phosphorus bonds under the reaction conditions.

It is important that the ether used to "quench" the reductive complexation reactions be dry; different chemistry if observed if wet ether or a protic solvent is used. When (R_P,R_P)-**7** was reacted with sodium naphthalenide until all the complex had been consumed, and the reaction was quenched with *wet* ether, several products were observed: (i) regenerated (R_P,R_P)-**7**, (ii) free phosphine ligand (R_P,R_P)-**2**, and (iii) a more polar material (TLC) which was characterized as complex **10** (Figure 5). Attempted isolation of amino–phosphine complex **10** via flash chromatography gave a sample contaminated with a small amount of (R_P,R_P)-**7**. At 25 °C in C_6D_6, the amino–phosphine complex **10** reverts to the bidentate phosphine complex (R_P,R_P)-**7** with a half-life of approximately 9 h (Figure 5).

Our rationale for these results is illustrated in Scheme I. Addition of a proton source to the crude reductive-cleavage reaction mixture gives "$Mo(CO)_4H_4$". Loss of two dihydrogen molecules from this molecule in the presence of the free phosphine (R_P,R_P)-**2** is apparently facile; hence, the five-membered chelate **10** is formed as the kinetic product. Complex **10** slowly rearranges to the more stable chelated bisphosphine (R_P,R_P)-**7**. These observations illustrated dimethylamino ligands can play a very active role in the organometallic chemistry of bisphosphine ligands **2** and related materials.[34,47]

Assignment of Stereochemistry for Ligands 1–3. In each ligand series, the R_P,S_P isomer is easily distinguished from the C_2-symmetric ones by NMR. To differentiate between the R_P,R_P and S_P,S_P isomers, it was most convenient to use X-ray diffraction methods; this could be achieved via just one structural determination for each ligand series. Ultimately, four complexes of the form $(OC)_4$Mo(phosphine ligand) were structurally characterized, i.e. those from (R_P,R_P)-**6**, (R_P,R_P)-**7**, (R_P,R_P)-**8**, and (S_P,S_P)-**8**. Consequently, the relative stereochemistries of all isomers of phosphines **6–8** were assigned (Figures 6–9, respectively). Crystallographic data and bond distances and angles are given in the supplementary material. The structures are typical of *cis*-bis(phosphine)$Mo(CO)_4$ complexes and will receive no further comment here.

Edge/face propeller-shaped arrangements of aromatic groups around a metal are generally considered to be ad-

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Scheme I. Reductive Cleavage of Complex (R_P,R_P)-7 with "Anhydrous" and "Protic" Workup Procedures

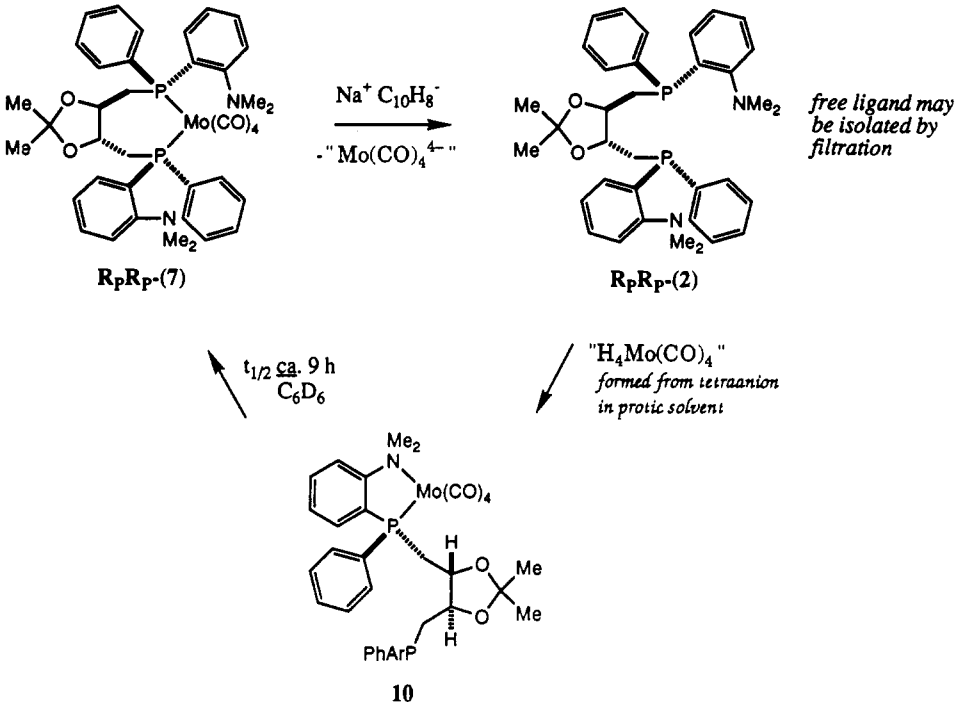

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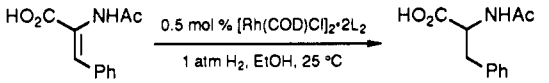
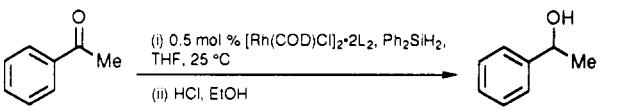
Table II. Reductions of a Dehydroamino Acid in the Presence of Epimeric Catalysts from Ligand 1



ligand (L_2)	% ee	product confign	ligand (L_2)	% ee	product confign
(*R*,*R*)-DIOP	72	*R*	(S_P,S_P)-1	70	*R*
(*R*,*R*)-PAMPOP	31	*S*	(R_P,S_P)-1	54	*R*
(S_P,S_P)-DIPAMP	94	*R*	(R_P,R_P)-1	20	*R*

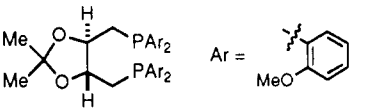
Table III. Hydrosilylations of Phenylethanone in the Presence of Epimeric Catalysts from Ligand 1



ligand (L_2)	% ee	product confign	ligand (L_2)	% ee	product confign
(*R*,*R*)-DIOP	28	*R*	(S_P,S_P)-1	43	*R*
(*R*,*R*)-PAMPOP	18	*R*	(R_P,S_P)-1	10	*R*
			(R_P,R_P)-1	13	*S*

vantageous with respect to asymmetric induction using chiral bidentate phosphine ligands. None of the molybdenum complexes examined have this conformation in the solid state. One might anticipate that a single diastereomer in each series would have a matched stereochemical environment that gives a more perfect C_2 arrangement of aromatic groups around the metal. All the solid-state structures show gross deviations from C_2 symmetry, however, even if just the aromatic groups are considered. Comparison of (R_P,R_P)-8 and (S_P,S_P)-8 reveals the former presents an aromatic edge and three aromatic faces to the metal, whereas the latter projects two aromatic edges around one phosphine atom and two aromatic faces around the other. The chiral backbone "sags" below the P–Mo–P plane for each of the structures examined, apparently a consequence of the ring constraints imposed in these seven-membered chelate structures. It is unwise to extrapolate conclusions from these structural studies to complexes of other metals, but these observations do imply that catalytically active complexes formed from these ligands are unlikely to have an "ideal" C_2-symmetric structure. Indeed, the ^{31}P NMR spectrum of (S_P,S_P)-7 at ambient temperature shows one broad peak, but as the temperature of the sample is decreased two peaks can be resolved (Figure 10). There appear to be two interconverting conformations of the complex for which $\Delta G^* = 49$ kJ mol^{-1} (T_c = 273 K).

Ligands 1 and 2 in Catalysis. The performance of these ligands in a selection of transition-metal-catalyzed reactions was examined. Data for hydrogenation of α-acetamidocinnamic acid with rhodium-based catalysts of DIOP,[2] PAMPOP,[48] DIPAMP,[7] and epimeric phosphines 1 are shown in Table II. The hybrid ligand (S_P,S_P)-1 gives



(*R*,*R*)-PAMPOP

approximately the same magnitude and sense of asymmetric induction (*R* configuration in the products) as (*R*,*R*)-DIOP, whereas (R_P,S_P)-1 and (R_P,R_P)-1 give progressively lower optical yields.[49] This trend shows evidence of productive and unproductive pairing of stereocenters[14] and indicates *backbone chirality is the dominant influence for ligands* 1 *in this reaction.* That (S_P,S_P)-DIPAMP and (S_P,S_P)-1 give the same enantiomer preferentially indicates the phosphorus chirality in these ligands operates in the same sense, whereas for (R_P,S_P)-1 and (R_P,R_P)-1 the 2-methoxyphenyl substituents on the chiral phosphorus centers disrupt the conformation imposed by the (*R*,*R*)-DIOP backbone. In the matched case ((S_P,S_P)-1) the ligand gives results similar to those of (*R*,*R*)-DIOP. The published[48] result for (*R*,*R*)-PAMPOP, however, il-

(48) Brown, J. M.; Murrer, B. A. *Tetrahedron Lett.* **1980**, *21*, 581.
(49) Hydrogenation mediated by the catalyst from (S_P,S_P)-1 was slow relative to reactions using the other epimeric phosphines; the conversion in the experiment quoted here is only 10%.

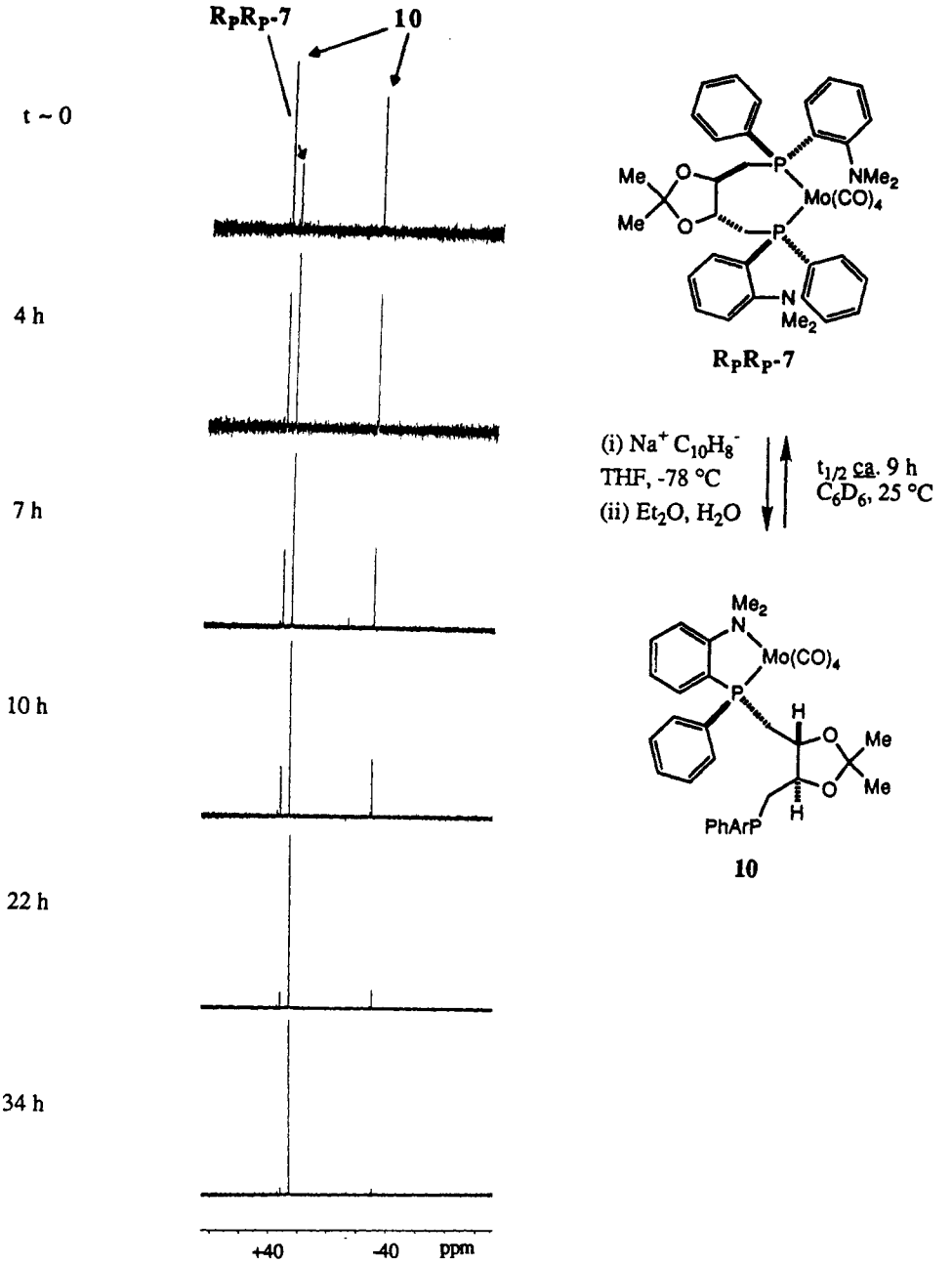


Figure 5. ^{31}P NMR data for the P,N-chelate to P,P-chelate rearrangement of 10 to (R_P,R_P)-7.

lustrates that seemingly small changes in ligand design can have profound effects on the outcome of the asymmetric catalysis; this tetramethoxy derivative selectively gives the *S* enantiomer, in contrast to all the other ligands in this series. Reasons for the anomalous behavior of (*R*,*R*)-PAMPOP in this reaction are unclear.

Asymmetric hydrosilylations of acetophenone in the presence of rhodium(1+) catalysts from matched and mismatched[14] ligands are depicted in Table III; all the enantioselectivities are low. In the best case, (S_P,S_P)-1 gives the same sense of induction as (*R*,*R*)-DIOP[50] and higher enantioselectivity. The R_P,S_P hybrid gives an optical yield significantly lower than that of (*R*,*R*)-DIOP, but the sense of the asymmetric induction remains the same. A small and *opposite* selectivity is observed using the R_P,R_P epimer; apparently the phosphorus chirality overrides the effect of the chiral backbone in this instance. Phosphorus-centered chirality has a more pronounced effect on the stereochemical outcome than backbone asymmetry; this is unlike the corresponding hydrogenation reactions. The remarkable reversal of selectivities observed for (*R*,*R*)-PAMPOP in the hydrogenation reactions (vide supra) is not evident in these *hydrosilylations*.

Data from rhodium-catalyzed hydroborations of alkenes[51,52] mediated by catalysts based upon stereoisomers of ligand 1 are shown in Table IV. All the catalysts, including that from (*R*,*R*)-DIOP,[53,54] give asymmetric induction in the same sense, implying that the backbone chirality of the hybrid is the dominant factor. The catalyzed hydroborations of indene and styrene are surprising,

(50) Dumont, W.; Poulin, J.-C.; Tang, T.-P.; Kagan, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 8295.

(51) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179.

(52) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426.

(53) Zhang, J.; Lou, B.; Guo, G.; Dai, L. *J. Org. Chem.* **1991**, *56*, 1670.

(54) The catalyst system in the DIOP-mediated reactions was obtained using tin(II) chloride as an additive; thus, those are not rigorously comparable with the results for the hydrid ligands reported here. Nevertheless, we feel the results are informative.

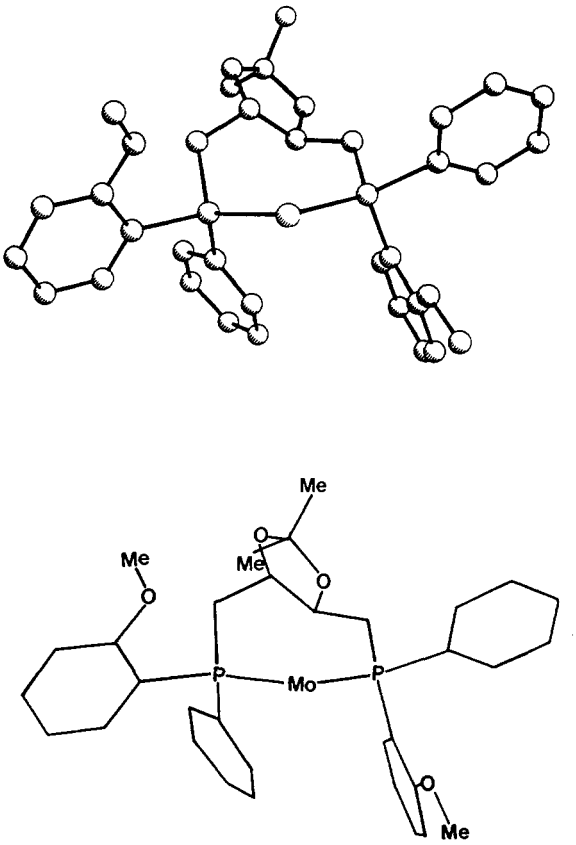
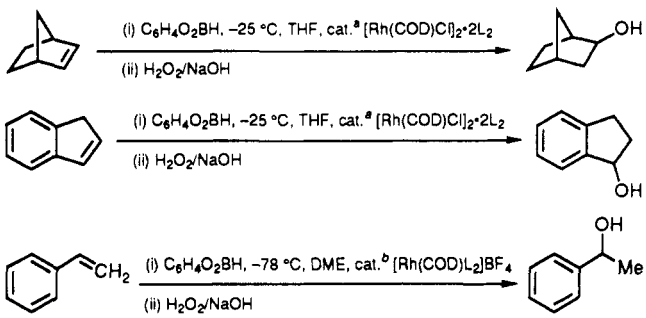


Figure 6. *Crystal structure and schematic representation of* (R_P,R_P)-**6** (carbonyl ligands omitted for clarity).

Table IV. Hydroborations in the Presence of Epimeric Catalysts from Ligand 1



	exo-norborneol		1-indanol		1-phenylethanol	
ligand (L_2)	% ee	config	% ee	config	% ee	config
(*R*,*R*)-DIOP	60	1*R*	74	*S*	48	*R*
(S_P,S_P)-**1**	84	1*R*	49	*S*	13	*R*
(R_P,S_P)-**1**	80	1*R*	77	*S*	19	*R*
(R_P,R_P)-**1**	60	1*R*	54	*S*	~0	*R*

[a] Catalyst is 0.5 mol % $[Rh(COD)Cl]_2$·2L_2. [b] Catalyst is 1.0 mol % $[Rh(COD)L_2]BF_4$, prepared in situ.

since the R_P,S_P hybrid gives the highest optical yield and no trend is evident.

Table V depicts the palladium(II)-catalyzed allylation of methyl *N*-(diphenylmethylene)glycinate using diastereomers of ligand **2** and the literature result[55] for the same reaction (the latter is expressed for (*R*,*R*)-DIOP when, in fact, (*S*,*S*)-DIOP was used). Optical yields for all epimers of **2** are lower than those reported for DIOP. The most striking feature of these data, however, is that induction

(55) Genet, J.-P.; Juge, S.; Achi, S.; Mallart, S.; Montes, J. R.; Levif, G. *Tetrahedron* **1988**, *44*, 5263.

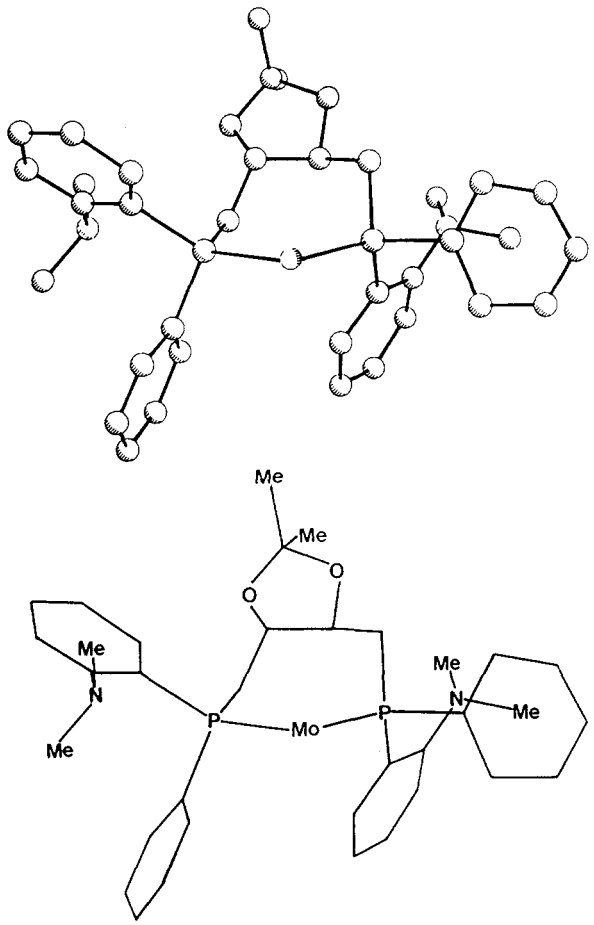
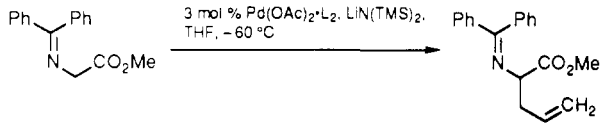


Figure 7. Crystal structure and schematic representation of (R_P,R_P)-**7** (carbonyl ligands omitted for clarity).

Table V. Allylation Reactions in the Presence of Epimeric Catalysts from Ligand 2



ligand (L_2)	% ee	config	ligand (L_2)	% ee	config
(*R*,*R*)-DIOP	68	*S*	(R_P,S_P)-**2**	15	*S*
(R_P,R_P)-**2**	18	*R*	(S_P,S_P)-**2**	22	*S*

from the R_P,R_P ligand is opposite to that obtained with (*R*,*R*)-DIOP. Moreover, the phosphorus chirality dominates; backbone chirality seems to have little effect in this series. A large variation of optical yield with reaction conditions (e.g. counterion effects) was observed for the DIOP-based catalysts;[55] it is possible that the unoptimized enantioselectivities quoted here could be increased appreciably by subtle changes in the reaction conditions.

Conclusions

Very few bisphosphines with asymmetric phosphorus atoms linked by a chiral backbone have been reported.[56] The first prepared was structure I, formed via nucleophilic

(56) Racemic bis(1,3,2-oxazaphospholidines) containing chiral phosphorus centers linked by a chiral biaryl unit have been prepared diastereomerically pure, but no coordination chemistry or applications of these compounds to catalysis have been reported: Pastor, S. D.; Hyun, J. L.; Odorisio, P. A.; Rodebaugh, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 6547. A series of P,N-chelating ligands with chiral phosphorus centers and with chiral N substituents have been prepared: Horner, L.; Simons, G. *Phosphorus Sulfur Relat. Elem.* **1984**, *19*, 65. Horner, L.; Dickerhof, K. *Phosphorus Sulfur Relat. Elem.* **1983**, *15*, 331.

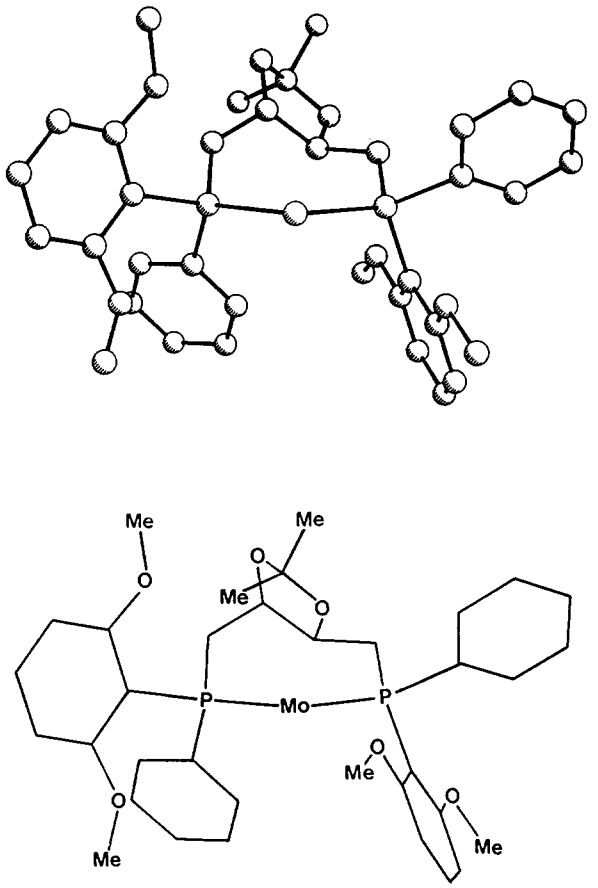
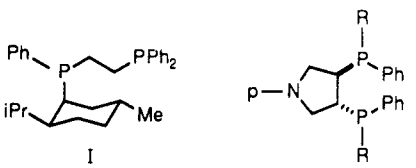


Figure 8. Crystal structure and schematic representation of (R_P,R_P)-8 (carbonyl ligands omitted for clarity).

attack of a phosphide on menthyl chloride and isolated by fractional crystallization.[57] There is, however, no reason to suspect bisphosphines I should be superior ligands for asymmetric catalysis, and indeed, the results described so far have not been outstanding.[57]



p = protecting group; R = alkyl, e.g. Me, CH_2Ph, $(CH_2)_2CN$

Nägel and co-workers have prepared stereoisomerically pure pyrrolidine-based phosphines of type II, by alkylation of the corresponding pyrrolidine-based secondary arylphosphines and separation.[22,23] Asymmetric hydrogenations of dehydroamino acid derivatives in the presence of catalysts containing these ligands, however, gave smaller optical yields than the parent bis(diphenylphosphino) compound (II, R = Ph). Nägel concluded that high enantioselectivities in reactions mediated by complexes of chiral phosphine-based catalysts are mainly due to the influence of axially situated phenyl groups at the phosphorus atoms.[24] One might infer from Nägel's work that *diarylphosphines* which are asymmetric at phosphorus could be more effective in enantioselective catalysis than their alkyl–aryl or dialkyl counterparts.

Solid-state structures of (R_P,R_P)-6, (R_P,R_P)-7, (R_P,R_P)-8, and (S_P,S_P)-8 indicate C_2 symmetry is difficult to attain

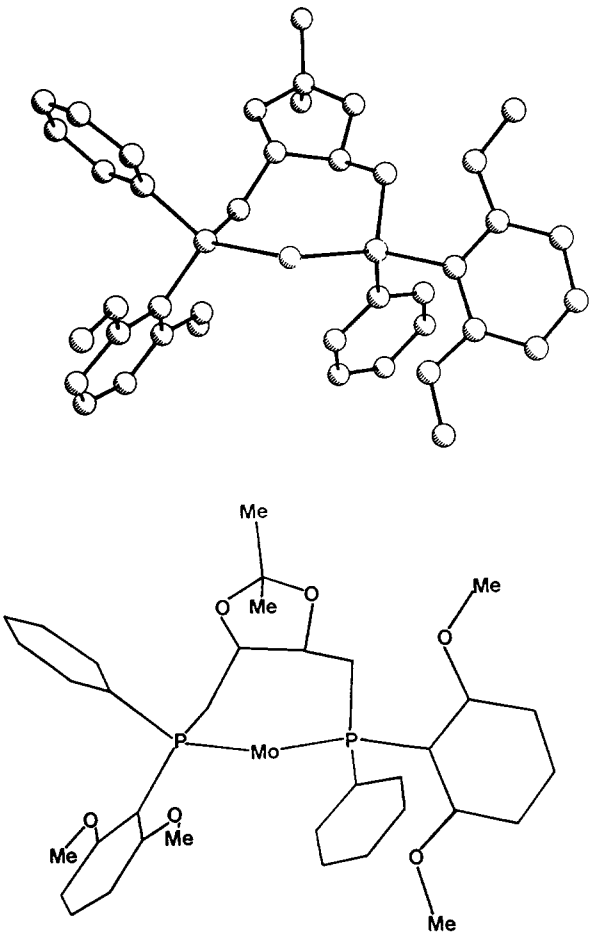
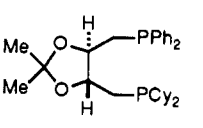


Figure 9. Crystal structure and schematic representation of (S_P,S_P)-8 (carbonyl ligands omitted for clarity).

in this series: seven-membered chelate structures tend to be too large to rest in the P–M–P plane; hence, the ligands pucker to relieve nonbonded contacts. Consequently, the terms "axial" and "equatorial" can only be applied loosely to these complexes, and the groups occupying positions most closely resembling the axial sites may not be ideally situated for chiral induction. Subtle conformational effects could also account for those surprising reactions in which complexes of R_P,S_P ligands give higher enantioselectivities than their S_P,S_P and R_P,R_P counterparts. Others have described catalyzed hydrogenation wherein unsymmetrical DIOP analogues (e.g. III) give higher induction than similar, but C_2 symmetric, ligands;[58,59] there may be some connection between these observations and the present study.



It is perhaps significant that the reactions for which phosphorus chirality is most important are allylations using the Me_2N-substituted phosphines 1. Coordination of 2-dimethylamino substituents on arylphosphines plays an active role in the chemistry of their organometallic complexes, as observed in this work and elsewhere.[34,47] Perhaps weak coordination of the dimethylamino functionality

(57) King, R. B.; Bakos, J.; Hoff, C. D.; Marko, L. *J. Org. Chem.* **1979**, *44*, 3095.

(58) Chiba, M.; Takahashi, H.; Takahashi, H.; Morimoto, T.; Achiwa, K. *Tetrahedron Lett.* **1987**, *28*, 3675.

(59) Morimoto, T.; Chiba, M.; Achiwa, K. *Tetrahedron Lett.* **1988**, *29*, 4755.

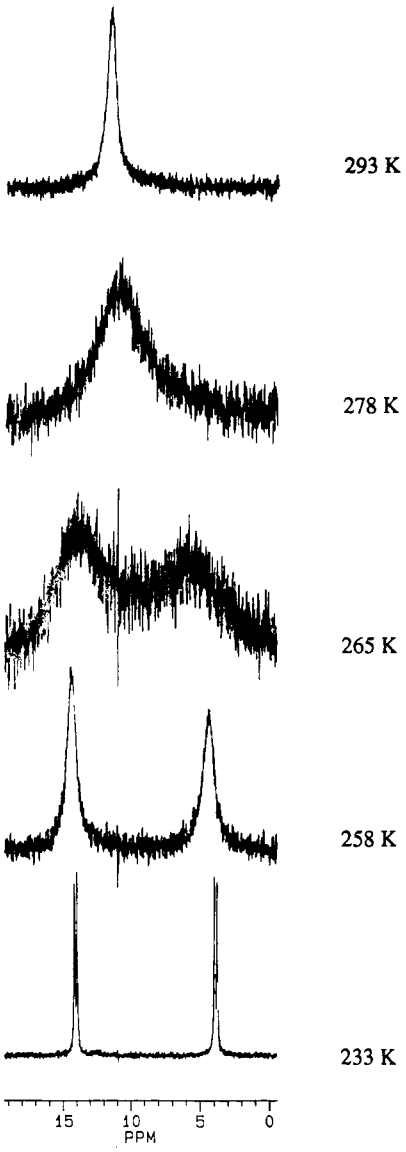


Figure 10. ^{31}P NMR spectra for (S_P,S_P)-**7** at reduced temperatures.

reinforces the chiral environment about the metal formed by the P-aryl groups.

Despite many complicating factors, trends do emerge in asymmetric catalysis using stereochemically matched and mismatched ligands, and dominant features with respect to induction sometimes can be identified. We have observed all the possible outcomes when ligands **1** and **2** are used in asymmetric catalysis. Chirality of the backbone dominates over the asymmetric phosphorus centers in hydrogenations of the dehydroamino acid shown in Table II; hydrosilylations of acetophenone (Table III) show a less pronounced trend, whereas phosphorus asymmetry seems to be crucial in the allylation reactions (Table V). No clear pattern is observed for rhodium-catalyzed hydroborations (Table IV); indeed, (R_P,S_P)-**1**, which one might expect to be neither completely matched nor completely mismatched, gives the best induction when indene is the substrate. Ligand **1** is sometimes better than DIOP in terms of induction; the bis(alkylarylphosphines) **II** have never been shown to be superior to the parent system (**II**, R = Ph).

Modest enantioselectivities have been observed with catalysts based on the hybrid ligands used in this paper, but exceptionally high values were not necessarily expected in this preliminary work. Enantioselectivities could be diminished as a result of puckering of the seven-numbered metal chelates away from ideal C_2 conformations; analogous bis(diarylphosphine) ligands which form *five*-membered ring chelates (e.g., CHIRAPHOS-DIPAMP hybrids) could be much more effective. We have shown that coupling phosphorus- and carbon-based asymmetry can have a profound effect on the performance of a chiral phosphine ligand in catalysis. Moreover, the syntheses of these ligands are no more difficult than any synthesis of DIPAMP.[7,60] The research presented here is a prelude to a long-term study of constructive stereochemical pairing to produce superior ligands for asymmetric induction. Extrapolation of this work to other ligand designs and metal complexes should afford an intriguing range of stereochemically matched (and mismatched) catalytic reagents for asymmetric catalysis.

Experimental Section

General Procedures. Melting points are uncorrected. High-field NMR spectra were recorded on a 300- or 250-MHz instrument using $CDCl_3$ solvent unless otherwise stated. Chemical shifts are reported in δ (ppm) relative, in most cases, to $CHCl_3$ as an internal reference (7.25 ppm for ^1H and 77.1 ppm for ^{13}C). Occasionally, MeOH (3.31 ppm for ^1H and 49.6 ppm for ^{13}C) and dioxane (3.53 ppm for ^1H and 66.5 ppm for ^{13}C) were used as internal references. ^{19}F NMR chemical shifts are reported relative to $CFCl_3$. Where abbreviated DEPT sequence experiments were carried out during ^{13}C NMR experments, the carbon multiplicities are listed as (C) quaternary, (CH_2) methylene, and (CH/CH_3) methine/methyl. The purity of all products was assessed as >95% via ^1H and ^{13}C NMR analyses. Thin-layer chromatography was performed on silica gel 60 F_{254} plates. Flash chromatography was performed on SP silica gel (230–400 mesh ASTM). Tetrahydrofuran (THF) was distilled immediately before use from sodium–benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled immediately before use from CaH_2.

(*R*,*R*)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis([2-methoxyphenyl]phenylphosphino)butane ((S_P,S_P)-1**, (S_P,R_P)-**1**, and (R_P,R_P)-**1**). Mixture of Epimers.** Potassium (1.80 g, 45 mmol) and 0.48 g (21 mmol) of sodium were melted together in a Schlenk tube under argon; 80 mL of dioxane was added, followed by 6.05 g (20 mmol) of bis(2-methoxyphenyl)-phenylphosphine. The mixture was stirred vigorously, and a somewhat exothermic reaction occurred as a yellow suspension of potassium (2-methoxyphenyl)phenylphosphide formed. After 3 h at room temperature, a solution of 4.7 g (10 mmol) of (*R*,*R*)-1,4-ditosyl-2,3-*O*-isopropylidene-L-threitol in 60 mL of toluene was added and the mixture stirred for 20 min, during which time the color of the solution faded. The mixture was filtered through Celite and the residue washed with 40 mL of toluene. Evaporation of the solvents gave the crude material as a viscous pale yellow oil, which was purified by flash chromatography with 20% ethyl acetate–80% hexane as eluent to give 3.84 g (6.8 mmol, 68%) of the bisphosphine **1**.

Formation of the Complexes 6 as a Mixture of Epimers and Separation of These. The epimeric bisphosphines **1** formed above (3.84 g, 6.9 mmol) were dissolved in 100 mL of dry ethanol against a stream of argon, and 2.0 g (7.6 mmol) of molybdenum hexacarbonyl was added followed by 0.45 g (14 mmol) of sodium borohydride. The mixture was stirred and refluxed for 3 h and then cooled to room temperature. Water (150 mL) was added in small portions to precipitate the dissolved complexes; these were filtered and dried in vacuo over P_2O_5 to give 4.55 g (5.9 mmol, 85%) of the mixture as a finely divided pale yellow solid. A 2.5-g sample of this material was flash chromatographed with 10% ethyl acetate–90% hexane as eluent to give 0.318 g (0.42 mmol, 12%) of (S_P,S_P)-**6**, 0.472 g (0.62 mmol, 19%) of (R_P,S_P)-**6** (19:1 mixture of R_P,S_P epimer to the other isomers), and 0.334 g (0.44 mmol, 13%) of (R_P,R_P)-**6**. Data for these isolated complexes as follows. (S_P,S_P)-**6**: R_f 0.32 (20% ethyl acetate–80% hexane); ^1H NMR

(60) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.

δ 1.26 (s, 6 H), 2.87 (m, 2 H), 3.12 (m, 2 H), 3.34 (s, 6 H), 4.13 (m, 2 H), 6.52 (m, 2 H), 6.83 (m, 2 H), 7.08 (m, 10 H), 7.77 (m, 4 H); ^{13}C NMR δ 26.6, 37.0 (m), 54.6, 78.4 (m), 108.0, 111.2, 120.2, 129.5, 129.9, 131.1, 133.2, 161.0; ^{31}P NMR δ 13.99; IR (Nujol) 3059, 2014, 1919, 1882, 1586, 1574, 1434, 1377, 1245, 1050, 1024, 751 cm^{-1}; $[\alpha]_D^{20}$ = 126° (c = 0.585, benzene). (R_P,S_P)-6: R_f 0.22 (20% ethyl acetate–80% hexane); ^{1}H NMR δ 1.24 (s, 3 H), 1.25 (s, 3 H), 2.62 (m, 1 H), 2.90 (s, 3 H), 2.96 (m, 1 H), 3.16 (m, 1 H), 3.31 (s, 3 H), 3.89 (m, 1 H), 3.96 (m, 1 H), 4.28 (m, 1 H), 6.33 (m, 1 H), 6.52 (m, 1 H), 6.82 (m, 1 H), 6.95 (m, 1 H), 7.09 (m, 9 H), 7.51 (m, 2 H), 7.78 (m, 2 H), 8.40 (m, 1 H); ^{13}C NMR δ 26.7, 32.0 (dd, J = 20.2, 1.9 Hz, CH_2), 34.5 (dd, J = 18.0, 1.6 Hz, CH_2), 54.5, 54.6, 78.9 (m), 107.8 (C), 111.2, 111.9, 120.4, 120.5, 120.6, 120.8, 128.1, 129.5, 129.7, 129.9, 131.2, 133.0, 133.2, 159.8 (C), 159.9 (C), 160.9 (C), 210.9 (m, carbonyl), 214.5 (m, carbonyl); ^{31}P NMR δ 13.67 (d, $^2J_{P-P}$ = 20.9 Hz), 22.47 (d, $^2J_{P-P}$ = 20.9 Hz); IR (Nujol) 2013, 1914, 1898, 1878, 1588, 1574, 1466, 1275, 1245, 1051, 1024 cm^{-1}. (R_P,R_P)-6: R_f 0.21 (20% ethyl acetate–80% hexane); ^{1}H NMR δ 1.17 (s, 6 H), 2.59 (m, 2 H), 3.01 (s, 6 H), 3.71 (m, 2 H), 4.27 (m, 2 H), 6.35 (m, 2 H), 6.83 (m, 2 H), 7.05 (m, 8 H), 7.49 (m, 4 H), 7.94 (m, 2 H); ^{13}C NMR δ 26.8, 33.9 (m, CH_2), 54.5, 79.0, 107.9, 111.6, 120.6, 127.6, 128.1, 130.5, 132.3, 135.6; ^{31}P NMR δ 18.8; IR (Nujol) 2012, 1916, 1897, 1877, 1587, 1571, 1466, 1275, 1242, 1053, 1073, 888 cm^{-1}; $[\alpha]_D^{20}$ = 77.9° (c = 0.57, benzene). Anal. Calcd: C, 57.97; H, 4.48. Found: C, 57.78; H, 4.74.

Liberation of the Ligands from the Isolated Complexes. (S_P,S_P)-1. A solution of 200 mg (0.26 mmol) of (S_P,S_P)-6 in 20 mL of THF was cooled to −78 °C with stirring under argon. Sodium naphthalenide (~0.5 M in THF) was added dropwise until all the starting material was consumed (determined by TLC). The resulting dark brown mixture was diluted with 60 mL of dry, air-free ether and filtered through Celite under argon. Evaporation of the solvents gave the crude material, which was purified by flash chromatography with 15% ethyl acetate in hexane as eluent to give 53 mg (0.095 mmol, 36%) of the bisphosphine (S_P,S_P)-1 as a clear viscous oil: R_f 0.39 (20% ethyl acetate–80% hexane); ^{1}H NMR δ 1.29 (s, 6 H), 2.52 (dd, J = 14.0, 6.7 Hz, 2 H), 2.82 (dd, J = 14.0, 5.1 Hz, 2 H), 3.23 (s, 6 H), 4.31 (s, 6 H), 6.45 (m, 2 H), 6.82 (m, 2 H), 7.08 (m, 8 H), 7.38 (m, 2 H), 7.56 (m, 4 H); ^{13}C NMR δ 27.2, 31.2 (dd, J = 16.8, 4.5 Hz, CH_2), 54.8, 80.7 (dd, J = 18.1, 7.5 Hz), 108.4 (C), 110.5, 120.80, 120.82, 120.9, 128.0, 128.10, 128.15, 128.21, 129.9, 133.0, 133.30, 133.34, 133.5, 138.9 (d, J = 14.4 Hz, C), 161.3 (d, J = 12.1 Hz, C); ^{31}P NMR δ −29.82; IR (CH_2Cl_2) 3054, 2986, 2937, 1586, 1573, 1474, 1463, 1433, 1380, 1371, 1242, 1042, 1026, 880 cm^{-1}. MS (70 eV, EI; m/e): calcd for $C_{33}H_{36}O_4P_2$ 558.2089, found 558.2075; calcd for M^+ ^{13}C 559.2122, found 559.2119; 558 (2), 343 (80), 285 (20), 230 (10), 215 (100). $[\alpha]_D^{20}$ = −13.6° (c = 2.6, benzene).

(R_P,S_P)-1. The preparation was carried out as for (S_P,S_P)-1 to give 53 mg (0.095 mmol, 37%) of the bisphosphine (R_P,S_P)-1 as a clear viscous oil: R_f 0.39 (20% ethyl acetate–80% hexane); ^{1}H NMR δ 3.31 (s, 3 H), 3.35 (s, 3 H), 2.43–2.73 (m, 4 H), 3.17 (s, 3 H), 3.18 (s, 3 H), 4.20–4.33 (m, 2 H), 6.43 (m, 2 H), 6.80 (m, 2 H), 7.06 (m, 8 H), 7.35 (m, 2 H), 7.57 (m, 4 H); ^{31}P NMR δ −29.87 (s), −30.69 (s); IR (CH_2Cl_2) 3054, 2986, 2937, 1586, 1573, 1474, 1463, 1433, 1242, 1042, 1026, 880 cm^{-1}. MS (70 eV, EI; m/e): calcd for $C_{33}H_{36}O_4P_2$: 558.2089, found 558.2075; M^+ ^{13}C calcd: 559.2122, found 559.2120; 558 (1), 543 (1), 343 (90), 285 (20), 215 (100). $[\alpha]_D^{20}$ = −12.4° (c = 2.65, benzene).

(R_P,R_P)-1. This compound was prepared by a procedure similar to that for (S_P,S_P)-1 to give 68 mg (0.12 mmol, 49%) of the bisphosphine (R_P,R_P)-1 as a clear viscous oil: R_f 0.39 (20% ethyl acetate–80% hexane); ^{1}H NMR δ 1.35 (s, 6 H), 2.42–2.68 (m, 4 H), 3.17 (s, 6 H), 4.24 (m, 2 H), 6.43 (m, 2 H), 6.79 (m, 2 H), 7.07 (m, 8 H), 7.29 (m, 2 H), 7.58 (m, 4 H); ^{13}C NMR δ 27.3, 30.6 (dd, J = 16.4, 2.9 Hz, CH_2), 54.8, 80.1 (dd, J = 15.2, 7.5 Hz), 108.4, 110.4, 120.8, 128.2, 128.3, 129.8, 132.9, 133.0, 133.2, 133.5, 138.9 (d, 14.3 Hz), 161.2 (d); ^{31}P NMR δ −30.87; IR (CH_2Cl_2) 3054, 2984, 2933, 2834, 1585, 1573, 1473, 1463, 1432, 1379, 1370, 1242, 1180, 1163, 1041, 1026, 889 cm^{-1}. MS (70 eV, EI; m/e): calcd for $C_{33}H_{36}O_4P_2$ 558.2089, found 558.2075 M^+ ^{13}C calcd 559.2122, found 559.2120; 558 (1), 533 (1), 343 (90), 285 (25), 215 (100). $[\alpha]_D^{20}$ −0.6° (c = 2.62, benzene).

(*R*,*R*)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis([2-(dimethylamino)phenyl]phenylphosphino)butane ((S_P,S_P)-2, (S_P,R_P)-2, and (R_P,R_P)-2). Mixture of Epimers. Potassium (1.8 g, 46 mmol) and sodium (0.4 g, 17.2 mmol) were melted together in a Schlenk tube under argon; then, 60 mL of dioxane was added. Bis(2-(dimethylamino)phenyl)phenylphosphine (7.0 g, 20 mmol) was added against a stream of argon, and the mixture was stirred vigorously at 25 °C for 2 h 45 min, during which time a suspension of (2-(dimethylamino)phenyl)phenylphosphide formed. 1,4-Ditosyl-2,3-*O*-isopropylidene-L-threitol (4.7 g, 10 mmol) was added as a solution in 60 mL of toluene, and the mixture was stirred at 25 °C for 15 min and then filtered through Celite under argon; the Celite was washed through with a further 20 mL of toluene. Evaporation of the solvents gave the crude bisphosphine as a viscous yellow oil; this was purified by flash chromatography with 5% ethyl acetate in hexane as eluent to give 4.57 g (7.8 mmol, 78%) of **2** as an approximately 1:2:1 mixture of R_P,R_P:R_P,S_P:S_P,S_P phosphine epimers.

Formation of the Complexes 7 as a Mixture of Epimers and Separation of These. The epimeric bisphosphine mixture formed above (1.33 g, 2.3 mmol) was dissolved in 50 mL of 95% ethanol; 0.64 g of molybdenum hexacarbonyl (2.42 mmol) was added, followed by 0.1 g of sodium borohydride (2.6 mmol), and the mixture was stirred and refluxed under argon for 3 h. The solution was cooled to 25 °C under argon; then 20 mL of water was added. The mixture was stored at −25 °C for 1 h and filtered, and the residue was dried in vacuo over P_2O_5, giving 1.55 g (1.96 mmol, 85%) of a mixture of isomeric molybdenum tetracarbonyl complexes **7**. Flash chromatography with 10% ethyl acetate–90% hexane as eluent gave pure samples of 0.275 g (0.35 mmol, 15%) of (R_P,R_P)-7, 0.497 g (0.63 mmol, 27%) of (R_P,S_P)-7, and 0.193 g (0.24 mmol, 10%) of (S_P,S_P)-7. Data for these complexes is as follows. (R_P,R_P)-7: R_f 0.34 (10% ethyl acetate–90% hexane); ^{1}H NMR δ 1.15 (s, 6 H), 1.93 (s, 12 H, broad), 2.63 (m, 2 H), 3.95 (m, 2 H), 4.27 (m, 2 H), 6.95 (m, 12 H), 7.34 (m, 4 H), 8.66 (m, 2 H); ^{13}C NMR δ 26.6, 31.6 (m, CH_2), 45, 79.2, 107.8, 125.4, 125.6, 127.9, 128.0, 128.1, 129.2, 129.3, 129.4, 132.9, 140.1, 140.3, 140.6, 158.8 (C), 210.8 (carbonyl); ^{31}P NMR δ 24.7; IR (Nujol) 3057, 2017, 1928, 1919, 1896, 1874, 1582, 1564, 1455, 1244, 1053, 887, 738, 692 cm^{-1}; MS (30 eV, EI) m/e 737 (<1), 709 (5), 677 (10), 356 (70), 228 (100); $[\alpha]_D^{20}$ = 224.5° (c = 0.86, benzene). Anal. Calcd for $C_{39}H_{42}N_2O_6P_2Mo$: C, 59.09; H, 5.34; N, 3.54. Found: C, 60.15; H, 3.98; N, 3.28. (R_P,S_P)-7: R_f 0.30 (10% ethyl acetate–90% hexane); ^{1}H NMR δ 1.16 (s, 3 H), 1.17 (s, 3 H), 1.91 (s, 6 H), 1.99 (s, 6 H), 2.59 (m, 1 H), 2.86 (m, 1 H), 3.24 (m, 1 H), 3.88 (m, 1 H), 4.06–4.24 (m, 2 H), 7.00 (m, 12 H), 7.28 (m, 1 H), 7.41 (m, 2 H), 7.66 (m, 2 H), 8.74 (m, 1 H); ^{13}C NMR δ 26.6, 26.7, 30.7 (m, CH_2), 35.6 (m, CH_2), 45.5, 45.8, 78.6, 107.8 (C), 124.4, 124.5, 125.35, 125.38, 125.64, 125.68, 125.8, 125.9, 127.8, 127.9, 128.0, 128.2, 128.3, 129.6, 129.8, 130.8, 132.9, 133.6, 133.8, 140.2, 140.7, 156.8 (m, C), 158.7 (m, C), 212.1 (carbonyl), 214.8 (carbonyl); ^{31}P NMR δ 11.4 (d, $^2J_{P-P}$ = 19.3), 26.0 (d, $^2J_{P-P}$ = 19.3 Hz); IR (Nujol) 3058, 2000, 1916, 1901, 1876, 1584, 1567, 1459, 1435, 1379, 1245, 1050, 880 cm^{-1}; MS (30 eV, EI) m/e 737 (<1), 709 (2), 677 (5), 356 (95), 228 (100). Anal. Calcd for $C_{39}H_{42}N_2O_6P_2Mo$: C, 59.09; H, 5.34; N, 3.54. Found: C, 59.19; H, 5.47; N, 3.47. (S_P,S_P)-7: R_f 0.25 (10% ethyl acetate–90% hexane); ^{1}H NMR δ 1.18 (s, 6 H), 2.08 (s, 12 H), 2.77 (m, 2 H), 3.13 (m, 2 H), 3.99 (m, 2 H), 7.07 (m, 12 H), 7.29 (m, 2 H), 7.72 (m, 4 H); ^{13}C NMR δ 26.7, 35.4 (m, CH_2), 45.9, 78.0 (m), 107.8 (C), 124.5, 125.56, 125.65, 128.0, 128.2, 128.4, 129.6, 130.9, 133.8, 135.4 (C), 135.9 (C), 157.1 (m, C), 211.5 (carbonyl); ^{31}P NMR δ 11.5 (broad s); IR (Nujol) 3058, 2015, 1999, 1915, 1885, 1474, 1458, 1433, 1378, 1372, 1242, 1048 cm^{-1}; MS (30 eV, EI) m/e 737 (<1), 709 (<1), 678 (2), 639 (2), 356 (95), 228 (100); $[\alpha]_D^{20}$ = 158° (c = 0.995, benzene). Anal. Calcd for $C_{39}H_{42}N_2O_6P_2Mo$: C, 59.09; H, 5.34; N, 3.54. Found: C, 59.2; H, 5.36; N, 3.42.

Liberation of the Ligands from the Isolated Complexes. (R_P,R_P)-2. A solution of 0.325 g of (R_P,R_P)-7 (0.41 mmol) in 20 mL of THF was cooled to −78 °C with stirring under argon. Sodium naphthalenide (~0.5 M in THF) was added dropwise until all the starting material was consumed (monitored by TLC). The cold mixture was diluted with 60 mL of dry, deoxygenated ether and then filtered through Celite under argon. Evaporation of the solvents gave the crude product, which was purified by flash chromatography with 5% ethyl acetate–95% hexane as eluent. A 0.130-g (0.223-mmol, 54%) sample of (R_P,R_P)-2 was obtained: R_f 0.21 (5% ethyl acetate–95% hexane); ^{1}H NMR (300 MHz, benzene-d_6) δ 1.37 (s, 6 H), 2.36–2.54 (m, 4 H), 2.44 (s, 12 H), 4.19 (m, 2 H), 6.90 (m, 4 H), 7.08 (m, 8 H), 7.31 (m, 2 H), 7.55 (m, 4

H); ^{13}C NMR (75.5 MHz, benzene-d_6) δ 27.5, 32.1 (dd, J = 17.1, 3.3 Hz, CH_2), 45.2, 80.5 (dd, J = 15.6, 7.4 Hz), 108.6, 120.3, 124.1, 127.9 (m), 129.1, 132.0, 133.1, 133.3, 136.8, (d, J = 14.6 Hz), 140.4 (d, J = 15.8 Hz), 157.8 (d, J = 17.2 Hz); ^{31}P NMR δ −29.7; IR (CH_2Cl_2) 3054, 2986, 2939, 2827, 2784, 1582, 1477, 1453, 1434, 1380, 1157, 1093, 1040, 943, 895 cm^{-1}. MS (70 eV, EI; m/e): calcd for $C_{35}H_{42}N_2O_2P_2$ 584.2721, found 584.2731; M^+ ^{13}C calcd 585.2755, found 585.2767; 584 (<1), 569 (<1), 356 (70), 228 (60), 150 (100). $[\alpha]_D^{20}$ = 12° (c = 0.865, benzene).

(R_P,S_P)-2. This compound was prepared as for the R_P,R_P isomer, but using 0.856 g of (R_P,S_P)-7 (1.08 mmol) to give 0.392 g (0.622 mmol, 62%) of (R_P,S_P)-2: R_f 0.21 (5% ethyl acetate–95% hexane); ^1H NMR δ 1.37 (s, 3 H), 1.39 (s, 3 H), 2.37–2.67 (m, 4 H), 2.47 (s, 6 H), 2.53 (s, 6 H), 4.21–4.38 (m, 2 H), 6.92–7.20 (m, 12 H), 7.38 (m, 2 H), 7.57 (m, 4 H); ^{13}C NMR δ 27.30, 27.35, 32.26 (dd, J = 4.8, 2.9 Hz, CH_2), 32.54 (dd, J = 4.8, 2.9 Hz, CH_2), 45.0, 80.27 (dd, J = 15.2, 7.6, Hz), 80.68 (dd, J = 18.1, 7.6 Hz), 108.4 (C), 120.5, 120.6, 120.7, 124.3, 124.5, 128.01, 128.06, 128.09, 128.17, 128.2, 129.4, 132.2, 132.5, 133.1, 133.2, 133.4, 133.5, 136.55 (m), 140.55 (m), 157.9, 158.1; ^{31}P NMR δ −29.9 (d, $^5J_{P-P}$ = 1.7 Hz), −30.3 (d, $^5J_{P-P}$ = 1.7 Hz); IR (CH_2Cl_2) 3054, 2985, 2938, 2861, 2826, 2785, 1582, 1477, 1453, 1434, 1380, 1371, 1157, 1093, 1040, 943, 889 cm^{-1}. MS (70 eV, EI; m/e): calcd for $C_{35}H_{42}N_2O_2P_2$ 584.272 127, found 584.273 15; M^+ ^{13}C calcd: 585.2755, found 585.2767; 584 (1), 569 (1), 356 (80), 218 (80), 250 (100). $[\alpha]_D^{20}$ = 12° (c = 0.865, benzene).

(S_P,S_P)-2. This compound was prepared as for the R_P,R_P isomer, using 0.443 g of (S_P,S_P)-7 (0.56 mmol) to give 0.185 g (0.316 mmol, 56%) of (S_P,S_P)-2: R_f 0.21 (5% ethyl acetate–95% hexane); ^1H NMR (300 MHz, benzene-d_6) δ 1.31 (s, 6 H), 2.47 (m, 2 H), 2.51 (s, 12 H), 2.69 (m, 2 H), 4.32 (m, 2 H), 6.94 (m, 4 H), 7.11 (m, 8 H), 7.34 (m, 2 H), 7.56 (m, 4 H); ^{13}C NMR (75.5 MHz, benzene-d_6) δ 27.6, 32.9 (m, CH_2), 45.3, 80.9 (C), 120.3, 124.2, 127.84, 127.87, 127.9, 129.1, 132.1, 133.1, 133.3, 136.7 (m, C), 140.2 (m, C), 157.8 (m, C); ^{31}P NMR δ −30.1; IR (CH_2Cl_2) 3054, 2984, 2938, 2861, 2826, 2783, 1582, 1568, 1476, 1453, 1434, 1380, 1370, 1157, 1093, 1039, 943, 888 cm^{-1}. MS (70 eV, EI; m/e): calcd for $C_{35}H_{42}N_2O_2P_2$ 584.272 127, found 584.273 15; M^+ ^{13}C calcd 585.2755, found 585.2767; 584 (1), 569 (1), 356 (90), 223 (80), 150 (100). $[\alpha]_D^{20}$ = −9° (c = 0.35, benzene).

Attempted Preparation of (*R*,*R*)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis([2,6-dimethoxyphenyl]phenylphosphino)butane ((S_P,S_P)-3, (S_P,R_P)-3, and (R_P,R_P)-3). Mixture of Epimers. Sodium (0.58 g, 25 mmol) and potassium (2.34 g, 60 mmol) were melted together under argon, and 80 mL of dioxane was added. Against a stream of argon, 11.47 g (30 mmol) of bis(2,5-dimethoxyphenyl)phenylphosphine was added and the mixture was stirred, *cautiously at first* (an exothermic reaction occurs) and then vigorously for 2 h 15 min. A precipitate of the phosphide forms soon after stirring has commenced. A solution of 7.05 g of (*R*,*R*)-1,4-ditosyl-2,3-*O*-isopropylidene-L-threitol (15 mmol) in 60 mL of toluene was added, and the mixture was stirred for 15 min at 25 °C and filtered through Celite under argon; the residue was washed with a further 60 mL of toluene. Evaporation of the combined filtrates gave the crude bisphosphine as a pale yellow oil, which crystallized on standing. Recrystallization from absolute ethanol gave a first crop of 2.88 g (4.9 mmol, 33%) of a 1:1 mixture of the R_P,R_P:S_P,S_P phosphine epimers. Recrystallization of the material recovered from the mother liquor gave 2.83 g (4.6 mmol, 31%) of a mixture of all three epimers enriched in the R_P,S_P isomer. Repeated recrystallization of this gave a small quantity (~0.3 g) of the R_P,S_P isomer as a 30:1 mixture with the R_P,R_P and S_P,S_P species. Data for this sample are as follows. (R_P,S_P)-3: R_f 0.17 (20% ethyl acetate–80% hexane); ^1H NMR δ 1.39 (s, 3 H), 1.43 (s, 3 H), 2.77 (m, 2 H), 3.20 (m, 2 H), 3.22 (s, 6 H), 3.29 (s, 6 H), 4.32 (m, 1 H), 4.47 (m, 1 H), 6.29 (m, 4 H), 7.07 (m, 8 H), 7.58 (m, 4 H); ^{13}C NMR δ 27.2, 27.3, 30.7 (overlapping m, CH_2), 55.1, 55.3, 81.2 (overlapping m, CH_2), 104.4, 104.5, 108.0, 126.2, 126.3, 127.5, 127.6, 127.7, 128.6, 130.58, 130.64, 130.87, 130.92, 131.5, 131.6, 131.7, 142.4 (overlapping m), 164.2 (overlapping m); ^{31}P NMR δ −38.7 (d, J = 1.3 Hz), −41.3 (d, J = 1.3 Hz); IR 3053, 2985, 2939, 2837, 1582, 1466, 1429, 1379, 1370, 1246, 1104, 888, 779 cm^{-1}; MS (70 eV, EI; m/e): calcd for $C_{35}H_{40}O_6P_2$: 618.2300, found 618.2288; M^+ ^{13}C calcd 619.2333, found 619.2323; 618 (<1), 603 (<1), 373 (90), 315 (10), 245 (100). Anal. Calcd for $C_{35}H_{40}O_6P_2$: C, 67.95; H, 6.52. Found: C, 68.00; H, 6.74.

Formation of R_P,R_P and S_P,S_P Complexes 8. A 1:1 mixture of 3.22 g of (R_P,R_P)-3 and (S_P,S_P)-3 (5.2 mmol) was dissolved in 100 mL of 95% ethanol; 1.59 g of molybdenum hexacarbonyl (6.0 mmol) was added, followed by 0.466 g (12 mmol) of sodium borohydride, and the mixture was stirred and refluxed under argon for 4 h. The mixture was cooled to room temperature under argon and then stored at −25 °C for 12 h. Filtration and drying of the residue in vacuo over P_2O_5 gave 4.56 g of a mixture of the complexes as a finely divided pale yellow solid. Flash chromatography of 3.4 g of this mixture gave 1.26 g (1.52 mmol, 37%) of (R_P,R_P)-8 and 1.06 g (1.28 mmol, 31%) of (S_P,S_P)-8. Data for these complexes are as follows. (R_P,R_P)-8: R_f 0.2 (10% ethyl acetate–90% hexane); ^1H NMR δ 1.26 (s, 6 H), 2.33 (s, 2 H), 3.29 (s, 12 H), 4.11 (m, 2 H), 4.80 (m, 2 H), 6.34 (m, 4 H), 7.05 (m, 8 H), 7.76 (m, 4 H); ^{13}C NMR δ 27.4, 42.6 (m, CH_2), 54.6, 80.7, 104.1, 107.7 (C), 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 131.2, 131.4, 131.5, 131.6, 131.9, 142.5 (m, C), 160.5 (C); ^{31}P NMR δ 17.9; IR (Nujol) 3062, 2018, 1915, 1886, 1869, 1584, 1436, 1250, 1107 cm^{-1}; MS (30 eV, EI) m/e 772 (<1), 715 (1), 373 (50), 260 (90), 245 (80), 228 (80), 124 (100); $[\alpha]_D^{20}$ = −86.5° (c = 0.93, benzene). Anal. Calcd for $C_{39}H_{40}O_{10}P_2Mo$: C, 56.66; H, 4.88. Found: C, 56.35; H, 4.97. (S_P,S_P)-8: R_f 0.13 (10% ethyl acetate–90% hexane); ^1H NMR δ 1.15 (s, 6 H), 3.24 (s, 12 H), 3.55 (m, 4 H), 3.84 (m, 2 H), 6.26 (m, 4 H), 7.13 (m, 8 H), 8.10 (m, 4 H); ^{13}C NMR δ 26.6, 36.5 (m, CH_2), 54.6, 79.3 (m), 104.4, 107.4 (C), 127.7, 127.8, 127.9, 128.0, 128.8, 131.2, 132.6, 132.7, 132.8, 138.9 (m, C), 160.2 (C), 211.4 (carbonyl); ^{31}P NMR δ 19.4; IR (Nujol) 2017, 1910, 1898, 1867, 1154, 1252, 1108, 1035 cm^{-1}; $[\alpha]_D^{20}$ = 88.5° (c = 1.03, benzene). Anal. Calcd for $C_{39}H_{40}O_{10}P_2Mo$: C, 56.66; H, 4.88. Found: C, 56.84; H, 4.90.

Attempted Liberation of the Ligands from the Isolated Complexes. (S_P,S_P)-3. A solution of 0.496 g (0.62 mmol) of (S_P,S_P)-8 in 20 mL of THF was cooled to −78 °C under argon. Sodium naphthalenide (~0.5 M in THF) was added with stirring until all the starting material was consumed. The solution was diluted with 60 mL of dry, air free ether and then filtered (cold) through Celite under argon. Evaporation of the solvents gave a crude material which was purified by flash chromatography with 10% ethyl acetate–90% hexane as eluent to give 58 mg (0.094 mmol, 16%) of (S_P,S_P-3: R_f 0.17 (20% ethyl acetate–80% hexane); ^1H NMR δ 1.41 (s, 6 H), 2.84 (m, 4 H), 3.21 (s, 12 H), 4.30 (m, 2 H), 6.25 (m, 4 H), 7.07 (m, 8 H), 7.58 (m, 4 H); ^{13}C NMR δ 27.3, 30.7 (dd, J = 17.2, 1.9 Hz, CH_2), 55.2, 81.6 (dd, J = 20.1, 8.7 Hz), 104.5, 108.0 (C), 126.2, 127.5, 127.6, 130.56, 130.64, 130.8, 131.6, 142.5 (d, J = 16.9 Hz, C), 164.1 (d, J = 8.3 Hz, C); ^{31}P NMR δ −38.2; IR (CH_2Cl_2) 3054, 2987, 1582, 1466, 1430, 1380, 1247, 1106, 1036, 896 cm^{-1}. MS (70 eV, EI; m/e): calcd for $C_{35}H_{40}O_6P_2$ 618.2300, found 618.2288; M^+ ^{13}C calcd 619.2333, found 619.2323; 618 (<1), 604 (<1), 373 (85), 315 (10), 245 (100), 167 (40). $[\alpha]_D^{20}$ = −38.7° (c = 2.9, benzene).

Attempts to liberate the phosphine ligands from the other complexes using similar procedures failed due to overreduction.

Typical Procedure for the Hydrogenation Reactions (Table II). A Schlenk tube was charged with 4.9 mg of chloro(1,5-cyclooctadiene)rhodium(1+) dimer (0.01 mmol), 12.3 mg (0.022 mmol) of (R_P,S_P)-1, and 4.4 mg (0.02 mmol) of sodium tetrafluoroborate; it was then evacuated and flushed with argon five times. The Schlenk tube was evacuated and then flooded with hydrogen, 1 mL of degassed ethanol was added, and the mixture was stirred at 25 °C for 10 min. A solution of 0.410 g (2.0 mmol) of α-acetamidocinnamic acid in 5 mL of degassed ethanol was added and the mixture stirred at 25 °C for 2 days. The solvent was evaporated and the residue dissolved in 0.5 M NaOH solution; this solution was then filtered. The filtrate was acidified with concentrated HCl, extracted with ether (2 × 100 mL), and dried over sodium sulfate. Evaporation of the solvent gave the crude acid with a rotation of $[\alpha]_D^{20}$ = −21° (c = 1.0, EtOH), which indicates the *R* configuration.

The methyl esters of the crude acids were formed by reaction with diazomethane. The optical activity of the methyl esters was determined by integration of the ^1H NMR using Eu(hfc)$_3$ shift reagent in comparison with the racemate.

Typical Procedure for Hydrosilation Reactions (Table III).[50] A Schlenk tube was charged with 2.6 mg of chloro(1,5-cyclooctadiene)rhodium(1+) dimer (0.0054 mmol) and 6.6 mg (0.012 mmol) of (S_P,S_P)-1 and then evacuated and flushed with

Table VI. X-ray Crystallographic Data Collection Parameters

	(R_P,R_P)-6	(R_P,R_P)-7	(R_P,R_P)-8·0.5CH_2Cl_2	(S_P,S_P)-8
fw	766.57	834.47	826.62	826.62
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 1)	$P2_12_12_1$ (No. 19)
cryst size, mm^3	0.5 × 0.5 × 0.5	0.1 × 0.4 × 0.4	0.2 × 0.3 × 0.5	0.2 × 0.4 × 0.5
lattice params				
a, Å	11.621 (3)	11.013 (6)	11.64 (1)	14.007 (3)
b, Å	10.676 (2)	21.134 (5)	16.05 (1)	27.419 (8)
c, Å	14.850 (2)	18.555 (6)	10.760 (7)	10.394 (3)
α, deg			94.06 (6)	
β, deg	101.59 (2)	101.32 (3)	97.05 (6)	
γ, deg			97.10 (7)	
V, $Å^3$	1804.8 (6)	4235 (2)	1973 (5)	3992 (2)
Z	2	4	2	4
R; R_w	0.029; 0.036	0.111; 0.122	0.098; 0.110	0.052; 0.054
no. of obsd data ($I > 3\sigma(I)$)	3866	3838	3142	2207
no. of variables	432	358	403	274
temp, °C	23	−85	23	23

argon three times. A 2-mL aliquot of THF was added, and the mixture was stirred at 25 °C for 10 min; 0.15 mL (0.146 g, 1.07 mmol) of phenylethanone was added, followed by 0.37 mL (0.37 g, 2 mmol) of diphenylsilane. The resulting bright yellow solution was stirred at 25 °C for 48 h; 2 mL of ethanol and one drop of concentrated HCl was added, and the mixture was stirred at 25 °C for 4 h. The mixture was neutralized with sodium bicarbonate solution, diluted with 50 mL of ether, washed with saturated aqueous NaCl, and dried over magnesium sulfate. Evaporation of the solvents gave the crude material, which was purified by flash chromatography with 10% ethyl acetate in hexane as eluent to give 0.13 g (1.06 mmol, 87%) of 1-phenylethanol. The optical yield was determined to be 43% from ^1H NMR using a $Eu(hfc)_3$ shift. The specific rotation was $[\alpha]_D^{20} = +16$ ($c = 3.94$, CH_2Cl_2), which gives an R absolute configuration of the product. Other reactions in this series were carried out under the same conditions.

Typical Procedure for the Catalyzed Hydroboration Reactions (Table IV).[61] A Schlenk tube was charged with 4.9 g (0.01 mmol) of chloro(1,5-cyclooctadiene)rhodium(1+) dimer and 10.5 mg (0.021 mmol) of DIOP and evacuated/flushed three times with argon. An aliquot of 2 mL of THF was added, and the resulting golden yellow solution was stirred at 20 °C for 15 min. A solution of 94 mg (1 mmol) of norbornene in 2 mL of THF was added, the mixture was cooled to −78 °C, and 144 mg of catecholborane was added. A white precipitate formed on stirring at −78 °C for 5 min. When the mixture was warmed −40 °C, the precipitate dissolved and the solution became lime green but returned to golden yellow within 1 h. The solution was allowed to stand at −40 °C for 72 h, and no further color change occurred. The solution was then cooled to −78 °C; 1 mL of ethanol, 1.7 mL of 3 M NaOH, and 0.7 mL of 30% H_2O_2 were added. The mixture was warmed to 25 °C over ca. 1 h and stirred for 12 h at that temperature. A solution of 10 mL of 1 M NaOH was added, and the organic material was extracted with ether (4 × 25 mL). The combined extracts were washed with 1 M NaOH and saturated aqueous NaCl and dried over $MgSO_4$. Removal of the solvents in vacuo gave 111 mg (99%) of crystalline *exo*-norborneol; this sample was contaminated with a small amount of phosphine oxides from the catalyst. The optical purity of this sample was accessed via ^1H NMR using $Eu(hfc)_3$ shift reagent.

Typical Procedure for Allylation Reactions (Table V).[55] To a solution of 1 mmol of $LiN(TMS)_2$ in 2 mL of THF was added a solution of 0.279 g (1.1 mmol) of methyl *N*-(diphenylmethylene)glycinate[62] in 2 mL of THF with stirring at −78 °C. The mixture was stirred at −78 °C for 1 h 15 min; then a solution of 0.120 g (0.13 mmol) of allyl acetate, 4.5 mg (0.02 mmol) of palladium acetate, and 23.4 mg (0.04 mmol) of (R_P,R_P)-7 in 2 mL THF was added; the mixture was stored at −60 °C for 4 h. The reaction was quenched by adding 1 mL of saturated aqueous NH_4Cl; the mixture was diluted with 100 mL of ether, washed with saturated aqueous NaCl (1 × 50 mL) and dried over Na_2SO_4. Evaporation of the solvents gave the crude material, which was purified by flash chromatography, with 5% ethyl acetate in hexane as eluent, to give 0.249 g (77%) of the product: $[\alpha]_D^{20} = +20.6°$ ($c = 4.08$, $CHCl_3$), which indicated 18% ee and the R configuration.

X-ray Crystallographic Studies. All data were collected on a Rigaku AFC5S fully automated single-crystal X-ray diffractometer using graphite-monochromated Mo Kα radiation. A summary of data collection parameters is given in Table VI. Data were corrected for Lorentz and polarization effects. The structures were solved using the direct-methods routine of the public domain program package SHELX86, which found the Mo and P atoms.[63,64] The models were completed by successive difference Fourier maps to locate the remaining lighter atoms. For (R_P,R_P)-6 all non-hydrogen atoms were refined anisotropically, but for (R_P,R_P)-7 only the Mo and P atoms were refined anisotropically. The data permitted the Mo, P, and O atoms of (R_P,R_P)-8, and (S_P,S_P)-8 to be refined anisotropically, except for O116a of (R_P,R_P)-8, which became nonpositive definitive upon anisotropic refinement and was left isotropic. The phenyl rings in (R_P,R_P)-8 were refined as rigid bodies with C–C distances of 1.395 Å and C–C–C angles of 120.0°. As can be seen from the high residuals, refinement of (R_P,R_P)-7 and (R_P,R_P)-8 suffered from having two independent molecules per asymmetric unit. Because of high residuals found for an initial room-temperature data collection, data for (R_P,R_P)-7 was recollected at −85 °C. The crystal morphology—a thin plate—and the presence of CH_2Cl_2 lattice solvent molecules in less than unitary amounts (two independent sites with occupanices of 0.60 and 0.40) contribute to high residuals, which persist in spite of low-temperature data collection. Due to the lack of improvement of the structure of (R_P,R_P)-7 with low-temperature data collection, low-temperature collection on (R_P,R_P)-8 was not attempted. It should be remembered for these two structures that the bond distances and angles may not be accurate. All of the space groups are by necessity acentric due to the chirality of the molecules. In each case the proper enantiomorph was chosen on the basis of the known stereochemistry of the starting $Me_2CO_2C_2H_2$ backbone. Hydrogen atoms were included in calculated positions but were not refined. PLUTO drawings of the phosphine backbone of the molecules are provided in Figures 6–9. Since the goal of the crystallographic analyses was to obtain the configuration of the phosphine ligand and since the structures are not exceptional, the crystallographic data have been placed in the supplementary material.

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Registry No. (R_P,R_P)-1, 143681-71-4; (S_P,R_P)-1, 143681-70-3; (S_P,S_P)-1, 143681-69-0; (R_P,R_P)-2, 143681-73-6; (S_P,R_P)-2, 143681-72-5; (S_P,S_P)-2, 143681-75-8; (R_P,R_P)-3, 143681-77-0; (S_P,R_P)-3, 143681-76-9; (S_P,S_P)-3, 143681-74-7; 5, 37002-45-2; (R_P,R_P)-6, 143681-81-6; (R_P,S_P)-6, 143730-75-0; (S_P,S_P)-6, 143730-74-9; (R_P,R_P)-7, 143681-82-7; (R_P,S_P)-7, 143730-76-1; (S_P,S_P)-7, 143730-77-2; (R_P,R_P)-8, 143681-83-8; (R_P,R_P)-8·0.5CH_2Cl_2, 143681-84-9; (S_P,S_P)-8, 143730-78-3; (*R*,*R*)-DIOP, 32305-98-9; (*R*,*R*)-PAMPOP, 71359-99-4; DIPAMP, 97858-62-3; (*R*)-CHNHAc(COOH)(CH_2Ph), 10172-89-1; (*S*)-CHNHAc(COOH)(CH_2Ph), 2018-61-3; PPh_2(2-$MeOC_6H_4$), 53111-20-9; PPh(2-$MeOC_6H_4$)$_2$, 36802-41-2; PPh_2(4-$MeOC_6H_4$), 896-89-9; PPh(2-$Me_2NC_6H_4$)$_2$, 4551-07-9; PPh_2(2-$Me_2NC_6H_4$), 4358-50-3; $MePPh_2$, 1486-28-8; $MePPh$(2-$MeOC_6H_4$), 1485-88-7; $MePPh$(4-$MeOC_6H_4$), 37042-93-6; $MeP(S)Ph$(2-$Me_2NC_6H_4$), 143681-80-5; $MeP(O)Ph_2$, 2129-89-7; PhAc, 98-86-2; (*R*)-CHOH(Ph)(Me), 1517-69-7; (*S*)-CHOH(Ph)(Me), 1445-91-6; Ph_2C=NCH_2COOMe, 81167-39-7; (*R*)-Ph_2C=NCH(COOMe)(CH_2CH=CH_2), 118169-13-4; (*S*)-Ph_2C=NCH(COOMe)(CH_2CH=CH_2), 118169-12-3; $Pd(OAc)_2$, 3375-31-3; Ph_2SiH_2, 775-12-2; $C_6H_4O_2BH$, 274-07-7; potassium (2-methoxyphenyl)phenylphosphide, 143681-85-0; molybdenum tetracarbonyl, 44780-98-5; (2-(dimethylamino)-phenyl)phenylphosphide, 143681-78-1; (2,6-bis(methoxy)-phenyl)phenylphosphide, 143681-79-2; chloro(1,5-cyclooctadiene)rhodium(1+) dimer, 12092-47-6; acetamidocinnamic acid, 5469-45-4; norbornene, 498-66-8; indene, 95-13-6; styrene, 100-42-5; (*R*)-*exo*-norborneol, 29583-34-4; (*S*)-1-indanol, 25501-32-0; allyl acetate, 591-87-7.

Supplementary Material Available: Tables of atomic coordinates, anisotropic displacement parameters, hydrogen atom positional parameters, and bond angles and distances and diagrams showing the atom-labeling and numbering system for (R_P,R_P)-6, (R_P,R_P)-7·CH_2Cl_2, (R_P,R_P)-8, and (S_P,S_P)-8 (85 pages). Ordering information is given on any current masthead page.

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Biphenyl-Bridged Metallocenes That Are Chiral, Configurationally Stable, and Free of Diastereomers[1]

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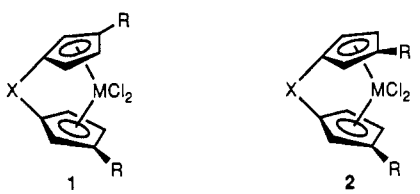
Formation of diastereomers is precluded when biphenyl-bridged bis(cyclopentadienyls) and transition-metal halides combine to give chiral *ansa*-metallocenes. These cyclopentadienyls must be symmetrically substituted. Syntheses and X-ray diffraction analyses are reported for four biphenyl-bridged *ansa*-metallocenes: titanocene dichlorides **17** and **22**, zirconocene dichloride **18**, and ferrocene **13**.

Introduction

Bridged chiral metallocenes—**1** for example—are the basis of reagents and catalysts that bring about a number of transformations stereoselectively.[2] However, syntheses



of these metallocenes are commonly encumbered by formation of their meso isomers **2**.[3] In only one case did the desired racemic structure predominate overwhelmingly,[3i,4] but even then not when the procedure was altered in a seemingly minor way.[3j] A design would, therefore, be desirable that would eliminate the meso isomers. A strategy that Halterman,[5] McLaughlin,[6] and Bosnich[7] used to achieve this goal is to connect chiral groups to the precursors in order to increase the forces favoring one diastereomer. An alternative, which we report here, is to

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