P-Modular Homochiral Bis(phosphanes) with 1,2-Disubstituted Cyclopentane Backbones in Asymmetric Hydrogenation[‡]

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Keywords: Chirality / Asymmetric synthesis / Hydrogenation / Chelate phosphanes / Rhodium

The review surveys synthetic aspects of a class of bidentate phosphanes based on the *trans*-1,2-disubstituted cyclopentane framework and the application of such ligands in transition-metal-catalyzed enantioselective hydrogenation. In particular, we address the preparative potential of the isomerically pure multi-purpose P–H and P–Cl reagents (*R*,*R*)- and (*S*,*S*)-$C_5H_8(PX_2)_2$ (X = H, Cl), which can serve to construct a family of optically active bis(phosphanes) with structural components ("modules") that are easily and systematically interchanged. The so-designed chelate ligands allow access to rhodium catalysts with stereodiscriminating properties, depending on parameters such as (i) presence of P-substituents that are equal or pairwise different in steric demand, (ii) spatial orientation of such substituents as defined by the *endo*- and *exo*-chelate P–C–C–P and P–Rh–P–C torsion angles, and (iii) existence of *C*- and *P*-chirogenic stereoelements in matched (or mismatched) combination.

Introduction

The discovery of soluble transition metal complexes which catalyze enantioselective hydrogenation and oxidation reactions is amongst the most outstanding developments of organometallic chemistry.[2] The first homogeneously catalyzed hydrogenations of olefins were reported independently by Knowles[3] and Horner,[4] who demonstrated that the use of Wilkinson-type complexes, bearing resolved chiral monodentate phosphane ligands in place of PPh_3, resulted in the formation of enantiomerically enriched products, albeit in low optical yields. Shortly after, Kagan introduced the easily prepared (4*R*,5*R*) and (4*S*,5*S*) enantiomers of 4,5-bis[(diphenylphosphanyl)methyl]-2,2-dimethyl-1,3-dioxolane (diop) as the first C_2-symmetric chelating bis(phosphanes), which were found to control the chiral induction in rhodium-catalyzed hydrogenation reactions much more precisely than monophosphane ligands, particularly in the reduction of *N*-acylated dehydroamino acids and their esters.[5] As an equally important contribution, Knowles and co-workers subsequently established the commercial L-DOPA process using *P*-chirogenic (R_P,$R_{P'}$)-bis[(2-methoxyphenyl)phenylphosphanyl]ethane, (*R*,*R*)-DIPAMP, as a steering ligand.[2a,6] These developments gave rise to the immediate supposition that homochiral bis(phosphanes) as such are endowed with superior properties, allowing the bidentate species to control the stereochemical outcome of the rate-determining step in catalysis more precisely than a monodentate phosphane. As a result, research aimed at the improvement of chiral catalysts of low performance has predominantly been concentrated on the design of new and possibly optimized chelate phosphanes, of

[‡] Chiral Bis(phosphanes), XV. Part XIV: Ref.[1]

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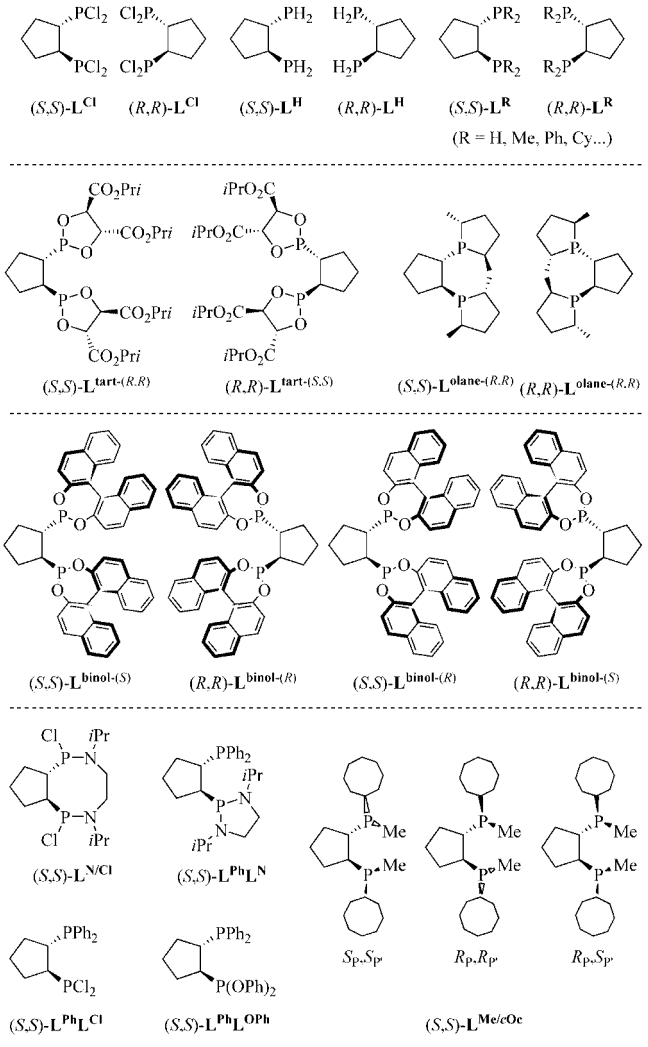
MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

which the DuPHOS-type *o*-phenylenebis(2,5-dialkylphospholanes)[7] and 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (BINAP)[2b] represent impressive examples. Note, however, that the generally accepted superiority of homochiral bidentate phosphanes in asymmetric hydrogenation has recently been challenged by the discovery that enantiopure monodentate P-ligands containing biaryl[8−13], spirobiindane,[14] oxaphosphinane[15] or carbohydrate[16] building blocks may likewise provide optical yields similar to those obtained with chelating phosphanes.[17]

Our approach to properly designed chiral hydrogenation catalysts has primarily been focussed on the construction of a class of optically active bidentate phosphanes with structural components (“modules” in Burk’s notation[7]) that can be systematically and easily interchanged in order to adapt the catalyst to a given purpose in the best possible fashion. Due to their “modular nature”[7] the so-defined ligands should be particularly suitable for adjusting the reactivity and catalytic behavior of metal complexes by judiciously selecting and changing parameters such as: (i) sets of donor groups, i.e., electronically different P−C-, P−N- or P−O-bonded substituents on the phosphorus atom; (ii) structural motifs, e.g., *P*- and/or *C*-chirality in, and steric demand of, substituent groups of that kind; (iii) torsion angles within the chelate framework, which in turn will influence the spatial orientation of selected parts of the ligand; and (iv) chelate bite angles, if variations of the backbone structure are also considered. Use of such ligands in transition-metal-mediated asymmetric catalysis can give insight into the relations and regularities existing between the performance of the catalytic system and the stereoelectronic characteristics of the metal−ligand template, provided viable synthetic schemes are available.

The traditional route to most of the widely used optically active bis(phosphanes), viz. those in which the phosphorus atoms bear two electron-withdrawing aryl groups, involves the alkylation of alkali metal diarylphosphides with disulfonates containing homochiral carbon backbones. The disadvantage of this protocol is that it cannot automatically be applied to the preparation of the more electron-rich *P*-alkylated analogues. Because of their high basicity, alkylated phosphide nucleophiles tend to engage in a number of troublesome side reactions to the effect that attempted displacement reactions using alkyl-substituted phosphide reagents will frequently result in products originating from metal−halogen exchange, P−P coupling and elimination[18] rather than substitution, especially when sterically hindered dialkylphosphides are used as nucleophiles.[18b] Previous work carried out in other laboratories has shown that these difficulties can be mastered either by the use of cyclic sulfates as substrates (particularly in displacement reactions employing relatively unhindered phosphide nucleophiles derived from primary phosphanes)[19] or, as an even more versatile method, by making use of less basic and, hence, less reactive phosphide−borane adducts.[20]

The key compounds of our synthetic strategy are the resolved enantiomers of bis(primary phosphanes), $H_2P^*\cap^*PH_2$, and bis(phosphonous dichlorides), $Cl_2P^*\cap^*PCl_2$, having their reactive $-PCl_2$ and $-PH_2$ functions supported on a rigid 1,2-*trans*-disubstituted cycloalkane backbone as represented, e.g., by the cyclopentane-based ligands $\mathbf{L^H}$ and $\mathbf{L^{Cl}}$ shown in the top row of Scheme 1. Their usefulness in the synthesis of optically active chelate phosphanes, to be discussed hereafter, is a result of the following features: First, the addition of P−H bonds across the >C=C< double bonds of different alkenes and cycloalkenes is likely to open a feasible route to various alkylated bis(secondary) and bis(tertiary) P_2 ligands with or without additional stereogenic centers at the phosphorus atom. Second, substitution reactions undergone by P−Cl functional phosphorus(III) compounds upon treatment with carbon, nitrogen or oxygen nucleophiles are among the most general and most easily accomplished coupling methods in organic chemistry. Finally, the possibility of incorporating virtually any other P−O-, P−N- or P−C-bonded residue into a homochiral bis(phosphane) framework should allow the preparation of a wide range of optically active chelate ligands having fine-tunable and, perhaps, rationally designable steric and electronic attributes.



Scheme 1. Collection of ligands and abbreviations

The Ligands

Resolution of the Enantiomers

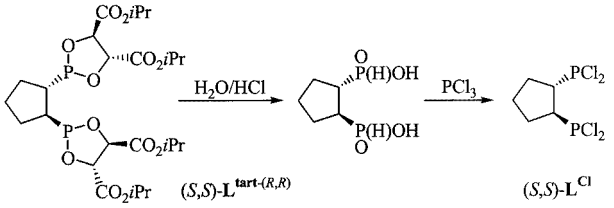
Analogous to the preparation of $Cl_2PC_2H_4PCl_2$ from ethylene, white phosphorus, and phosphorus trichloride,[21] racemic $C_5H_8(PCl_2)_2$, *rac*-**L**^{Cl}, can be obtained easily by heating cyclopentene with P_4 and PCl_3 at 220 °C in an autoclave, as reported by Green et al. as early as 1983.[22a]

Treatment of the racemate with Grignard reagents RMgBr (R = Me, Ph) afforded (±)-$C_5H_8(PR_2)_2$, **L**^{Me} and **L**^{Ph}, as the first P−C-substituted derivatives.[22] Resolution of the isomeric mixture was originally achieved by reaction with $NiBr_2$ in dichloromethane giving [$NiBr_2$(**L**^{Ph})]·CH_2Cl_2. Upon separation from solution, the complex underwent spontaneous resolution to deposit a conglomerate of crystals which were separated by hand and treated with sodium cyanide to yield **L**^{Ph} as its (*R*,*R*) and (*S*,*S*) stereoisomers.[22a]

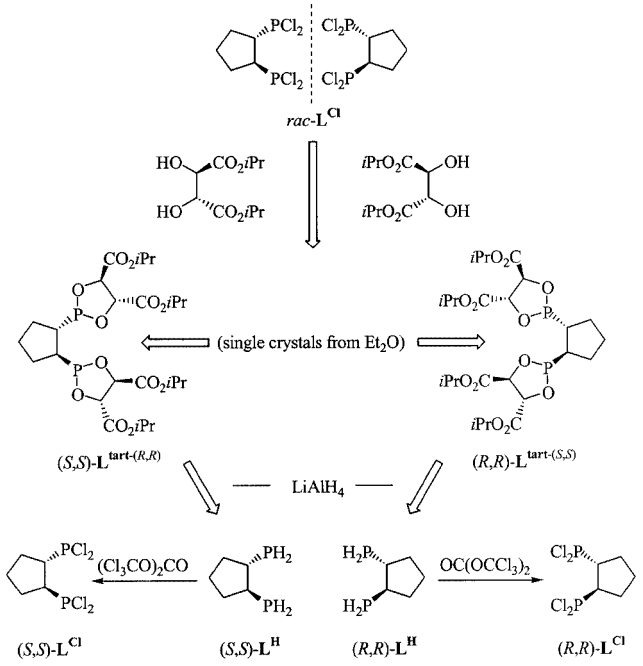
We entered the field in 1995 in an early attempt to accomplish stereodiscriminative C−H activation by treating 2,2′-disubstituted biphenyls and binaphthyls as racemates with the (+)- and (−)-enantiomers of the (hydrido)neopentylplatinum complex [{$C_5H_8(PCy_2)_2$}Pt(H)CH_2CMe_3] bearing the bis(dicyclohexylphosphane) ligand $C_5H_8(PCy_2)_2$ (**L**^{Cy}) in the optically active form.[23] For this particular bis(phosphane), effective resolution was brought about according to the strategy previously developed by Brunner and Pieronczyk for the separation of the stereoisomers of 2,3-bis(diphenylphosphanyl)norbornene (NORPHOS),[24] i.e., reduction with Ph_2SiH_2 of the *P*,*P*′-dioxides (+)- and (−)-C_5H_8{P(O)Cy_2}$_2$, which themselves were isolated by resolving their racemic mixture with (+)-di-*O*-benzoyltartaric acid.[23]

As an important breakthrough in the resolution of the enantiomers of the bis(phosphonous dichloride) **L**^{Cl}, we found that the cyclopentane-1,2-diyl[bis(1′,3′,2′-dioxaphospholane] **L**^{tart} resulting from the reaction of *rac*-**L**^{Cl} with (2*R*,3*R*)-(+)-diisopropyl tartrate (Scheme 2) could be crystallized from the isomeric mixture as a single (1*S*,2*S*,4′*R*,5′*R*) diastereomer, (*S*,*S*)-**L**$^{tart\text{-}(R,R)}$.[25] As expected, the (1*R*,2*R*,4′*S*,5′*S*) enantiomer, (*R*,*R*)-**L**$^{tart\text{-}(S,S)}$, was isolated, isomerically pure, from a similar reaction employing (2*S*,3*S*)-(−)-diisopropyl tartrate as the diol component.[26a] Reduction, with $LiAlH_4$, of these two phosphonites gave the bis(primary phosphane) **L**^{H} as resolved (*S*,*S*) and (*R*,*R*) enantiomers, and subsequent oxidation of the P−H bonds with bis(trichloromethyl)carbonate ("triphosgene") allowed for the routine preparation of either antipode of the multi-purpose P−Cl reagent **L**^{Cl}.[25,26b,27,28a]

In an alternative approach to the optically pure isomers of **L**^{Cl}, Brunner and co-workers preferred to hydrolyze the phosphonite enantiomers (*S*,*S*)-**L**$^{tart\text{-}(R,R)}$ and (*R*,*R*)-**L**$^{tart\text{-}(S,S)}$ to the free phosphinic acids, from which the resolved bis(phosphonous dichloride) enantiomers were recovered by chlorination with PCl_3 (Scheme 3).[29]



Scheme 3. Preparation of the optically pure $C_5H_8(PCl_2)_2$ enantiomers according to Brunner[29]



Scheme 2. Resolution of *rac*-$C_5H_8(PCl_2)_2$ into (*R*,*R*)- and (*S*,*S*)-$C_5H_8(PCl_2)_2$ via (*R*,*R*)- and (*S*,*S*)-$C_5H_8(PH_2)_2$[25,26b,27,28a]

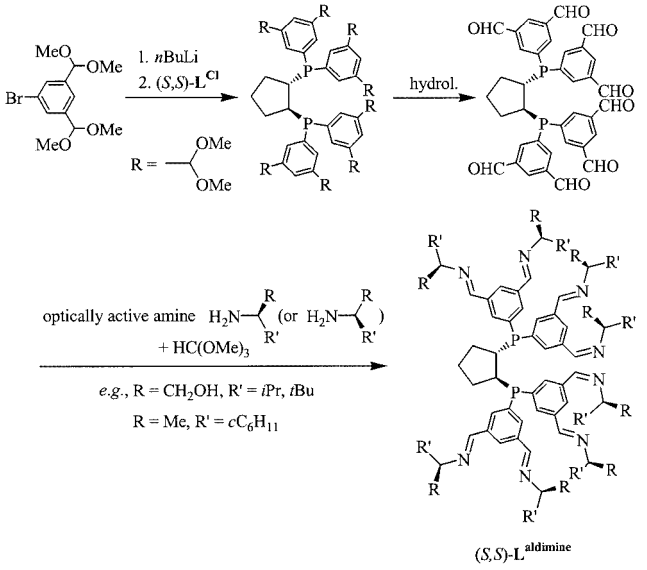
Representative Examples

From the abundance of optically pure diphosphorus ligands containing various P−C-, P−N- and P−O-bonded donor groups that have been prepared by treating **L**^{Cl}, as either mirror image isomer, with alcohols, phenols, diols, secondary amines, Grignard reagents, or organolithium compounds,[26b,27−32] we will outline only selected cases that serve to illuminate the synthetic potential of the isomerically pure PCl_2-functional starting materials.

By combining the two enantiomers with both (*R*)-(+)- and (*S*)-(−)-1,1′-bi(2-naphthol) we were able to isolate the four diastereomeric forms of the cyclic bis(phosphonous acid diester) **L**^{binol} depicted in Scheme 1, which offered the opportunity to study matching and mismatching effects on the outcome of asymmetric hydrogenation reactions (vide infra), as caused by the mutual interaction of the different stereogenic elements in such steering ligands.[32]

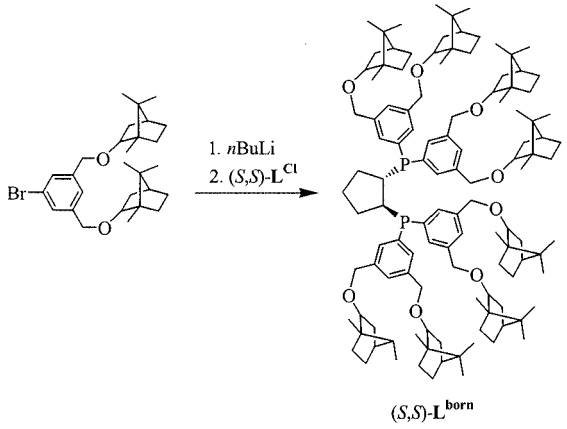
The Brunner group described both divergent and convergent reaction sequences leading from enantiomers (*S*,*S*)-**L**^{Cl} and (*R*,*R*)-**L**^{Cl} to a second generation of optically active dendritically expanded bis(phosphanes).[29] These contained their stereochemically uniform dendritic extensions

supported on a homochiral 1,2-disubstituted cycloalkane framework as defined by the phosphanes under discussion rather than on achiral 1,2-ethylene- or *ortho*-phenylene linkages as were originally used for optically active expanded P_2 ligands.[33] In the divergent synthetic approach, the enantiomerically pure $\mathbf{L^{Cl}}$ starting material was first coupled to branched aryllithium building blocks bearing acetal-protected formyl functions. Following deprotection of the acetals, multiple homochiral units were then introduced into the periphery of the expanded molecules by condensation of the aldehyde groups with different optically active amines and amino alcohols to afford branched ligands of the "$\mathbf{L^{aldimine}}$" type, as shown in Scheme 4. The alternative convergent strategy made use of pre-built branched aromatic bromides bearing (−)-borneol groups attached as benzylic ethers. Metallation followed by reaction with (*S*,*S*)-$\mathbf{L^{Cl}}$ and (*R*,*R*)-$\mathbf{L^{Cl}}$, respectively, produced the corresponding expanded "octaborneol-bis(phosphane)" ligand $\mathbf{L^{born}}$ depicted in Scheme 5 as either of the two possible diastereomers.



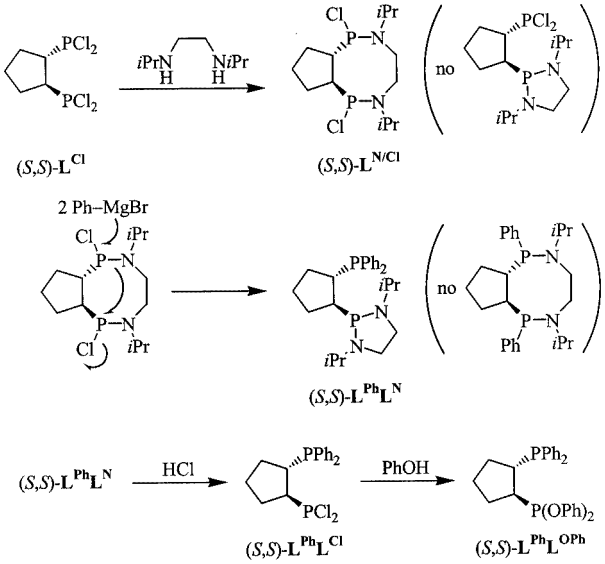
Scheme 4. Divergent approach to dendritically expanded bis(phosphanes)[29]

Dissymmetric P_2 ligands such as phosphane-phosphites[34] or bis(phosphanes) bearing different donor groups[35,36] have attracted considerable attention in homogeneous catalysis, in particular because of the impressive performance of their rhodium complexes as carbonylation and hydrogenation catalysts. Bis(phosphanes) with C_1 symmetry of the type $Ar_2PC_2H_4PAr'_2$ have previously been prepared either by base-catalyzed addition of a diarylphosphane to a suitable diarylvinylphosphane[35a] or by combining the phosphane-phosphonous dichloride $Ph_2PC_2H_4PCl_2$ with an appropriate Grignard or organolithium reagent.[35b] Analogous key intermediates having a rigid 1,2-disubstituted cyclopentane backbone rather than a flexible ethylene linkage, $C_5H_8(PPh_2)(PCl_2)$, were obtained as pure (*S*,*S*) and (*R*,*R*) enantiomers by the reaction sequence outlined in



Scheme 5. Convergent approach to a dendritically expanded "octaborneol-bis(phosphane)"[29]

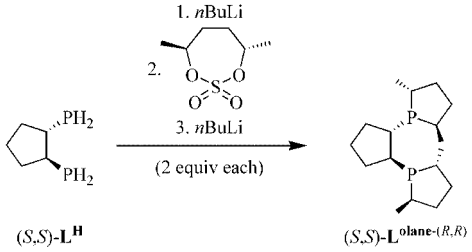
Scheme 6. The exclusive formation of the still C_2-symmetric initial product containing an eight-membered perhydro-1,6,2,5-diazadiphosphocine ring, $\mathbf{L^{N/Cl}}$ [$\delta(^{31}P)$ = 161.4 (s) ppm], was unexpected as was its subsequent reaction with phenylmagnesium bromide yielding the now C_1-symmetric $C_5H_8(PPh_2)\{P[N(iPr)CH_2]_2\text{-}c\}$ ($\mathbf{L^{Ph}L^{N}}$) {$\delta(^{31}P)$ = 5.7, 115.6 [both d, J(PP) = 9.3 Hz] ppm} − probably as a result of nucleophilically induced ring contraction. Cleavage of the P−N bonds with HCl proceeded smoothly to afford the desired dissymmetric phosphane-phosphonous dichloride 1,2-$C_5H_8(PPh_2)(PCl_2)$ ($\mathbf{L^{Ph}L^{Cl}}$) {$\delta(^{31}P)$ = 9.5, 211.8 [both d, J(PP) = 13.0 Hz] ppm}, which similar to 1,2-$C_5H_8(PCl_2)_2$ proved to be a convenient starting material for further derivatization, e.g., to $C_5H_8(PPh_2)_2\{P(OPh)_2\}$ ($\mathbf{L^{Ph}L^{OPh}}$).[31]



Scheme 6. Dissymmetric cyclopentane-based *P*,*P*′ ligands from C_2-symmetric $C_5H_8(PCl_2)_2$[31]

The more important diphosphorus ligands derived from the resolved bis(primary phosphane) $\mathbf{L^{H}}$ include the diastereomeric 1,2-bis(phospholano)cyclopentanes (*S*,*S*)- and

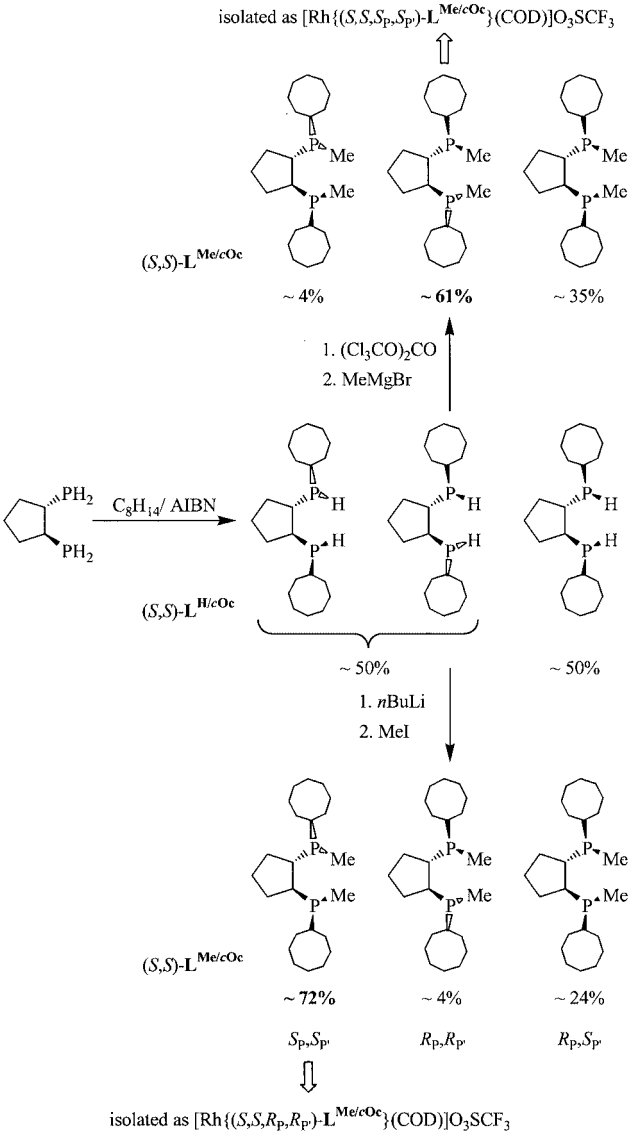
(*R*,*R*)-$C_5H_8\{P[(R)\text{-}CH(Me)CH_2]_2\text{-}c\}_2$ [$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$], described by Pringle et al.,[37] and the stereoisomers of the *C*- and *P*-chirogenic bis(phosphanes) $C_5H_8\{P(Me)R\}_2$ ($\mathbf{L}^{\mathbf{Me/R}}$), prepared in our laboratory.[32,38] The former were constructed in order to demonstrate how the enantioselectivity in asymmetric hydrogenation reactions of a rhodium catalyst which bears the flexible ethylene-bridged (*R*,*R*)-bis(phospholano)ethane ligand $1,2\text{-}C_2H_4\{P[(R)\text{-}CH(Me)CH_2]_2\text{-}c\}_2$ and, hence, exists in solution as an equilibrium mixture of interconverting λ and δ chelate conformers, can be rationally improved by placing an inflexible carbon skeleton between the two phosphorus atoms (vide infra). Similar to other bis(phosphanes) containing 2,5-dialkylphospholane building blocks, the two diastereomeric [$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$] ligands resulted from consecutive treatment of the pertinent $\mathbf{L}^{\mathbf{H}}$ enantiomer with *n*BuLi (2 equiv.), followed by the required 1,4-diol cyclic sulfate and another 2 equiv. of butyllithium as summarized by Scheme 7.[37]



Scheme 7. Synthesis of bis(phospholane) ligands with cyclopentane skeletons[37]

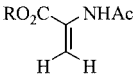
In the first step of the synthesis leading to the *C*,*P*-chirogenic bis(phosphanes) $\mathbf{L}^{\mathbf{Me/R}}$, which are to be regarded as conformationally rigid counterparts of Imamoto's "(S_P,$S_{P'}$)-bisP*" ligands $1,2\text{-}C_2H_4\{(S)\text{-}P(Me)R\}_2$ (R = *i*Pr, *t*Bu, Et_3C, cC_5H_9, cC_6H_{11}, $cC_6H_{10}Me$, 1-adamantyl),[39] a radical-initiated addition of the $-PH_2$ functions of optically pure $\mathbf{L}^{\mathbf{H}}$, across the carbon−carbon double bonds of cycloalkenes C_nH_{2n-2} (n = 5−8), was employed as a method of preparation for the bis(secondary phosphanes) $C_5H_8\{P(H)R\}_2$, where R = cC_5H_9, cC_6H_{11}, cC_7H_{13}, or cC_8H_{15}.[38a]

As exemplified in Scheme 8 for the product obtained with cyclooctene ($\mathbf{L}^{\mathbf{H/cOc}}$), formation of higher alkylated byproducts originating from consecutive P−H/>C=C< addition steps did not occur. Although the dialkylated bis(phosphanes) were formed without any notable diastereoselectivity and, hence, were isolated as more or less statistical mixtures of their (R_P,$R_{P'}$), (R_P,$S_{P'}$) [= (S_P,$R_{P'}$)], and (S_P,$S_{P'}$) diastereomers, separation of these stereoisomers was feasible by further derivatization and subsequent metal complex formation.[32,38] Thus, treatment of the isomeric mixtures with alkyllithium compounds, followed by alkylation with methyl iodide, caused the diastereomeric distributions to change in favor of the (*S*,*S*)-$C_5H_8\{(S)\text{-}P(Me)C_8H_{15}c\}_2$ and (*R*,*R*)-$C_5H_8\{(R)\text{-}P(Me)C_8H_{15}c\}_2$ stereoisomers,[38a] the rhodium(I) complexes of which − $[Rh\{(S,S)\text{-}C_5H_8[(R)\text{-}P(Me)C_8H_{15}c]_2\}(COD)]O_3SCF_3$ and $[Rh\{(R,R)\text{-}C_5H_8[(S)\text{-}P(Me)C_8H_{15}c]_2\}(COD)]O_3SCF_3$, respectively − were isolated as diastereomerically pure crystals by precipitation from a THF/diethyl ether solvent mixture.[32,38b] Conversely, successive combination of the bis(secondary phosphane) isomers $\mathbf{L}^{\mathbf{H/cOc}}$ first with "triphosgene" (vide supra) and then with methylmagnesium bromide led to an enrichment of the (*S*,*S*)-$C_5H_8\{(R)\text{-}P(Me)C_8H_{15}c\}_2$ and (*R*,*R*)-$C_5H_8\{(S)\text{-}P(Me)C_8H_{15}c\}_2$ stereoisomers, which in turn were treated with $[Rh(COD)_2]O_3SCF_3$ to furnish diastereomerically pure $[Rh\{(S,S)\text{-}C_5H_8[(S)\text{-}P(Me)C_8H_{15}c]_2\}(COD)]O_3SCF_3$ and $[Rh\{(R,R)\text{-}C_5H_8[(R)\text{-}P(Me)C_8H_{15}c]_2\}(COD)]O_3SCF_3$, following chromatographic workup (Scheme 8).[32]

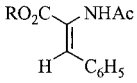


Scheme 8. Conversion of $C_5H_8(PH_2)_2$ to *C*,*P*-chirogenic bisphosphanes[32,38]

Catalytic Hydrogenation: Results of Comparative Studies



R = H: **acrH**; R = Me: **acrMe**



R = H: **cinH**; R = Me: **cinMe**

One of the most useful features of the ligands derived from the $\mathbf{L^H}$ and $\mathbf{L^{Cl}}$ precursors is their adjustability which enables the possibility of influencing the enantioselectivity by varying the substituents on the phosphorus atoms. Many of these optically active ligands have therefore been examined by us and others for their utility in Rh-catalyzed asymmetric hydrogenations of standard enamide substrates such as (acetylamino)acrylic (**acrH**) and -cinnamic (**cinH**) acid and their corresponding methyl esters **acrMe** and **cinMe**, respectively. The main purpose of these investigations was to reveal potential correlations between the outcome of the hydrogenation reactions and structural properties of the metal complexes in order to elucidate the factors governing the stereoselectivity of the catalysts. The results of these studies are collected in Table 1. For the sake of comparison, the catalytic results obtained with Rh catalysts derived from structurally related P_2 ligands[29,37,39a,39d,40] are also included in Table 1.

A first conclusion that can be drawn from Table 1 is that the catalytic activity of the different $[Rh(\mathbf{L})(COD)]^+$ complexes, as judged from the reaction times needed for full substrate conversion, increases with increasing electron-richness of the phosphorus atoms: $\mathbf{L^{binol}} << \mathbf{L^{Ph}} < \mathbf{L^{Me/cOc}}$. One further conclusion to be drawn for hydrogenations using either unsubstituted $\mathbf{L^{Ph}}$ steering ligands or dendritically expanded homologues with different multiple homochiral units in the periphery is that the generally high enantioselectivity for the (*S*)- or (*R*)-products displayed by the rhodium catalysts summarized under Entries **2** and **3** in Table 1 is governed by the (*R*,*R*) or (*S*,*S*) configuration and, respectively, λ or δ conformation of the chiral cyclopentane backbone rather than being controlled by the chiral dendritic expansions.[29] The rhodium chelate complexes of these ligands thus follow the empirical λ/δ rule predicting that a λ chelate will give the (*S*) enantiomer, while a δ chelate will produce the (*R*) enantiomer.[41] While this holds true for all ligands bearing two aryl substituents, the 1,1′-bi(2-naphthol)-derived bis(phosphonous acid diesters) $\mathbf{L^{binol}}$ reveal such a strong influence of the axially chiral binaphthoxy groups on the orientation of induction that their sense of chirality can override the contribution of the chiral ligand core. Thus, the catalyst complexes bearing (*R*,*R*)-

Table 1. Enantioselective hydrogenations of standard enamide substrates with [Rh(ligand)(diolefin)]X precatalysts

Entry[a]	Ligand	acrH *t* [h]	acrH *ee* [%]	acrMe *t* [h]	acrMe *ee* [%]	cinH *t* [h]	cinH *ee* [%]	cinMe *t* [h]	cinMe *ee* [%]
1a	(*S*,*S*)-$\mathbf{L^{binol\text{-}(S)}}$	16	96 (*R*)	16	89 (*R*)	16	78 (*R*)	16	85 (*R*)
1b	(*R*,*R*)-$\mathbf{L^{binol\text{-}(R)}}$	16	92 (*S*)	16	86 (*S*)	16	77 (*S*)	16	85 (*S*)
1c	(*S*,*S*)-$\mathbf{L^{binol\text{-}(R)}}$	16	28 (*S*)	16	29 (*S*)	16	24 (*S*)	16	36 (*S*)
1d	(*R*,*R*)-$\mathbf{L^{binol\text{-}(S)}}$	16	27 (*R*)		not det.	16	20 (*R*)	16	36 (*R*)
2a	(*S*,*S*)-$\mathbf{L^{Ph}}$[b]	4	91 (*R*)	4	85 (*R*)	2	93 (*R*)	2	91 (*R*)
2b	(*R*,*R*)-$\mathbf{L^{Ph}}$	4	92 (*S*)	4	86 (*S*)	2	95 (*S*)	2	91 (*S*)
3a	(*S*,*S*)-$\mathbf{L^{born}}$[c]						94 (*R*)		
3b	(*R*,*R*)-$\mathbf{L^{born}}$						96 (*S*)		
3c	(*S*,*S*)-$\mathbf{L^{aldimine}}$ [c]						93−96 (*R*)		
4a	(*S*,*S*)-$\mathbf{L^{olane\text{-}(R,R)}}$				95 (*R*)				98 (*R*)
4b	(*R*,*R*)-$\mathbf{L^{olane\text{-}(R,R)}}$				73 (*R*)				77 (*R*)
5	(*R*,*R*)-Me-BPE[d]			1	91 (*R*)			1	85 (*R*)
6a	(S,S,S_P,$S_{P'}$)-$\mathbf{L^{Me/cOc}}$[e]	1.5	21 (*S*)	1.5	29 (*S*)	2	26 (*S*)	2	35 (*S*)
6b	(R,R,R_P,$R_{P'}$)-$\mathbf{L^{Me/cOc}}$	1.5	23 (*R*)	1.5	28 (*R*)	2	28 (*R*)	2	34 (*R*)
6c	(S,S,R_P,$R_{P'}$)-$\mathbf{L^{Me/cOc}}$	1.5	90 (*R*)	1.5	82 (*R*)	2	74 (*R*)	2	86 (*R*)
6d	(R,R,S_P,$S_{P'}$)-$\mathbf{L^{Me/cOc}}$	1.5	90 (*S*)	1.5	83 (*S*)	2	73 (*S*)	2	86 (*S*)
7a	(S_P,$S_{P'}$)-*t*Bu-bisP*[e]			1	98 (*R*)	1	98 (*R*)	1	>99 (*R*)
7b	(S_P,$S_{P'}$)-1-Ad-bisP*			1	>99 (*R*)			1	>99 (*R*)
7c	(S_P,$S_{P'}$)-*c*C_5H_9-bisP*	1	33 (*R*)	1	80 (*R*)			1	43 (*R*)
8a	(R,R,R_P,$R_{P'}$)-pyrL$^{Me/Ph}$[e]						64 (*S*)		
8b	(R,R,S_P,$S_{P'}$)-pyrL$^{Me/Ph}$						34 (*S*)		
8c	(R,R,R_P,$S_{P'}$)-pyrL$^{Me/Ph}$						21 (*S*)		

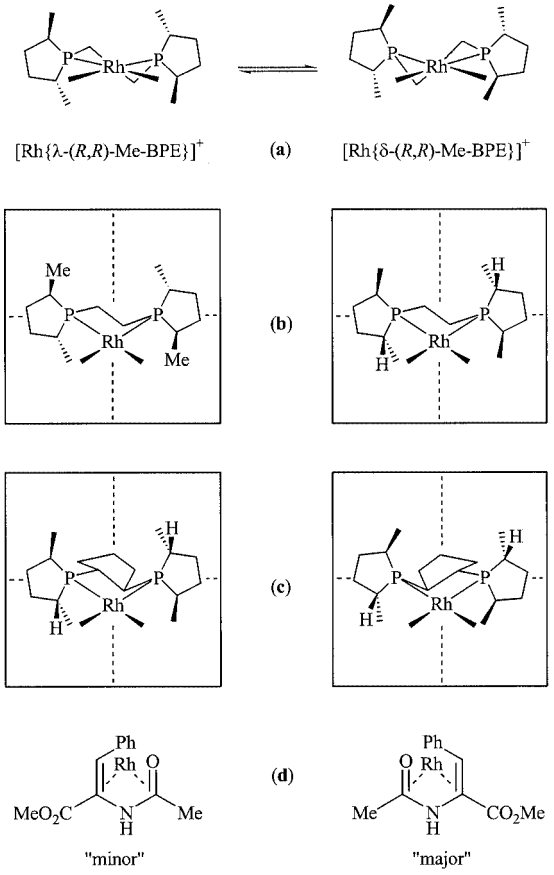
[a] Diolefin = 1,5-cyclooctadiene (Entries **1**,[32] **2**,[32] **3**,[29] **4**,[37] **5**,[19a,19c] **6**,[32,38b] and **8**[40]) or norbornadiene (Entry **7**[39a,39d]); $X^- = Cl^-$ {Entry **3**: in situ catalysts generated from $[Rh(\mu\text{-}Cl)(COD)]_2$ and bis(phosphane) ligands}, BF_4^- (Entries **4**, **7**, and **8**) or $F_3CSO_3^-$ (Entries **1**, **2**, **5**, and **6**). Experimental conditions: methanol or ethanol solvents (the latter only for Entry **7c** with **acrH** or **acrMe** as substrates); ambient temperature; initial H_2 pressure either ambient (Entries **1**−**3**, **6**, and **8**) or ca. 2 bar (Entries **4**, **5**, and **7**); typical Rh/substrate ratios of about $1-2 \times 10^{-3}$ (Entries **4**, **5**, and **7**), $3-5 \times 10^{-3}$ (Entries **1** and **2**), and 10^{-2} (Entries **3**, **6**, and **8**), respectively. Reaction times given for 100% conversion; *ee* values of Entries **3**, **4**, and **8** (no reaction times detailed in the original literature) likewise determined after complete hydrogenation. [b] For the hydrogenation of (benzoylamino)acrylic and -cinnamic acid using an in situ catalyst composed of $[Rh(\mu\text{-}Cl)(COD)]_2$ and (*S*,*S*)-$\mathbf{L^{Ph}}$ in methanol, Green et al. reported *ee* values of 100 ± 2%.[22a] [c] See Schemes 4 and 5.[29] [d] 1,2-C_2H_4{P-[(*R*)-CH(Me)CH_2]$_2$-*c*}$_2$. [e] ($R_{P(P')}$) and ($S_{P(P')}$) denote the configuration at the phosphorus atom for the *free* ligands, which is inverted upon coordination to the rhodium atom as a consequence of the CIP sequence rules; see also Table 2 and Scheme 8.

or (*S*,*S*)-$\mathbf{L}^{\mathbf{binol}\text{-}(R)}$ ligands invariably afforded hydrogenation products with (*S*) configuration (Entries **1b** and **1c**) whereas the (*R*) enantiomers predominated in the isomeric mixtures formed with the two diastereomeric Rh−$\mathbf{L}^{\mathbf{binol}\text{-}(S)}$ catalysts (**1a** and **1d**). From the results collected in Table 1 it is also clear that the optical yields achieved with (*S*,*S*)-$\mathbf{L}^{\mathbf{binol}\text{-}(S)}$ are by far superior to those obtained with (*S*,*S*)-$\mathbf{L}^{\mathbf{binol}\text{-}(R)}$ and that the (*R*,*R*)-$\mathbf{L}^{\mathbf{binol}\text{-}(R)}$ ligand is much more selective than its (*R*,*R*)-$\mathbf{L}^{\mathbf{binol}\text{-}(S)}$ diastereomer. Obviously, the (*R*,*R*)-$\mathbf{L}^{\mathbf{binol}\text{-}(R)}$ and (*S*,*S*)-$\mathbf{L}^{\mathbf{binol}\text{-}(S)}$ enantiomers represent the beneficial matched combination of stereochemical elements while the (*R*,*R*)-$\mathbf{L}^{\mathbf{binol}\text{-}(S)}$ and (*S*,*S*)-$\mathbf{L}^{\mathbf{binol}\text{-}(R)}$ forms must be looked at as the disadvantageous mismatched counterparts.[32]

Distinct matched−mismatched effects in enantioselective hydrogenation also occur for the >C=C< reductions catalyzed by the more electron-rich rhodium complexes possessing either the diastereomeric $\mathbf{L}^{\mathbf{olanc}}$ or the *C*,*P*-chirogenic $\mathbf{L}^{\mathbf{Me}/c\mathbf{Oc}}$ ligands of Entries **4**[37] and **6**.[32,38b]

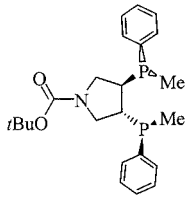
The bis(phospholane) (*S*,*S*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$ clearly exhibits a stronger ability for chiral discrimination than its (*R*,*R*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$ stereoisomer. Interestingly, the enantiodiscriminating properties of the derived rhodium complex [Rh{(*S*,*S*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$}(COD)]$BF_4$ ("**Rh-4a**" hereafter) are also superior to those of the more flexible ethylene-bridged Rh−(*R*,*R*)-Me-BPE catalyst (Entry **5**[19a,19c]), which in turn is seen to be superior to [Rh{(*R*,*R*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$}(COD)]$BF_4$ (**Rh-4b**), in spite of existing, in solution, as a labile mixture of readily interconverting λ and δ conformers; Scheme 9 (a).

On the one hand, these observations further corroborate the previously drawn conclusion that greater conformational rigidity of the backbones of bis(phospholane) chelate ligands will result in a more efficient transfer of chirality during Rh^I-catalyzed asymmetric hydrogenation.[19c] On the other hand, the finding that the Rh−(*S*,*S*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$ complex with δ backbone stereochemistry proved to be much more selective for the (*R*) products than the λ-Rh−(*R*,*R*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$ catalyst was unexpected:[37] So far, the heuristic stereochemical model used for the understanding of the origin of enantioselection by Rh−(*R*,*R*)-Me-DuPHOS and Rh−(*R*,*R*)-Me-BPE catalysts was based on the premise that two of the four equatorially aligned phospholane substituents adjacent to the phosphorus atoms effectively block the top left and bottom right "coordination quadrants"[6c] indicated on the left of Scheme 9 (b).[7,19c] In the more stable (less reactive) enamide adduct, the substrate should therefore be coordinated through its *si* face, the less favored (more reactive) adduct diastereomer being that in which the enamide is *re*-face-bound. Since Rh−DuPHOS catalysts have been confirmed both experimentally[19d] and theoretically[42b,42c,42d] to nicely reproduce the Halpern-Brown-type "anti-lock-and-key"[42] mechanistic behavior in which the major product enantiomer is formed by hydrogenation of the less favorably bonded enantioface,[43,44] both the excellent (*R*)-selectivity of the Rh−(*S*,*S*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$ complex and the somewhat lower (*R*)-discriminating ability of the Rh−(*R*,*R*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$ diastereomer are indicative of *si*-face binding of the substrate in the less stable adducts and, respectively, of *re*-face binding in the sterically favored

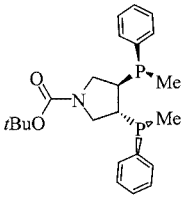


Scheme 9. (**a**): λ/δ equilibrium of Rh−(*R*,*R*)-Me-BPE catalysts; (**b**): quadrant-blocking in Rh−(*R*,*R*)-Me-BPE chelate complexes by equatorial methyl groups (left) or, alternatively, by axial hydrogen atoms (right); (**c**) and (**d**): quadrant-blocking in λ- and δ-shaped Rh−$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$ complexes together with "minor" *si*- and "major" *re*-face binding of substrate enamides as proposed by Pringle[37]

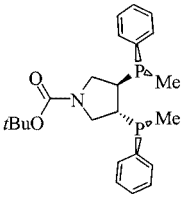
intermediates. In sharp contrast to the original stereochemical model proposed for chelate complexes of bis(phospholane) ligands, Pringle et al. therefore concluded that it is the bottom left and top right quadrants which are more effectively blocked in the ground-state geometries of the two diastereomers than the quadrants left side up and right side down − actually, to a higher degree in matched δ-[Rh{(*S*,*S*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$}(COD)]$^+$ but to a lesser extent in mismatched λ-[Rh{(*R*,*R*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$}(COD)]$^+$. Indeed, crystal structures of two model complexes, δ-[PtI_2{(*S*,*S*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$}] (**Pt-4a**) and λ-[$PtI_2${(*R*,*R*)-$\mathbf{L}^{\mathbf{olane}\text{-}(R,R)}$}] (**Pt-4b**) confirmed that the equatorial methyl substituents of the phospholane rings shielding the top left and bottom right quadrants are ca. 0.5 Å closer to the iodo binding sites in the λ than in the δ conformer, whereas the axial α-hydrogen atoms occupying the quadrants left side down and right side up are ca. 0.3 Å closer to the other ligands in the δ than in the λ diastereomer. It was therefore proposed that it is the steric interaction of the enamide substrate with these hydrogen atoms which crucially contributes to the facially discriminating abilities of the catalyst complexes; Scheme 8 (c).[37] For a different interpretation, however, see below.



$R,R,R_P,R_{P'}$-pyrL$^{Me/Ph}$



$R,R,S_P,S_{P'}$-pyrL$^{Me/Ph}$



$R,R,R_P,S_{P'}$-pyrL$^{Me/Ph}$

With regard to the diastereomeric complexes bearing the four stereochemically different **L$^{Me/cOc}$** ligands, Entries **6a**−**d** of Table 1 make it clear that it is the bis(phosphanes) with opposite configuration at the carbon and phosphorus atoms (Note footnote[e] of Table 1!) that lead to the superior hydrogenation catalysts. Although less stereodiscriminating than Imamoto's catalysts with alkylated (S_P,$S_{P'}$)-bisP* ligands $C_2H_4\{(S)\text{-P(Me)R}\}_2$ having voluminous *P*-bound *tert*-butyl or 1-adamantyl groups in addition to the methyl residue (Entries **7a** and **7b**, Table 1),[39a,39d] the rhodium complexes of the two ($S,S,R_P,R_{P'}$)-**L$^{Me/cOc}$** and ($R,R,S_P,S_{P'}$)-**L$^{Me/cOc}$** enantiomers appear to perform better than those derived from (S_P,$S_{P'}$)-cC$_5$H$_9$-bisP* (Entry **7c**, Table 1), which has a cyclopentyl substituent roughly comparable in steric demand near the metal center to cyclooctyl. Also of interest is a comparison with Nagel's diastereomeric *N*-(*tert*-butoxycarbonyl)-3,4-bis[methyl(phenyl)phosphanyl]pyrrolidines ($R,R,R_P,R_{P'}$)-, ($R,R,S_P,S_{P'}$)-, and ($R,R,R_P,S_{P'}$)-pyrL$^{Me/Ph}$. Rhodium(I) chelate complexes of these ligands are λ-shaped as are Imamoto's Rh−bisP* catalysts; but unlike the latter, which yield (*R*) hydrogenation products[39a,39d] unless the enamide contains a very bulky α-substituent,[39c,39f] Nagel's catalysts induce the preferential formation of amino acids and esters as (*S*) enantiomers irrespective of the stereochemistry at the two phosphorus atoms; the different −P(Me)Ph configurations are only seen to modulate the extent of the enantiomeric excess (Entries **8a**−**c**, Table 1).[40] Thus, it is the configuration of the backbone carbon atoms that controls the sign of chiral induction imposed by the Rh−pyrL$^{Me/Ph}$ catalysts and, vice versa, it is the configuration at the phosphorus atom that outplays the influence of the carbon skeleton in hydrogenations catalyzed by Rh−bisP* complexes. In other words, while the Rh−pyrL$^{Me/Ph}$ catalysts obey the λ/δ rule (vide supra), this empirical rule is not valid for catalysts possessing the very successful electron-rich bisP* steering ligands![39b] Rhodium complexes derived from the four diastereomeric electron-rich **L$^{Me/cOc}$** bis(phosphanes) (Entries **6a**−**6d**, Table 1) and also from the more electron-poor Rh−**L^{binol}** complexes (Entries **1a**−**d**, Table 1), are intermediate in that the ligands showing the matched combination of stereoelements (Entries **1a**, **1b**, **6c**, **6d**, Table 1) follow the rule, whereas the mismatched catalysts (Entries **1c**, **1d**, **6a**, **6b**, Table 1) do not. It should be noted that the catalytic results obtained with Pringle's diastereomeric Rh−**L^{olane}** complexes **Rh-4a** and **Rh-4b** are akin: the matched δ-conformer **Rh-4a** provokes (*R*) stereoselection and thus conforms to the rule; mismatched λ-shaped **Rh-4b** similarly yields amino acids with (*R*) configuration and, hence, breaks the rule.

Although no structural data are currently at hand for metal complexes containing bis(phosphonites) of the **L^{binol}** type, substantial structural information exists on complexes possessing **L$^{Me/cOc}$** ligands and other bis(phosphanes) with P−C-bonded substituents, which strongly suggests that the very different enantioselectivities displayed by the Rh−**L$^{Me/cOc}$** systems with *like* or *unlike* stereochemistry at the donor and backbone atoms is causally related to slight differences in the spatial orientation of the bulky cycloalkyl rings in the diastereomeric complex cations.[32,38]

Molecular Structures of Complexes and Concluding Remarks on Enantioselectivity

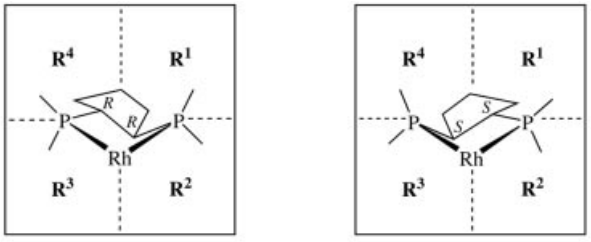
In order to gain insight into correlations that may exist between the structural features displayed by the different

Table 2. Selected torsion angles and diene twists [°] in structurally characterized Rh and Pt complexes with optically active cyclopentane-bridged P_2 ligands

Complex[a]	P−C−C−P	P−Rh−P−R^1	P−Rh−P−R^2	P−Rh−P−R^3	P−Rh−P−R^4	COD twist	*ee*[b]
[Rh{(*S,S*)-**L^{Ph}**}(COD)]O$_3$SCF$_3$ (**Rh-2a**)[32]	+48.8 (δ)	+109.1	−129.0	+147.0	−89.2	+3.9	91 (*R*)
[Rh{(*R,R*)-**L^{Ph}**}(COD)]O$_3$SCF$_3$ (**Rh-2b**)[31][32]	−49.4 (λ)[c]	+88.5	−147.0	+129.2	−108.6	−4.1	91 (*S*)
	−57.7 (λ)[d]	+99.3	−140.4	+134.7	−99.0	+3.4	
[Rh{($S,S,R_P,R_{P'}$)-**L$^{Me/cOc}$**}(COD)]O$_3$SCF$_3$ (**Rh-6a**)[38b][e]	+52.7 (δ)	+137.2	−99.8	+131.5	−106.7	+1.5	35 (*S*)
[Rh{($R,R,R_P,R_{P'}$)-**L$^{Me/cOc}$**}(COD)]O$_3$SCF$_3$ (**Rh-6d**)[32] [e] [f]	−44.7 (λ)	+114.3	−125.1	+113.8	−125.2	+7.8	86 (*S*)
[Rh{($R_P,R_{P'}$)-*t*Bu-bisP*}(C$_7$H$_8$)]BF$_4$ (**Rh-7a**)[39a][39d] [e]	−45.5 (λ)	+109.1	−127.1	+96.8	−139.5	ca. +1	> 99 (*R*)
[PtI$_2${(*S,S*)-**L$^{olane-(R,R)}$**}] (**Pt-4a**)[37]	+58.0 (δ)	−131.2	−110.7	+143.7	−99.6		98 (*R*)
[PtI$_2${(*R,R*)-**L$^{olane-(R,R)}$**}] (**Pt-4b**)[37]	−46.3(λ)	+113.2	−131.1	+113.2	−131.1		77 (*R*)

[a] For definition of R^1−R^4, see Scheme 10. [b] Data refer to the optical yields obtained in the reduction of methyl (*Z*)-2-acetamidocinnamate (**cinMe**). [c] Crystal chosen from a recrystallized sample of optically pure [Rh{(*R,R*)-**L^{Ph}**}(COD)]O$_3$SCF$_3$.[32] [d] Specimen **Rh-2b*** separated by hand from the conglomerate obtained by crystallizing [Rh(*rac*-**L^{Ph}**)(COD)]O$_3$SCF$_3$.[31] [e] ($R_PR_{P'}$) indicates the configuration at the phosphorus atom for the *coordinated* ligands; cf. footnote[e] of Table 1 and Scheme 8. [f] Values taken from the structural analysis of racemic [Rh{(*RS,RS*,R_PS_P,$R_{P'}S_{P'}$-**L$^{Me/cOc}$**}(COD)]O$_3$SCF$_3$ (**Rh-6c/6d**); torsion and twist angles for the [Rh{($S,S,S_P,S_{P'}$)-**L$^{Me/cOc}$**}(COD)]O$_3$SCF$_3$ enantiomer (**Rh-6c**) with opposite sign.

λ,δ conformer precatalysts $[Rh(\mathbf{L})(COD)]^+$ and the sign and the extent of the stereoinduction that can be achieved with the actual catalysts, X-ray data have been collected for several of the cationic Rh^I precursors. The most important stereochemical features of these complexes comprise (i) the chelate torsion angle P−C−C−P analytically describing the folding of the chelate ring, (ii) the exocyclic torsion angles P−Rh−P−R defining the orientation (axial or equatorial) of the four *P*-bonded substituents R with respect to the coordination plane, and (iii) the twist angle between the P−Rh−P plane and the plane spanned by the central metal and the midpoints of the two coordinated olefinic bonds. A tabulation of these values is presented in Table 2 (see also Scheme 10 and Figures 1−5) So far we have been unable to isolate the diastereomerically pure complex $[Rh\{(R,R,R_P,R_{P'})\text{-}\mathbf{L^{Me/cOc}}\}(COD)]O_3SCF_3$ (**Rh-6d**) or its enantiomer $[Rh\{(S,S,S_P,S_{P'})\text{-}\mathbf{L^{Me/cOc}}\}(COD)]O_3SCF_3$ (**Rh-6c**) as crystals suitable for X-ray crystallography. By way of alternative, we therefore derived the stereochemical features discussed below for **Rh-6d** from the structure of $[Rh\{(RS,RS,R_PS_P,R_{P'}S_{P'}\text{-}\mathbf{L^{Me/cOc}}\}(COD)]O_3SCF_3$ (**Rh-6c/6d**), made up of equal proportions of either mirror image isomer. For the sake of brevity, the salient stereochemical features of only one of the two enantiomeric forms present in the racemic crystal are considered; see also footnote [e] of Table 2.



Rh-2b:	R^1–$R^4 = C_6H_5$	**Rh-2a:**	R^1–$R^4 = C_6H_5$
Rh-6d:	$R^1 = R^3 = cC_8H_{15}$	**Rh-6a:**	$R^1 = R^3 = cC_8H_{15}$
	$R^2 = R^4 = CH_3$		$R^2 = R^4 = CH_3$
Rh-7a:	$R^1 = R^3 = CH_3$		
	$R^2 = R^4 = C(CH_3)_3$	(C_2H_4-bridged)	
Rh(Pt)-4b:	$R^1 = R^3 = C^5(H)_{ax}$	**Rh(Pt)-4a:**	$R^1 = R^3 = C^5(H)_{ax}$
	$R^2 = R^4 = C^2(CH_3)_{eq}$		$R^2 = R^4 = C^2(CH_3)_{eq}$

Scheme 10. Definition of P-substituents R^1−R^4 for structurally characterized metal complexes

For the purpose of comparison, data for the two platinum compounds $[PtI_2\{(S,S)\text{-}\mathbf{L^{olane\text{-}(R,R)}}\}]$ (**Pt-4a**) and $[PtI_2\{(R,R)\text{-}\mathbf{L^{olane\text{-}(R,R)}}\}]$ (**Pt-4b**) modelling the related rhodium catalysts **Rh-4a** and **Rh-4b**[37] are also included, as are the pertinent parameters of ethylene-bridged $[Rh\{C_2H_4[(R)\text{-}P(Me)But]_2\}(C_7H_8)]BF_4$ (**Rh-7a**) (Note footnote [d] of Table 2!).[39a,39d]

As expected, all rhodium complexes containing $C_5H_8(PR_2)_2$ chelate phosphanes show torsion angles spanned by the two endocyclic P−CH bonds and the connecting ethylene chain of similar magnitude but opposite sign for the λ and δ conformations imposed by the (*R*,*R*) and (*S*,*S*) forms of the individual ligands. For λ-shaped $[Rh\{(R,R,R_P,R_{P'})\text{-}\mathbf{L^{Me/cOc}}\}(COD)]O_3SCF_3$ (**Rh-6d**), the value of the P−C−C−P torsion angle almost coincides with that of the *t*Bu-bisP* compound **Rh-7a**, in which the λ conformation is stabilized by the bulky CMe_3 substituents. A major structural difference between **Rh-7a** and **Rh-6d** arises from the contrasting orientations of the sterically demanding *tert*-butyl and cyclooctyl groups with respect to the P−Rh−P coordination plane; these are equatorial in the former (R^2 and R^4 in Scheme 10 and Table 2; torsion angles P−Rh−P−CMe_3, −127.1 and −139.5°) but tend to be axial in the latter (R^1 and R^3 in Scheme 10 and Table 2; torsion angles P−Rh−P−$C_8H_{15}c$, +114.3 and +113.8°; cf. Figure 2.)

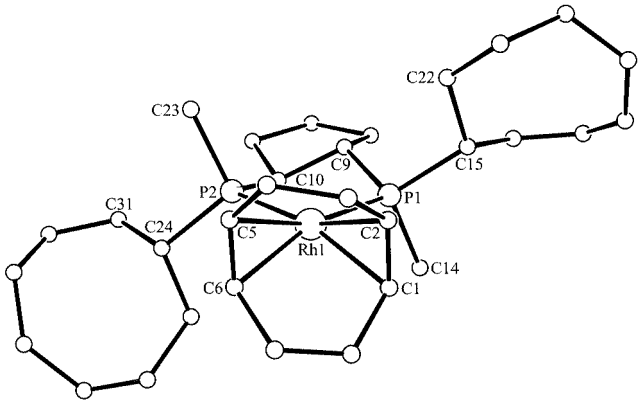


Figure 1. Perspective view of the cation $[Rh\{(S,S,R_P,R_{P'})\text{-}\mathbf{L^{Me/c\text{-}Oc}}\}(COD)]^+$ (**Rh-6a$^+$**); selected bond lengths [A] and angles [°]: Rh1−P1, 2.305(1); Rh1−P2, 2.316(1); Rh1−C1, 2.216(5); Rh1−C2, 2.226(5); Rh1−C5, 2.238(5); Rh1−C6, 2.227(6). P1−Rh−P2, 84.33(3)[38b]

$[Rh\{(S,S,R_P,R_{P'})\text{-}\mathbf{L^{Me/cOc}}\}(COD)]O_3SCF_3$ (**Rh-6a**), on the other hand, resembles **Rh-7a** in the equatorial arrangement of the large substituents (R^1 and R^3 in Scheme 10 and Table 2; torsion angles P−Rh−P−$C_8H_{15}c$, +137.2 and +131.5°; see Figure 1), with the methyl groups pointing to an axial direction in both cases. From the optical inductions achieved in the asymmetric hydrogenation of, e.g., methyl acetamidocinnamate it is clear, however, that the bisP* complex **Rh-7a** is much more enantioselective than **Rh-6a** containing the mismatched combination of *C*- and *P*-chirogenic stereoelements and is also superior in its stereodiscriminating power to that of the matched catalyst **Rh-6d**. This raises the question as to how the spatial orientation of the sterically demanding substituents in **Rh-6a**, **Rh-6d**, and **Rh-7a** contribute to the varying degrees of enantioselectivity

observed in >C=C< hydrogenations catalyzed by these complexes.

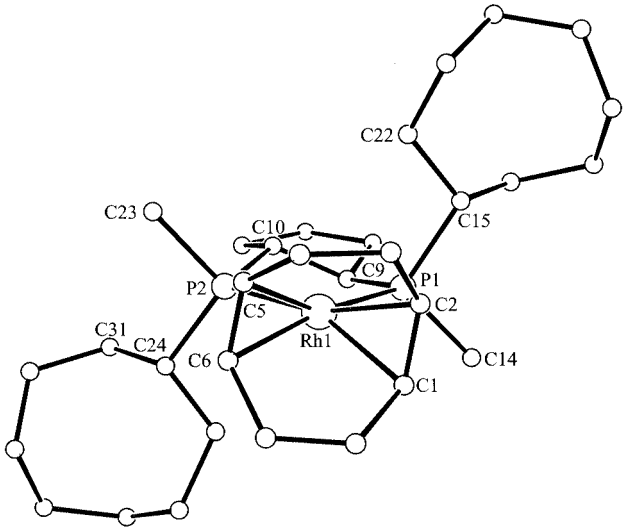
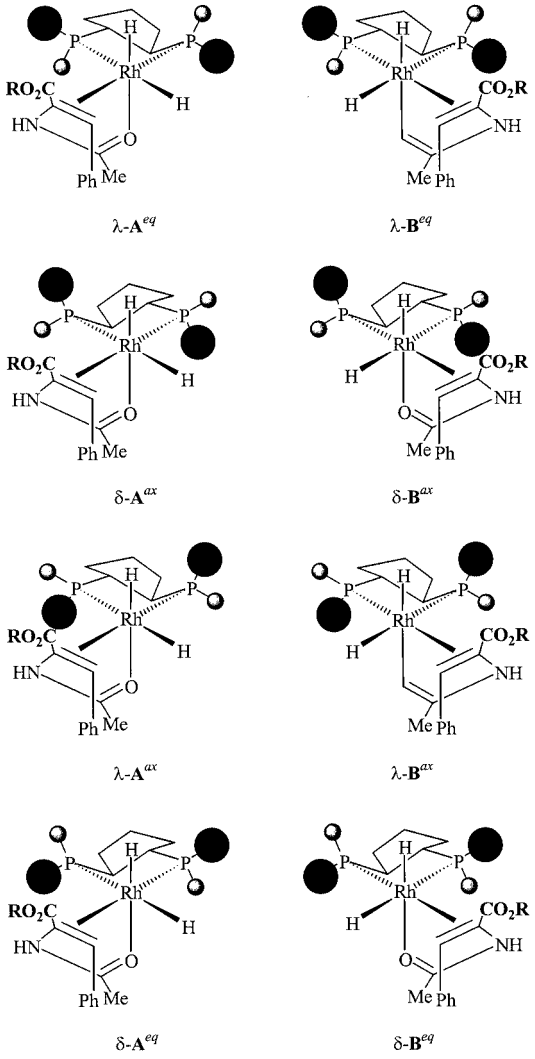


Figure 2. Perspective view of the cation [Rh{(*R*,*R*,R_P,$R_{P'}$)-$L^{Me/c\text{-}Oc}$}(COD)]$^+$ (**Rh-6d$^+$**), as present in the structure of [Rh{(*RS*,*RS*,$R_P$$S_P$,$R_{P'}$$S_{P'}$-$L^{Me/c\text{-}Oc}$}(COD)]$O_3SCF_3$ (**Rh-6c/6d**); selected bond lengths [Å] and angles [°]: Rh1−P1, 2.312(2); Rh1−P2, 2.323(2); Rh1−C1, 2.230(7); Rh1−C2, 2.237(7); Rh1−C5, 2.249(7); Rh1−C6, 2.249(7). P1−Rh−P2, 85.20(6)[32,47]

According to the "quadrant classification" established by Knowles in 1983,[6c] Gridnev and Imamoto[39b] as well as Ohashi[36d] have recently presented convincing evidence that any rhodium catalyst with C_2- or C_1-symmetric *P*-chirogenic bis(phosphanes), in which the difference in size between the terminal substituents is as apparent as in **Rh-6a**, **Rh-6d**, and **Rh-7a**, will furnish (*R*) hydrogenation products irrespective of a λ or δ conformation of the backbone, if the more voluminous groups are arranged in the upper left and lower right quadrants (cf. **Rh-7a**), while opposite orientation (as in **Rh-6a** and **Rh-6d**) will provoke (*S*) stereoselection.[39b] This is because the migratory insertion of the enamide to form an alkyl hydride, which has been identified as the enantiodetermining irreversible step of asymmetric hydrogenation both experimentally[39b−39g] and computationally,[42a] is controlled in an enantiofacially discriminating fashion by repulsive interaction between the chelate ring made up by the substrate and the bulky P-substituents in short-lived diastereomeric dihydrido enamide intermediates as depicted in Scheme 11. For **Rh-7a**, e.g., the (ethylene-connected) diastereomer λ-**A**^{eq}, containing the substrate bonded through its *si* face to give (*R*)-amino acids as observed, is definitely lower in energy than λ-**B**^{eq} because it is the smaller *P*-bound residue that undergoes direct steric repulsion with the carboxyl group attached to the chelate cycle.

For the three structurally characterized compounds under discussion, steric blocking of two diagonally arranged quadrants is most complete in the most stereoselective catalyst **Rh-7a**, where the bulky but nevertheless compact *tert*-butyl groups *exclusively* shield the quadrants left side up and right side down. Thus, the two $(H_3C)_3C$ hydrogen



Scheme 11. Possible diastereomers of cationic dihydrido enamide intermediates with chiral bis(phosphane) ligands having P-substituents pairwise differing in size (after Gridnev and Imamoto)[39b]

atoms that are closest to the >C=C< binding sites (H-11 and H-21 in the original publication[39a]) are located *within* the area spanned by the two quadrants and − equally important − are directed towards the diolefin in such a fashion that they are almost in a straight line with the central metal atom, the distances of the three atoms from the least-squares plane defined by the four olefinic carbon atoms being 1.53 and 1.51 Å for the two hydrogen atoms and 1.73 Å for the rhodium atom (angle H···Rh··H, 169.4°). As a result of their distinct equatorial alignment, the spatially expanded cyclooctyl rings of mismatched complex **Rh-6a** (Figure 1), on the other hand, not only fill out the two top right and bottom left quadrants but slightly penetrate into the adjacent parts of the coordination sphere as well, thereby contributing to some *unwanted shielding* of the upper left and lower right quadrants.[38b] Moreover, owing to the "face-on" orientation of the equatorial pairs of cyclooctyl groups the degree of *favorable quadrant-blocking*, thought to make δ-**B**^{eq} more readily accessible than δ-**A**^{eq},

is much less effective in **Rh-6a** than in **Rh-7a** (in this context, note also the decreased *ee* values achieved on substituting cC_5H_9 for *t*Bu or 1-Ad in Rh−bisP* catalysts!), as is evident from the deviations of the central metal atom and the *ipso*-C-bonded hydrogen atoms from the calculated least-square plane through the four coordinated >C=C< carbon atoms, which are 2.26 and 2.44 Å for the two hydrogen atoms but only 1.58 Å for rhodium (angle H···Rh··H, 155.5°). Matched catalyst **Rh-6d** which (as outlined above) is superior in stereodiscriminating power to **Rh-6a** but inferior to **Rh-7a**, differs in structure from mismatched **Rh-6a** by a more axial arrangement of the cyclooctyl rings, the methyl substituents being more equatorially aligned (Figure 2). This results in steric blocking of *only* the top right and bottom left quadrants, making λ-$\mathbf{B}^{ax}$ lower in energy than λ-$\mathbf{A}^{ax}$. Exclusive shielding of these two quadrants seems to be the main factor contributing to the stereoselective abilities of **Rh-6d**, since the "face-on" orientation of the cyclooctyl substituents is similar to **Rh-6a** and results in even slightly longer distances (2.36 and 2.70 Å) of the two *ipso*-C-bonded hydrogen atoms from the $(>C=C<)_2$ least-squares plane.

Interestingly, the Pt−$\mathbf{L}^{olane}$ complex **Pt-4a**, which served as an analogue of the matched catalyst [Rh{(*S*,*S*)-$\mathbf{L}^{olane\text{-}(R,R)}$}(COD)]$BF_4$ (**Rh-4a**),[37] similarly features quadrant-blocking methyl groups at the 2,5 positions of the phospholane ring showing a decidedly *axial* alignment in the upper left and lower right coordination quadrants (torsion angles P−Rh−P−$C^{2,5}$, −99.6/−110.7°). This arrangement should favor dihydride intermediate δ-$\mathbf{A}^{ax}$ over δ-$\mathbf{B}^{ax}$ to give high optical yields of the (*R*) hydrogenation products as observed. In marked contrast, the **Pt-4b** diastereomer, which was used to model the structure of mismatched [Rh{(*R*,*R*)-$\mathbf{L}^{olane\text{-}(R,R)}$}(COD)]$BF_4$ (**Rh-4b**), presents the same two methyl groups in the same quadrants in *equatorial* orientation (torsion angles P−Rh−P−$C^{2,5}$, −131.1° each), which can safely be predicted to lower the energy of λ-$\mathbf{A}^{eq}$ as compared to λ-$\mathbf{B}^{eq}$, but because of the equatorial alignment of the quadrant-shielding residues to a lesser degree than anticipated for δ-$\mathbf{A}^{ax}$ vs. δ-$\mathbf{B}^{ax}$. As the location of the phospholane substituents in the quadrants is independent of the λ or δ conformation of the five-membered chelate ring in the case of the two platinum complexes (large CH_3 groups top left and bottom right; small H atoms bottom left and top right) and as both rhodium analogues **Rh-4a** and **Rh-4b** induce (*R*) stereoselection, it becomes clear that Pringle's Rh−(*S*,*S*)-$\mathbf{L}^{olane\text{-}(R,R)}$ and Rh−(*R*,*R*)-$\mathbf{L}^{olane\text{-}(R,R)}$ catalysts also fit the aforementioned Gridnev/Imamoto rule for catalysts bearing *P*-chirogenic bis(phosphanes) with substituents pairwise differing in size.

We furthermore emphasize that the enhancement of enantioselectivity achieved by changing the alignment of a large substituent from a more equatorial to a more axial orientation as observed on going from **Rh-6a** to **Rh-6d** and, respectively, from **Rh-4b** to **Rh-4a** satisfies a prediction formulated by Nagel years ago: "We feel that to build a good catalyst for the hydrogenation of *N*-acylacrylic acid derivatives, it is necessary to have two large groups in the chelating diphosphane as axial as possible".[40] In view of the excellent enantioselectivities obtained with Imamoto's Rh−bisP* catalysts bearing compact bulky substituents in an equatorial arrangement, "axial" should, however, be qualified by "axial or focused to a single quadrant" rather than be understood as a sine qua non.

The results of the X-ray structure analyses carried out on the enantiomers [Rh{(*S*,*S*)-$\mathbf{L}^{Ph}$}(COD)]O_3SCF_3 (**Rh-2a**) and [Rh{(*R*,*R*)-$\mathbf{L}^{Ph}$}(COD)]O_3SCF_3 (**Rh-2b**) are worth mentioning regarding several aspects. As anticipated, single-crystals of the two complexes belonged to the same space group, $P2_1$, but because of different conditions of crystal growth, the unit-cell volumes of two of the three specimens investigated differed significantly: V = 1789.8(7) $Å^3$ and, comparably, V = 1791.1(5) $Å^3$ for the mirror image isomers taken from recrystallized samples of the enantiomerically pure complexes,[32] but V = 1772.3(5) $Å^3$ for a crystal of **Rh-2b** (**Rh-2b*** hereafter) picked from a conglomerate of [Rh(*rac*-$\mathbf{L}^{Ph}$)(COD)]O_3SCF_3, which − similar to the nickel complex [$NiBr_2$($\mathbf{L}^{Ph}$)]·CH_2Cl_2 [22a] − underwent spontaneous resolution upon crystallization from THF/*n*-pentane.[31] As a result of the different crystal packing in **Rh-2b** and **Rh-2b***, the endo- and exocyclic torsion angles measured for these two chelate systems were found to diverge considerably (Table 2) as did some of the bond lengths and angles (see captions of Figures 3−5). This demonstrates unequivocally that the two enantiomeric P_2 ligands do not build up absolutely inflexible coordination spheres but that some conformational freedom is associated with the ligand backbones. Previously, Oliver and Riley have pointed out that such adaptability of putatively stiff chiral phosphanes may be essential for high hydrogenation rates.[45] As a further and rather unexpected consequence, the diene ligand of the *same* enantiomers **Rh-2b** and **Rh-2b*** is seen to be skewed with respect to the P−Rh−P coordination plane *in opposite senses* (clockwise by +3.4° and anticlockwise by −4.1°). This clearly disproves the view that the sense of diene rotation is intimately correlated with the handedness of the catalyst pocket made up by the chiral steering ligand.[46] As complexes **Rh-2a** and **Rh-2b** catalyze the hydrogenation of standard enamide substrates giving high optical yields with opposite sign, it is furthermore concluded that no correlation whatsoever can be made between the sense of the diene twist and the enantioselectivity displayed by the catalysts. This goes against an early hypothesis of Kyba et al. that the forces causing the diolefin rotation would be the same that would induce the stereodiscrimination,[46] but corresponds to conclusions of Imamoto et al. that no interdependencies whatsoever exist between enantioselectivity and the sign of the diene skewness in the case of the bisP*−Rh catalysts, since these are highly stereoselective irrespective of an essentially ideal diene coordination with the double bonds perpendicular to the P−Rh−P plane.[39a,39b,39d]

Similar to several structures discussed in detail by Oliver and Riley already in 1983,[45] the arrangement of the phenyl rings in molecules **Rh-2a**, **Rh-2b**, and **Rh-2b*** does not obey the *ax*.−*eq*.−*ax*.−*eq*.-"edge−face−edge−face" relation[6c]

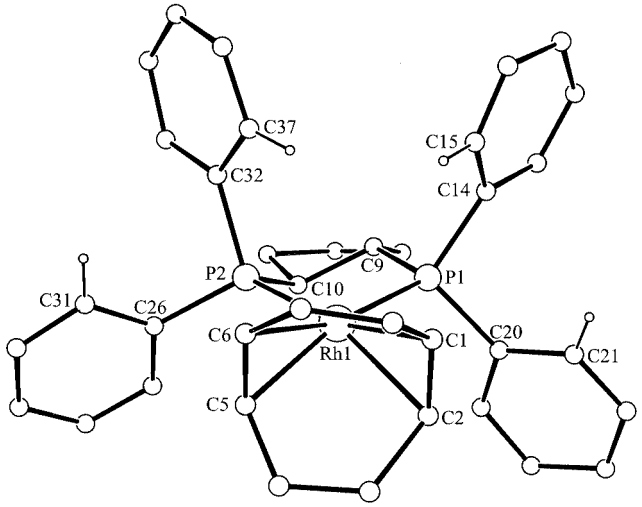


Figure 3. Perspective view of the cation [Rh{(*S*,*S*)-$\mathbf{L^{Ph}}$}(COD)]$^+$ (**Rh-2a**$^+$); selected bond lengths [Å] and angles [°]: Rh1−P1, 2.315(4); Rh1−P2, 2.306(4); Rh1−C1, 2.24(2); Rh1−C2, 2.27(2); Rh1−C5, 2.24(1); Rh1−C6, 2.25(1). P1−Rh−P2, 84.42(8); torsion angles Rh−P−C_{ipso}−C_{ortho} [°]: Rh1−P1−C14−C15, −7.1; Rh1−P1−C20−C21, −93.5; Rh1−P2−C26−C31, 91.5; Rh1−P2−C32−C37, 0.9[32,47]

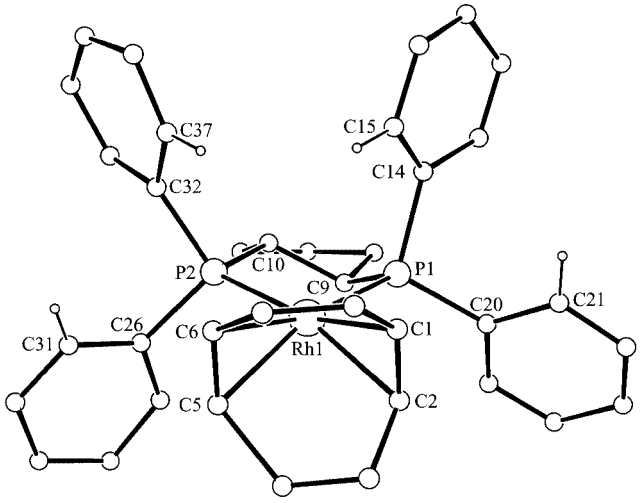


Figure 4. Perspective view of the cation [Rh{(*R*,*R*)-$\mathbf{L^{Ph}}$}(COD)]$^+$ of specimen **Rh-2b**; selected bond lengths [Å] and angles [°]: Rh1−P1, 2.328(4); Rh1−P2, 2.328(4); Rh1−C1, 2.31(4); Rh1−C2, 2.22(1); Rh1−C5, 2.24(1); Rh1−C6, 2.17(1). P1−Rh−P2, 84.19(10); torsion angles Rh−P−C_{ipso}−C_{ortho} [°]: Rh1−P1−C14−C15, 0.4; Rh1−P1−C20−C21, −93.7; Rh1−P2−C26−C31, 91.5; Rh1−P2−C32−C37, 6.9[32,47]

generally assumed for square-planar rhodium complexes with chiral bis(phosphane) ligands having terminal $-PPh_2$ donor groups: On moving from the upper right quadrant in a clockwise sense, one best describes the alignment of the phenyl substituents with respect to the five-membered chelate structures of the three molecules as *ax.*−*eq.*−*eq.*−*ax.*, as is readily evidenced from the magnitudes of the P−Rh−P−C_{ipso} torsion angles collected in Table 2. In the same sense, the Rh−P−C_{ipso}−C_{ortho} torsion angles given in the captions to Figures 3−5 define the

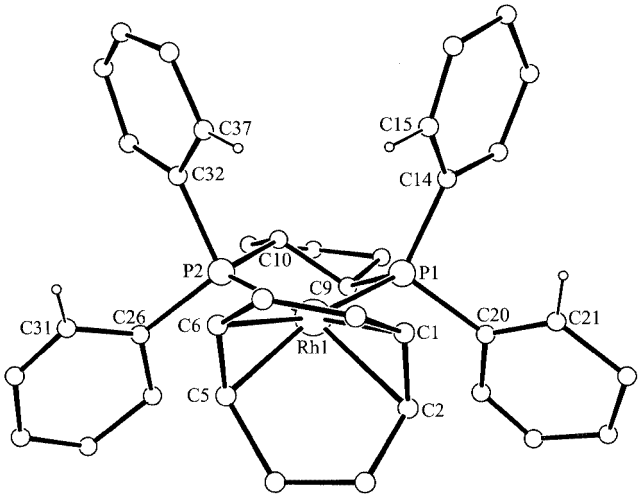


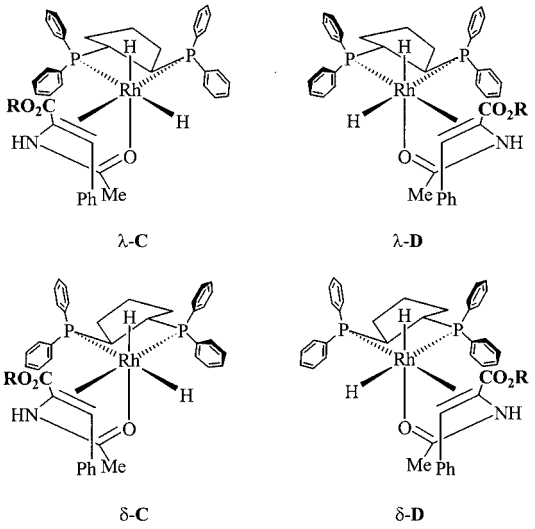
Figure 5. Perspective view of the cation [Rh{(*R*,*R*)-$\mathbf{L^{Ph}}$}(COD)]$^+$ of specimen **Rh-2b***; selected bond lengths [Å] and angles [°]: Rh1−P1, 2.309(2); Rh1−P2, 2.293(2); Rh1−C1, 2 .188(9); Rh1−C2, 2.312(7); Rh1−C5, 2.158(9); Rh1−C6, 2.264(7). P1−Rh−P2, 84.08(5); torsion angles Rh−P−C_{ipso}−C_{ortho} [°]: Rh1−P1−C14−C15, −6.2; Rh1−P1−C20−C21, −94.4; Rh1−P2−C26−C31, 91.1; Rh1−P2−C32−C37, 1.5[31,47]

orientations of the aromatic rings with respect to the binding sites of the diene as close to "edge−face−face−edge". Thus, while the backbone symmetry of the P_2 ligands in the stable conformation of the three complexes is C_2, the local symmetry at the metal atom as determined by the spatial orientation of the phenyl rings in the donor groups at first glance seems to approach C_s − were there not some subtleties that make the difference!

In **Rh-2a** we see the *ortho*-hydrogen atoms in the top right and bottom right quadrants at distances of 2.27 and 2.13 Å from the least-squares plane through the coordinated olefinic carbon atoms, the separations between that plane and the *ortho*-H atoms in the quadrants left side up and left side down amounting to 2.73 and 2.53 Å. For enantiomer **Rh-2b** (recrystallized sample), we face the opposite arrangement of the four *ortho*-hydrogen atoms with respect to the $(>C=C<)_2$ least-squares plane: 2.39 (2.28) Å and 1.96 (2.15) Å for the separations in the upper left and lower left quadrants vs. twice 2.76 (2.63, 2.48) Å for the corresponding distances in the quadrants right side up and right side down (values for specimen **Rh-2b*** picked from the conglomerate given parenthetically).

In view of the enhanced axial interactions in octahedral dihydro complexes directly preceding the enantiodetermining migratory insertion step (vide supra) it has been suggested that in RhP_2 complexes with backbone chirality and four equivalent phenyl substituents on the phosphorus atom, i.e., in catalysts *conforming* to the λ/δ rule, it is the axial phenyl rings which lend the decisive steric hindrance to the stereodiscriminating step.[39b,40] We conclude that the two phenyl groups in the top right and top left quadrants of **Rh-2a** and **Rh-2b** or **Rh-2b*** are identified by the substrate as being larger than the aryl residues in the quadrants that are bottom right and bottom left. In the critical dihydro enamide intermediates with *trans*-positioned hydride

and acetyl ligands, steric crowding would therefore be minimized if the axial phenyl substituents point away from the equatorial plane containing the enamide chelate in addition to the five-membered metal−bis(phosphane) ring. As a consequence, the equatorially aligned aryl groups would be forced into the plane spanned by the metal atom and the >C=C< double bond of the substrate; see structures **C** and **D** in Scheme 12. Comparing the relative bulkiness of the phenyl substituents as estimated from the distances between the *ortho*-H atoms and the least-squares plane made up by the olefinic carbon atoms in the enantiomeric diene precursors, we would anticipate more steric repulsion between the enamide chelate and the phenyl groups in the top and bottom right quadrants of **Rh-2a** and, vice versa, in the upper and lower left quadrants of **Rh-2b** and **Rh-2b***, respectively. The corollary of this conclusion is that in a dihydro enamide complex resulting from **Rh-2a**, the chelated substrate should experience the least steric strain if bonded through its *si* face as in δ-**C** to give, by migratory insertion, the experimentally observed (*R*) hydrogenation products; *re*-face-bonding with formation of the (*S*) enantiomers would only be expected if the least repulsive interactions occur in the quadrants right side up and right side down, i.e., in dihydride intermediates of type λ-**D** for which **Rh-2b** and **Rh-2b*** are suitable precursors. The preferred coordination of the enamide substrate as described by structures λ-**D** and δ-**C** not only minimizes the axial repulsions but also reduces steric crowding between the enamide chelate cycle and those equatorially aligned substituents that are nearest to the olefinic binding sites in the ground state structures of the diene precursors **Rh-2a** (bottom right) and **Rh-2b** or **Rh-2b*** (bottom left). Even if the equatorial interactions have been considered as less important for stereoselection than the axial repulsions,[39b,40] they can help to make isomers λ-**D** and δ-**C** more readily accessible than their diastereomers λ-**C** and δ-**D** featuring an unfavorable close contact between the chelate cycle and the phenyl substituents. Interpreted like this, the quadrant rule changes into a "left−right" criterion, valid for RhP_2 (pre)catalysts which, from a structural point of view, do not adhere to the *ax.*−*eq.*−*ax.*−*eq.*-"edge−face−edge−face" relation.



Scheme 12. Possible diastereomers of cationic dihydrido enamide intermediates with chiral bis(phosphane) ligands that have phenyl substituents of equal size but do not conform to the *ax.*−*eq.*−*ax.*−*eq.*-"edge−face−edge−face" relation

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. The author is also indebted to Degussa AG for many generous gifts of platinum salts. Furthermore, it is a pleasure to thank all coworkers who contributed to the success of this project over the past years, in particular Dr. Andrea Saare, Dr. Corinna Becker, Dr. Christine Eckert, Dr. Volker Kurth, Dr. Stefan Mertel, Dr. Nils Osthoff, Dr. Andreas Wühr, and Dipl.-Chem. Anja Kaunert. Finally, I wish to thank Mrs. Susanne Kammerer for skilful technical assistance.

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[47] Crystal structures: Enraf−Nonius CAD 4 (Mo-K_α radiation, λ = 0.71073 Å; T = 293 ± 2 K). **Rh-2a**: space group $P2_1$ (no. 4), a = 10.4024(9), b = 14.854(5), c = 11.665(2) Å, β = 96.803(8)°, V = 1789.8(7) Å, Z = 2, μ = 0.677 mm^{-1}; $2\theta_{max}$ = 50.36°, reflections collected (including Friedel pairs)/unique: 7048/6440 (R_{int} = 0.0324), 4720 $F_o \geq 4\sigma(F_o)$, 433 parameters, wR_2 (all data) = 0.1381, R_1 ($F \geq 4\sigma$) = 0.0566; absolute structure parameter: 0.10(7).[32] **Rh-2b**: space group $P2_1$ (no. 4), a = 10.416(1), b = 14.880(4), c = 11.631(1) Å, β = 96.50(1)°, V = 1791.1(7) Å, Z = 2, μ = 0.676 mm^{-1}; $2\theta_{max}$ = 48.56°, reflections collected (including Friedel pairs)/unique: 6398/5792 (R_{int} = 0.0570), 3252 $F_o \geq 4\sigma(F_o)$, 433 parameters, wR_2 (all data) = 0.1691, R_1 ($F \geq 4\sigma$) = 0.0761; absolute structure parameter: 0.22(11).[32] **Rh-2b***: space group $P2_1$ (no. 4), a = 10.3515(8), b = 14.827(4), c = 11.6246(8) Å, β = 96.610(7)°, V = 1772.3(5) Å, Z = 2, μ = 0.683 mm^{-1}; $2\theta_{max}$ = 47.94°, reflections collected/unique: 5787/2899 (R_{int} = 0.0482), 2163 $F_o \geq 4\sigma(F_o)$, 433 parameters, wR_2 (all data) = 0.0930, R_1 ($F \geq 4\sigma$) = 0.0371; absolute structure parameter: 0.09(10).[31] **Rh-6c/**

6d: space group $P2_1/c$ (no. 14), $a = 9.716(1)$, $b = 19.348(2)$, $c = 18.828(4)$ Å, $\beta = 99.80(1)°$, $V = 3487.7(9)$ Å, $Z = 4$, $\mu = 0.688$ mm^{-1}; $2\theta_{max} = 52.14°$, reflections collected/unique: 14610/6889 ($R_{int} = 0.0385$), 4483 $F_o \geq 4\sigma(F_o)$, 399 parameters, wR_2 (all data) = 0.1640, R_1 ($F \geq 4\sigma$) = 0.0647.[32] CCDC-200009 (**Rh-2b***), -200010 (**Rh-6c/6d**), -200011 (**Rh-2a**) and -200012 (**Rh-2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received December 27, 2002

