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Review

P-Modular bis(phosphines) based on the 1,2-*trans*-disubstituted cyclopentane framework in synthesis, coordination chemistry, and catalysis

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Contents

Abstract

The review describes a class of versatile bidentate phosphines having a homochiral 1,2-disubstituted cyclopentane backbone, the use of such ligands in coordination chemistry, and their application in transition metal-catalyzed synthesis, including C−H activation, C−C coupling,

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>C=C< hydrogenation, and hydroformylation. In particular, the synthetic potential of the multi-purpose P–H and P–Cl reagents (*R*,*R*)- and (*S*,*S*)-$C_5H_8(PX_2)_2$ (X = H, Cl) is highlighted, since these open up the possibility to incorporate virtually any other P–O-, P–N- or P–C-bonded residue ("module") into the homochiral bis(phosphine) framework. The resulting chelate ligands allow access to transition metal catalysts with stereodiscriminating properties determined by parameters such as (i) the presence of *P*-substituents that are equal or pairwise different in steric demand, (ii) the spatial orientation of such substituents with respect to the coordination plane of the catalyst complex, and (iii) the combination of *C*- and *P*-chirogenic stereoelements in matched (or mismatched) fashion. A comparative discussion of the crystal structures that are currently available for the free ligands and their transition metal complexes is also presented.
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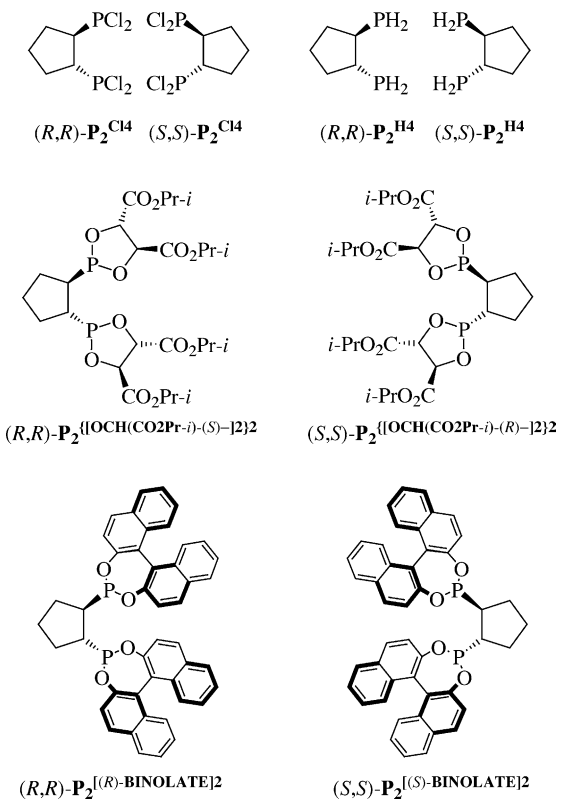
Keywords: Chelate phosphines; Chirality; Transition metal complexes; Catalysis; Crystal structures

1. Introduction

Optically active bidentate phosphines exhibiting C_2-symmetry due to a chiral carbon framework or a chiral substitution of the donor sets are among the most successful steering ligands used in transition metal-catalyzed enantioselective synthesis. Since the pioneering presentation of the readily accessible (4*R*,5*R*) and (4*S*,5*S*) enantiomers of 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane, DIOP, as the first C_2 chiral chelating bis(phosphines) by Kagan [1] and the use of *P*-chirogenic bidentate (R_P, $R_{P'}$)-bis{(2-methoxyphenyl)phenylphosphino}ethane, (*R*, *R*)-DIPAMP, in the commercial L-DOPA process established shortly after by Knowles et al. at Monsanto [2,3a], virtually hundreds of chiral P_2 ligands have been synthesized [4] in order to improve metal catalysts of up to then low performance. Impressive examples of chelate phosphines that have been optimized for various applications are given by 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, BINAP [3b], and the DuPHOS-type *o*-phenylene-bis(2,5-dialkylphospholanes) [5].

Many of the widely used optically active bis(phosphines), especially those in which the phosphorus atoms bear two electron-withdrawing aryl groups, are synthesized by alkylating lithiated diarylphosphides, $LiPAr_2$, with disulfonates containing chiral carbon scaffolds. The disadvantage of this protocol is that it cannot routinely be used in the synthesis of P_2 ligands possessing more electron-rich *P*-alkylated donor groups. Due to their pronounced basicity, alkyl phosphide nucleophiles, particularly those with sterically demanding substituents such as $LiP(Bu\text{-}t)_2$ or $LiP(C_6H_{11}\text{-}c)_2$, tend to favor various annoying side reactions frequently resulting in products formed by metal–halogen exchange, elimination or P–P coupling rather than substitution [6]. To some extent, these difficulties can be mastered either by making use of less basic and, hence, less reactive phosphide–borane adducts [7] or – in displacement reactions employing relatively unhindered phosphide nucleophiles derived from primary phosphines – by the use of cyclic sulfates as substrates [5].

Our recent research in the field covered by this review has been focussed on the development of variable methods of synthesis for optically active bidentate phosphorus ligands containing *P*-bound structural components ("modules" in Burk's notation [5e]) that can be interchanged systematically and easily. Important key compounds of the synthetic strategy we have adopted are given by the resolved enantiomers of bis(primary phosphines), $H_2P^*\cap^*PH_2$, and bis(phosphonous dichlorides), $Cl_2P^*\cap^*PCl_2$, having synthetically versatile reactive $-PCl_2$ and $-PH_2$ functions supported on a rigid 1,2-*trans*-disubstituted cycloalkane backbone, such as exemplified by the enantiopure cyclopentane-based precursors $C_5H_8(PH_2)_2$, $\mathbf{P_2^{H_4}}$, and $C_5H_8(PCl_2)_2$, $\mathbf{P_2^{Cl_4}}$, shown in Scheme 1.



Scheme 1. Selection of cylopentane-based bis(phosphines) illustrating the acronyms used throughout this paper.

2. Ligands

2.1. Historical development and scope

By analogy to the straightforward preparation of $Cl_2PC_2H_4PCl_2$ from ethylene, white phosphorus and

phosphorus trichloride [8], Green and co-workers obtained racemic 1,2-*trans*- $C_5H_8(PCl_2)_2$, *rac*-$\mathbf{P_2^{Cl_4}}$, as early as 1983 on a multi-gram scale by heating cyclopentene with P_4 and PCl_3 in an autoclave at 215 °C for 40 h [9a,b]. Only trace amounts of the *cis* isomer and the monoadduct $C_5H_9PCl_2$ were formed and were removed by distillation. Treatment of *rac*-$\mathbf{P_2^{Cl_4}}$ with RMgBr in THF (R = Me, Cy, Ph) [9a–c] gave the corresponding bis(tertiary phosphines) *rac*-$C_5H_8(PR_2)_2$, *rac*-$\mathbf{P_2^{R_4}}$, of which *rac*-$\mathbf{P_2^{Ph_4}}$ was fully characterized by X-ray structure analysis (Section 2.4) [9a,b].

Similar to 1,2-*trans*-$C_5H_8(PCl_2)_2$, the cyclohexane- and norbornane-based bis(phosphonous dichlorides) 1,2-*trans*-$C_6H_{10}(PCl_2)_2$ and 2,3-*trans*-$C_7H_{10}(PCl_2)_2$ were isolated as racemates in quantities of up to 100 g from autoclave reactions of the respective cycloalkenes with P_4 and PCl_3 at 220–225 °C and then derivatized to 1,2-*trans*-$C_6H_{10}(PPh_2)_2$ [9a] and 2,3-t*rans*-$C_7H_{10}[P(C_6H_{11}$-*c*$)_2]_2$ [10a,d], respectively. However, these two chelate phosphines are excluded from further discussion because they feature a largely undeveloped coordination chemistry, $[NiX_2\{$*rac*-$C_6H_{10}(PPh_2)_2\}]$ (X = Cl, Br), $[Mo(CO)_4\{$*rac*-$C_6H_{10}(PPh_2)_2\}]$ [9a], $[Pt(X)(CH_2$Bu-*t*$)\{$*rac*-$C_7H_{10}[P(C_6H_{11}$-*c*$)_2]_2\}]$ (X = H, CH_2Bu-*t*, (1*S*)-camphor-10-sulfonate) [10a,d], and $[Rh(\eta^4$-$C_8H_{12})\{(+)$-$C_7H_{10}[P(C_6H_{11}$-*c*$)_2]_2\}]ClO_4$ [11] being the only metal complexes hitherto described. The $C_7H_{10}[P(C_6H_{11}$-*c*$)_2]_2$ ligand system forms a closely related analogue of 2,3-*trans*-bis(diphenylphosphino)norbornene and its reduced congener 2,3-*trans*-bis(diphenylphosphino)norbornane, which have become famous in asymmetric catalysis under the acronyms NOPRPHOS [12] and RENOPRPHOS [13], respectively. The broad application of the latter two bis(phosphines) – notably of NORPHOS [4a] – is predominantly owed to the pioneering contributions of Brunner and co-workers and, hence, remains beyond the scope of this article.

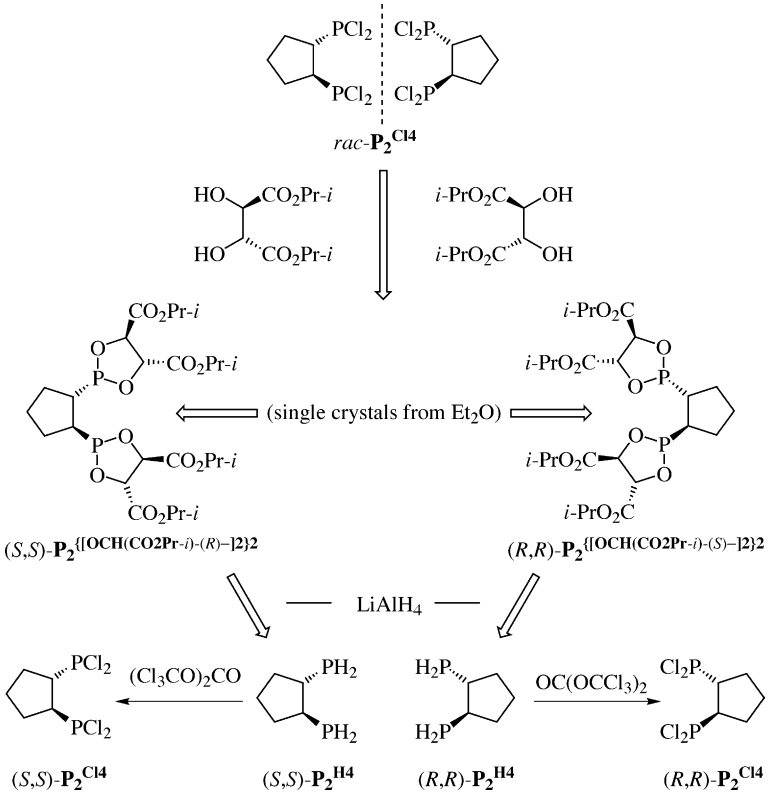
Although the thermally unstable phosphorus(II) chloride P_2Cl_4, which begins to decompose at 0 °C by disproportionation yielding PCl_3 together with $(PCl)_x$ [14], is certainly not involved as an intermediate in the high-temperature reactions between olefins, white phosphorus and phosphorus trichloride, it is interesting to see that this subhalide undergoes clean >C=C< addition with stereospecific formation of 1,2-*trans*-$C_6H_{10}(PCl_2)_2$, if allowed to interact with cyclohexene under mild conditions [14].

2.2. Ligand precursors and optical resolution

In the particular case of *rac*-$\mathbf{P_2^{Ph_4}}$, resolution of the racemic mixture was originally achieved by reacting the racemate with $NiBr_2$ in ethanol–water (95:5) to form $[NiBr_2($*rac*-$\mathbf{P_2^{Ph_4}})]$. Crystallization of the product from dichloromethane yielded large crystals of the CH_2Cl_2 solvate, the structure analysis of which showed the specimen investigated to contain only one enantiomer, $[NiBr_2\{(R,R)$-$\mathbf{P_2^{Ph_4}}\}]\cdot CH_2Cl_2$. The nickel(II) complex thus underwent spontaneous resolution upon crystallization depositing a conglomerate of enantiomerically pure single crystals. Separation of the conglomerate into (+)-$[NiBr_2\{(R,R)$-$\mathbf{P_2^{Ph_4}}\}]\cdot CH_2Cl_2$ and (−)-$[NiBr_2\{(R,R)$-$\mathbf{P_2^{Ph_4}}\}]\cdot CH_2Cl_2$ was accomplished manually by crystal picking, and (−)-(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$ and (+)-(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$ were subsequently recovered by treating the dextrorotatory and, respectively, laevorotatory complex isomers with sodium cyanide [9a,b].

We entered the field in the late 1980s on the occasion of an attempt to bring about enantiodiscriminative C–H activation by oxidative addition of racemic 2,2′-disubstituted biphenyls and binaphthyls to angular carbene-type [15] 14e complex fragments of Pt(0) bearing optically active P_2 chelating ligands. At that time, Whitesides and Hackett had already established an extensive carbene-like C–H insertion reactivity for the non-linear d^{10}-ML_2 equivalent $\{Pt[(c$-$C_6H_{11})_2P(CH_2)_2P(C_6H_{11}$-*c*$)_2]\}$ which they showed to be smoothly released into solution upon mild thermolysis of the readily accessible alkyl hydrido platinum(II) precursor $[Pt(H)(CH_2$Bu-*t*$)\{(c$-$C_6H_{11})_2P(CH_2)_2P(C_6H_{11}$-*c*$)_2\}]$ [16]. These results inspired us to probe the stereodiscriminatory properties of enantiomerically pure angular dicoordinate Pt(0) fragments containing the bis(dicyclohexylphosphino) ligand $C_5H_8[P(C_6H_{11}$-*c*$)_2]_2$, $\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$, in optically active form (see Section 4.1) [10]. For the synthesis of the required starting complexes $[Pt(H)(CH_2$Bu-*t*$)\{(+)$-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}\}]$ and $[Pt(H)(CH_2$Bu-*t*$)\{(-)$-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}\}]$, resolution of the racemic ligand was effected following the strategy previously developed by Brunner and Pieronczyk for the separation of NORPHOS into its (2*R*,3*R*)- and (2*S*,3*S*)-$C_7H_8(PPh_2)_2$ enantiomers [12], i.e., *rac*-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$ was first transformed, by oxidation with H_2O_2, to the *P*,*P*′-dioxide which was subsequently separated into (+)- and (−)-$C_5H_8[P(O)(C_6H_{11}$-*c*$)_2]_2$ using (2*S*,3*S*)-(+)-di-*o*-benzoyl tartaric acid as resolving agent. Several crystallizations of the P=O···HO-bridged diastereomeric adducts between the phosphine oxide enantiomers and the tartaric acid derivative from THF/pentane followed by cleavage of the hydrogen bonds with aqueous KOH afforded the dioxide as enantiopure isomers, which were eventually converted back to their parent (+)- and (−)-$C_5H_8[P(C_6H_{11}$-*c*$)_2]_2$ enantiomers using diphenyl silane as a reductant [10]. A similar procedure was used by Consiglio and Indolese to make the $\mathbf{P_2^{Ph_4}}$ ligand and its *p*-methoxyphenyl analogue $\mathbf{P_2^{[C_6H_4OMe\text{-}(4)]_4}}$ in optically active form [17].

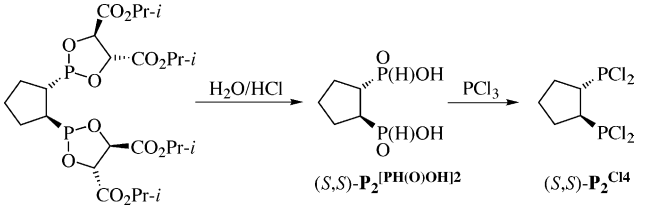
The observation that the cyclopentane-1,2-diyl-bis(1′,3′,2′-dioxaphospholane) $\mathbf{P_2}^{\{[OCH(CO_2Pr\text{-}i)-]_2\}_2}$, formed by reacting racemic $\mathbf{P_2^{Cl_4}}$ with (2*R*,3*R*)-(+)-diisopropyl tartrate, crystallized from the resulting isomeric mixture as a single (1*S*,2*S*,4′*R*,5′*R*) diastereomer, (*S*,*S*)-$\mathbf{P_2}^{\{[OCH(CO_2Pr\text{-}i)\text{-}(R)-]_2\}_2}$ [18a], meant a considerable step forward on the way to optically active cyclopentane-based P_2 ligands containing a wide range of different P–C-, P–N- or P–O-bonded donor groups: as anticipated, the enantiomeric bis(phosphonite) with (1*R*,2*R*,4′*S*,5′*S*) configuration, (*R*,*R*)-$\mathbf{P_2}^{\{[OCH(CO_2Pr\text{-}i)\text{-}(S)-]_2\}_2}$, could be isolated in diastereomerically pure form from a similar reaction between *rac*-$\mathbf{P_2^{Cl_4}}$



Scheme 2. Resolution of *rac*-$\mathbf{P_2^{Cl4}}$ via diastereomerically pure bis(dioxaphospholane) key intermediates [18a,19,20].

and (2*S*,3*S*)-(−)-diisopropyl tartrate [19a]. Subsequent reduction, with $LiAlH_4$, allowed the bis(primary phosphine) $C_5H_8(PH_2)_2$, to be isolated as either optical antipode, from which bis(phosphonous dichloride) $C_5H_8(PCl_2)_2$ was recovered as resolved (1*R*,2*R*) and (1*S*,2*S*) enantiomers by oxidizing the P–H bonds with bis(trichloromethyl) carbonate ("triphosgene") (Scheme 2) [18,19b,20,21a].

In a different approach to the mirror image isomers of the multi-purpose P–Cl reagent $\mathbf{P_2^{Cl4}}$, Brunner and co-workers chose to hydrolyse the resolved bis(1′,3′,2′-dioxaphospholanes) (*R*,*R*)-$\mathbf{P_2^{\{[OCH(CO_2Pr\text{-}i)\text{-}(S)\text{-}]_2\}_2}}$ and (*S*,*S*)-$\mathbf{P_2^{\{[OCH(CO_2Pr\text{-}i)\text{-}(R)\text{-}]_2\}_2}}$ to the free phosphinic acids (*R*,*R*)- and (*S*,*S*)-$C_5H_8[PH(O)OH]_2$, from which the pure enantiomers (*R*,*R*)- and (*S*,*S*)-$\mathbf{P_2^{Cl4}}$, were recovered by chlorination with PCl_3 (Scheme 3) [22a,b].



Scheme 3. Preparation of enantiopure (*S*,*S*)-$\mathbf{P_2^{Cl4}}$ by hydrolysis of diastereomerically pure (*S*,*S*)-$\mathbf{P_2^{\{[OCH(CO_2Pr\text{-}i)\text{-}(R)\text{-}]_2\}_2}}$ and chlorination [22a,b].

The advantage of having both $\mathbf{P_2^{H4}}$ and $\mathbf{P_2^{Cl4}}$ as enantiomerically pure compounds at one's disposal rests on the following features: First, both P–H/>C=C< addition reactions and "P–H → P–Li → P–R" metallation–alkylation sequences open practicable ways to alkylated bis(secondary) and bis(tertiary) P_2 ligands with or without additional chirogenic centers at phosphorus. Second, substitution reactions at the P–Cl bond using carbon, nitrogen or oxygen nucleophiles are among the most general and most easily accomplished coupling methods in organic chemistry. Finally, the possibility to incorporate virtually any P–C–, P–N– or P–O-bonded residue into the homochiral $C_5H_8(PX_2)_2$ framework allows the preparation of a wide range of optically active chelate ligands and metal complexes having fine-tunable steric and electronic attributes.

2.3. Ligand preparation

2.3.1. Bis(tertiary phosphines) $C_5H_8(PR_2)_2$

2.3.1.1. Bis(tertiary phosphines) with aliphatic and cycloaliphatic substituents. Treatment of *rac*-$\mathbf{P_2^{Cl4}}$ with the appropriate Grignard reagent RMgX (X = Cl, Br) in diethyl ether or THF afforded the racemic bis(phosphines) $C_5H_8(PR_2)_2$, where R = methyl [9] or cyclohexyl [9b,10a,d,23a]. In a similar fashion, the optically active ligands (1*S*,2*S*)-$C_5H_8[P(Bu\text{-}n)_2]_2$, (*S*,*S*)-$\mathbf{P_2^{(Bu\text{-}n)_4}}$ [24b], and (1*S*,2*S*)-$C_5H_8[P(C_6H_{11}\text{-}c)_2]_2$, (*S*,*S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$ [19b],

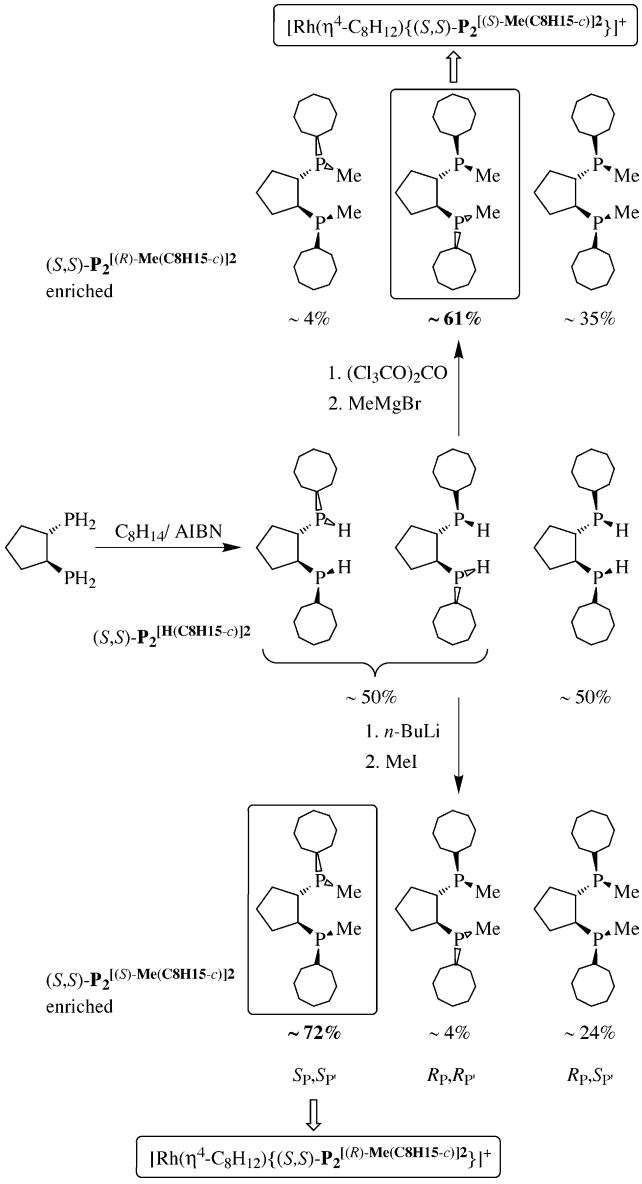
were isolated by reacting the (*S*,*S*)-$\mathbf{P_2^{Cl_4}}$ enantiomer with *n*-BuMgCl and *c*-$C_6H_{11}MgBr$, respectively.

Starting from bis(primary phosphine) $\mathbf{P_2^{H_4}}$, *P*-alkylated $C_5H_8(PR_2)_2$ and $C_5H_8[P(R)R']_2$ ligands have been prepared by either metallation–substitution sequences or P–H/>C=C< addition reactions. Lithiation of *rac*-$\mathbf{P_2^{H_4}}$ with *n*-butyllithium in THF at −78 °C, followed by the addition of the required amount of methyl iodide, thus furnished *rac*-$\mathbf{P_2^{Me_4}}$ in high yield. The tetra- and dilithio derivatives *rac*-$C_5H_8(PLi_2)_2$ and *rac*-$C_5H_8(PHLi)_2$ could be isolated as highly reactive solids which likewise gave good yields of *rac*-$\mathbf{P_2^{Me_4}}$ following alkylation and, respectively, metallation–methylation [18b].

Radical-initiated P–H addition of the $-PH_2$ functions of (1*S*,2*S*)- or (1*R*,2*R*)-$C_5H_8(PH_2)_2$ to the carbon–carbon double bonds of cycloalkenes C_nH_{2n-2} ($n = 5$–8) gave the bis(secondary phosphines) (1*R*,2*R*)- and (1*S*,2*S*)-$C_5H_8[PH(C_nH_{2n-1})]_2$ as statistical mixtures of their (R_P,$R_{P'}$), (R_P,$S_{P'}$) [=(S_P,$R_{P'}$)], and (S_P,$S_{P'}$) diastereomers [20,24a,25]. As exemplified in Scheme 4 for the cyclooctene adducts (*S*,*S*)-$\mathbf{P_2^{[H(C_8H_{15}\text{-}c)]_2}}$, separation of the stereoisomers was accomplished by further derivatization and metal complex formation. Thus, treatment of the isomeric mixtures with *n*-butyllithium followed by alkylation with methyl iodide led to an enrichment of the stereoisomers with like chirality at phosphorus and carbon, (*R*,*R*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$ and (*S*,*S*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$, the rhodium(I) complexes of which – $[Rh(\eta^4\text{-}C_8H_{12})\{(R,R)\text{-}\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}\}]O_3SCF_3$ and $[Rh(\eta^4\text{-}C_8H_{12})\{(S,S)\text{-}\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}\}]O_3SCF_3$ – were isolated in isomerically pure form by crystallization from THF/diethyl ether solvent mixtures [24b,25]. Conversely, reaction of the bis(secondary phosphine) stereoisomers $\mathbf{P_2^{[H(C_8H_{15}\text{-}c)]_2}}$ first with $(Cl_3CO)_2CO$ [20] and then with methyl magnesium bromide caused the isomeric distributions to change in favor of the (*R*,*R*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$ and (*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$ isomers, which were subsequently reacted with $[Rh(\eta^4\text{-}C_8H_{12})_2]O_3SCF_3$ to furnish $[Rh(\eta^4\text{-}C_8H_{12})\{(R,R)\text{-}\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}\}]O_3SCF_3$ and $[Rh(\eta^4\text{-}C_8H_{12})\{(S,S)\text{-}\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}\}]O_3SCF_3$ following work-up by column chromatography [25].

Two hydroxyalkyl-substituted derivatives, (1*S*,2*S*)-$C_5H_8[P(CH_2OH)_2]_2$, (*S*,*S*)-$\mathbf{P_2^{(CH_2OH)_4}}$, and (1*S*,2*S*)-$C_5H_8[P(C_3H_6OH)_2]_2$, (*S*,*S*)-$\mathbf{P_2^{(C_3H_6OH)_4}}$, have been described as being soluble in water. Both were made from (*S*,*S*)-$\mathbf{P_2^{H_4}}$, the former by catalytic formylation of the P–H bonds using aqueous CH_2O in the presence of $K_2[PtCl_4]$ [22a,b], the latter by radical-initiated P–H addition to allyl alcohol [24b].

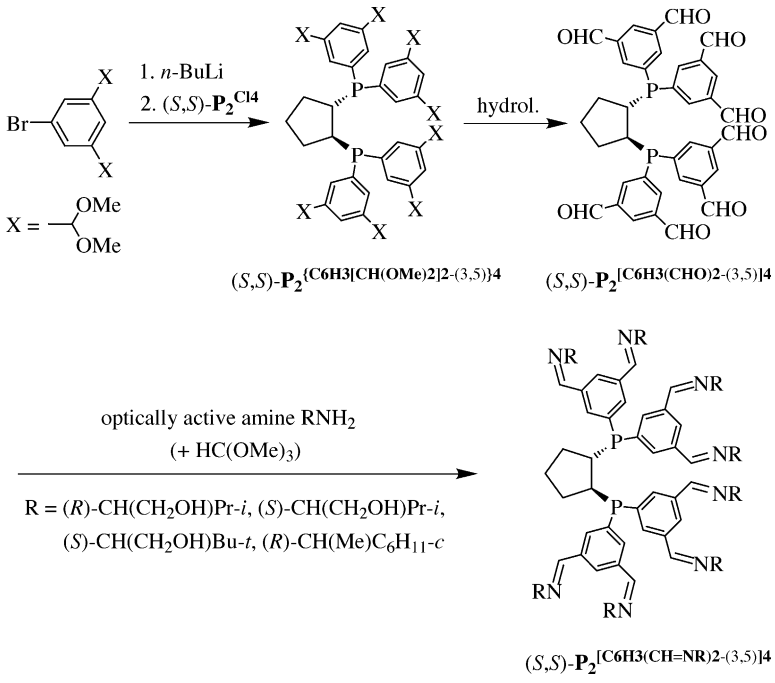
2.3.1.2. Bis(tertiary phosphines) with aromatic and heteroaromatic substituents. Grignard reactions between $\mathbf{P_2^{Cl_4}}$ and ArMgX (Ar = C_6H_5, C_6H_4OMe-(2), C_6H_4OMe-(4), C_6F_5; X = Cl, Br) yielded the phenyl-, anisyl-, and pentafluorophenyl-substituted bis(tertiary phosphines) $C_5H_8(PAr_2)_2$, both as racemic products, *rac*-$\mathbf{P_2^{Ph_4}}$ [9a,b], *rac*-$\mathbf{P_2^{[C_6H_4OMe\text{-}(2)]_4}}$, *rac*-$\mathbf{P_2^{[C_6H_4OMe\text{-}(4)]_4}}$ [17], and *rac*-$\mathbf{P_2^{(C_6F_5)_4}}$ [23b], and as enantiomerically pure compounds—(*R*,*R*)- or (*S*,*S*)-$\mathbf{P_2^{Ph_4}}$ [21b,23b], (*R*,*R*)-$\mathbf{P_2^{[C_6H_4OMe\text{-}(2)]_4}}$, (*S*,*S*)-$\mathbf{P_2^{[C_6H_4OMe\text{-}(4)]_4}}$ [17], and (*S*,*S*)-$\mathbf{P_2^{(C_6F_5)_4}}$ [23b], respectively.



Scheme 4. Preparation, enrichment, and isolation of *C*,*P*-chirogenic bis(phosphines) (*S*,*S*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$ and (*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$ [24b,25].

The racemic *o*-*N*,*N*-dimethylaminophenyl and 2-pyridyl-substituted ligands *rac*-$C_5H_8\{P[C_6H_4NMe_2\text{-}(2)]_2\}_2$, *rac*-$\mathbf{P_2^{[C_6H_4NMe_2\text{-}(2)]_4}}$ and *rac*-$C_5H_8\{P[C_5H_4N\text{-}(2)]_2\}_2$, *rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$, were synthesized by treating *rac*-$\mathbf{P_2^{Cl_4}}$ with the 2-lithio derivatives of *N*,*N*-dimethylaniline or pyridine, which themselves were generated in situ from *n*-BuLi and the corresponding aryl bromides [26b,c].

Brunner and co-workers described both divergent and convergent reaction sequences leading from enantiomers (*R*,*R*)- and (*S*,*S*)-$\mathbf{P_2^{Cl_4}}$ to a second generation of optically active dendritically expanded bis(phosphines)



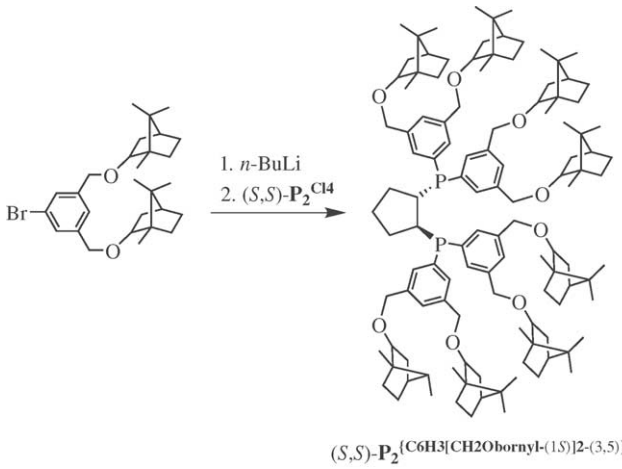
Scheme 5. Divergent approach to dendritically expanded bis(phosphines) bearing eight peripheral aldimine functions [22a,b].

containing their stereochemically uniform dendritic extensions supported on the homochiral 1,2-disubstituted cyclopentane framework [22a,b] rather than on achiral 1,2-ethylene- or *ortho*-phenylene bridges as were used in the first generation of optically active expanded P_2 ligands [27]. In the first step of the divergent approach, (*S*,*S*)-$\mathbf{P_2^{Cl4}}$ was coupled to aryllithium building blocks bearing acetal-protected formyl functions to form the tetra- and octaacetals (1*S*,2*S*)-$C_5H_8\{P[C_6H_4CH(OMe)_2\text{-}(2)]_2\}_2$, (*S*,*S*)-$\mathbf{P_2^{[C_6H_4CH(OMe)_2\text{-}(2)]_4}}$, and (1*S*,2*S*)-$C_5H_8\{P[C_6H_3\{CH(OMe)_2\text{-}\}_2\text{-}(3,5)]_2\}_2$, (*S*,*S*)-$\mathbf{P_2^{\{C_6H_3[CH(OMe)_2]_2\text{-}(3,5)\}_4}}$. Acetal cleavage with half-concentrated hydrochloric acid afforded the tetra- and octaformyl bis(phosphines) (1*S*,2*S*)-$C_5H_8\{P[C_6H_4CHO\text{-}(2)]_2\}_2$, (*S*,*S*)-$\mathbf{P_2^{[C_6H_4CHO\text{-}(2)]_4}}$, and (1*S*,2*S*)-$C_5H_8\{P[C_6H_3(CHO)_2\text{-}(3,5)]_2\}_2$, (*S*,*S*)-$\mathbf{P_2^{[C_6H_3(CHO)_2\text{-}(3,5)]_4}}$, from which various expanded tetra- and octaaldimine type ligands (*S*,*S*)-$\mathbf{P_2^{[C_6H_4CH=NR\text{-}(2)]_4}}$ and (*S*,*S*)-$\mathbf{P_2^{[C_6H_3(CH=NR)_2\text{-}(3,5)]_4}}$ were prepared by condensation with D-(−)- and L-(+)-valinol, L-(+)-*tert*-leucinol, and, respectively, (*R*)-1-cyclohexylethylamine, as shown in Scheme 5 for the synthesis of the octasubstituted bis(phosphines).

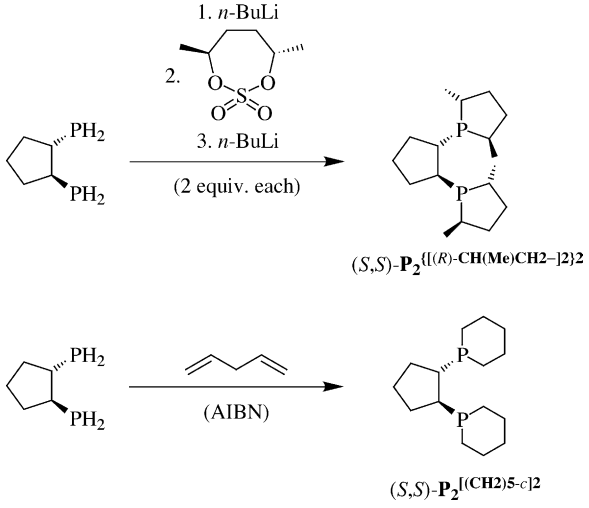
The convergent strategy started from pre-built aryl bromides bearing two (−)-borneol groups attached as benzylic ethers to the 3,5-positions of the aromatic ring. Lithiation and subsequent combination with (*R*,*R*)- or (*S*,*S*)-$\mathbf{P_2^{Cl4}}$ produced either of the two diastereomeric dendritically expanded "octaborneol-bis(phosphine)" ligands (*R*,*R*)- and (*S*,*S*)-$\mathbf{P_2^{\{C_6H_3[CH_2Obornyl\text{-}(1S)]_2\text{-}(3,5)\}_4}}$ depicted in Scheme 6 [22a,b].

Treatment of (*S*,*S*)-$\mathbf{P_2^{[C_6H_3(CHO)_2\text{-}(3,5)]_4}}$ with $NaHSO_3$ gave the sulfite adduct (*S*,*S*)-$\mathbf{P_2^{\{C_6H_3[CH(OH)(SO_3^-Na^+)]_2\text{-}(3,5)\}_4}}$ [22c].

2.3.1.3. Bis(tertiary phosphines) with phospholane and phosphorinane donor groups. The diastereomeric 1,2-bis(phospholano)cyclopentanes (1*R*,2*R*)- and (1*S*,2*S*)-$C_5H_8\{P[(R)\text{-}CH(Me)CH_2\text{–}]_2\}_2$, (*R*,*R*)- and (*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2\text{-}]_2\}_2}}$, resulted from consecutive treatment of the required $\mathbf{P_2^{H4}}$ enantiomer with 2 equiv. of *n*-BuLi, followed by 2 equiv. of (2*S*,5*S*)-2,5-hexanediol cyclic sulfate, and then followed by another 2 equiv. of *n*-butyllithium [28]. The phosphorinane-substituted ligand (1*S*,2*S*)-$C_5H_8[P(CH_2)_5\text{-}c]_2$, (*S*,*S*)-$\mathbf{P_2^{[(CH_2)_5\text{-}c]_2}}$, was obtained by radical-initiated P–H addition of (*S*,*S*)-$\mathbf{P_2^{H4}}$ to 1,4-pentadiene (Scheme 7) [24b].



Scheme 6. Convergent synthesis of a dendritically expanded bis(phosphine) with eight peripheral (1*S*)-borneoxymethyl groups [22a,b].



Scheme 7. Synthesis of optically active cyclopentane-based bis(phospholanes) [28] and bis(phosphorinanes) [24b].

2.3.2. *Bis(phosphonous diamides) $C_5H_8[P(NR_2)_2]_2$*

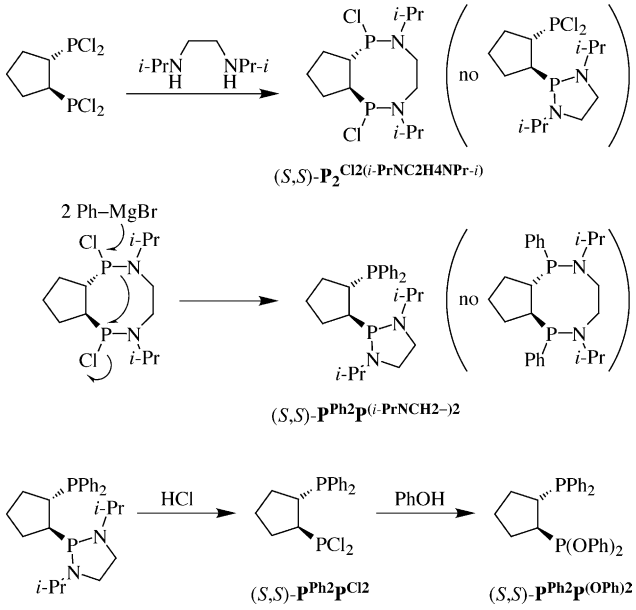
Known compounds include *rac*-$C_5H_8[P(NC_5H_{10}\text{-}c)_2]_2$, *rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$, (1*S*,2*S*)-$C_5H_8[P(NC_5H_{10}\text{-}c)_2]_2$, *rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$, *rac*-$C_5H_8\{P[N(C_2H_4)_2O\text{-}c]_2\}_2$, *rac*-$\mathbf{P_2^{[N(C_2H_4)_2O\text{-}c]_4}}$, and *rac*-$C_5H_8\{P[N(CH_2CHMe)_2O\text{-}c]_2\}_2$, *rac*-$\mathbf{P_2^{[N(CH_2CHMe)_2O\text{-}c]_4}}$, which resulted from condensation reactions of racemic or resolved $\mathbf{P_2^{Cl_4}}$ with piperidine [19b,29], morpholine [20,29], and 2,6-dimethylmorpholine [21a], respectively.

2.3.3. *Bis(phosphonites) $C_5H_8[P(OR)_2]_2$*

In addition to the enantiomeric cyclopentane-1,2-diyl-bis(1′,3′,2′-dioxaphospholanes) (*R*,*R*)-$\mathbf{P_2^{\{[OCH(CO_2Pr\text{-}i)\text{-}(S)\text{—}]_2\}_2}}$ and (*S*,*S*)-$\mathbf{P_2^{\{[OCH(CO_2Pr\text{-}i)\text{-}(R)\text{—}]_2\}_2}}$ used for the resolution of racemic $C_5H_8(PCl_2)_2$ (Section 2.2), the bis(phosphonites) *rac*-$\mathbf{P_2^{(OMe)_4}}$ [29], (*S*,*S*)-$\mathbf{P_2^{(OMe)_4}}$ [19b,20], *rac*-$\mathbf{P_2^{[OBu\text{-}s\text{-}(S)]_4}}$ (1:1 diastereomeric mixture) [29], (*S*,*S*)-$\mathbf{P_2^{[OBu\text{-}s\text{-}(S)]_4}}$ [19b], *rac*-$\mathbf{P_2^{[Omenthyl\text{-}(1'R,2'S,5'R)]_4}}$ (1:1 diastereomeric mixture) [29], *rac*-$\mathbf{P_2^{(OPh)_4}}$ [29], (*R*,*R*)-$\mathbf{P_2^{(OPh)_4}}$ [21b,23b], (*S*,*S*)-$\mathbf{P_2^{(OPh)_4}}$ [19b,20,21b,23b], *rac*-$\mathbf{P_2^{[OC_6H_3(CF_3)_2\text{-}(3,5)]_4}}$, (*S*,*S*)-$\mathbf{P_2^{[OC_6H_3(CF_3)_2\text{-}(3,5)]_4}}$, *rac*-$\mathbf{P_2^{[OC_6H_3F_2\text{-}(2,6)]_4}}$, (*S*,*S*)-$\mathbf{P_2^{[OC_6H_3F_2\text{-}(2,6)]_4}}$, *rac*-$\mathbf{P_2^{[OC_6H_3F_2\text{-}(3,5)]_4}}$, (*S*,*S*)-$\mathbf{P_2^{[OC_6H_3F_2\text{-}(3,5)]_4}}$, *rac*-$\mathbf{P_2^{[OC_6H_2F_3\text{-}(2,4,6)]_4}}$, (*S*,*S*)-$\mathbf{P_2^{[OC_6H_2F_3\text{-}(2,4,6)]_4}}$, (*S*,*S*)-$\mathbf{P_2^{(OC_6F_5)_4}}$ [23b], (*R*,*R*)-$\mathbf{P_2^{[(R)\text{-BINOLATE}]_2}}$, (*R*,*R*)-$\mathbf{P_2^{[(S)\text{-BINOLATE}]_2}}$, (*S*,*S*)-$\mathbf{P_2^{[(S)\text{-BINOLATE}]_2}}$, and (*S*,*S*)-$\mathbf{P_2^{[(R)\text{-BINOLATE}]_2}}$ [25] have been prepared by treating $\mathbf{P_2^{Cl_4}}$, either as a racemate or as an enantiopure stereoisomer, with the pertinent alcohol, phenol, or diol. For the free acid, which exists as the phosphinic tautomer $C_5H_8[PH(O)OH]_2$, $\mathbf{P_2^{[H(O)OH]_2}}$ [22a], see Section 2.2 (Scheme 3).

2.3.4. *C_1-symmetric ligands $C_5H_8(PPh_2)[P(NR_2)_2]$ and $C_5H_8(PPh_2)[P(OR)_2]$*

Dissymmetric P_2 ligands of the general type $Ar_2P(CH_2)_2PAr'_2$ have previously been synthesized either by base-catalyzed P–H/>C=C< addition of a diarylphosphine Ar_2PH to a suitable diarylvinylphosphine $Ar'_2PCH{=}CH_2$ [30–32] or by nucleophilic substitution of $Ph_2P(CH_2)_2PCl_2$ with an appropriate aryllithium or arylmagnesium reagent [33]. An analogous phosphine–phosphonous dichloride with a rigid cyclopentane backbone, $C_5H_8(PPh_2)(PCl_2)$, $\mathbf{P^{Ph_2}P^{Cl_2}}$, was obtained both as a racemic mixture and as resolved (*R*,*R*) and (*S*,*S*) enantiomers by the reaction sequence depicted in Scheme 8 for the (*S*,*S*) stereoisomers.



Scheme 8. Reaction sequence leading from C_2-symmetric (1*S*,2*S*)-$C_5H_8(PCl_2)_2$ to C_1-symmetric cyclopentane-based *P*,*P*′ ligands [23c].

Treatment of $\mathbf{P_2^{Cl_4}}$ with *N*,*N*′-diisopropylethylenediamine afforded the still C_2-symmetric perhydro-1,6,2,5-diazaphosphocine $C_5H_8[P(Cl)N(Pr\text{-}i)C_2H_4N(Pr\text{-}i)P(Cl)]$, $\mathbf{P_2^{Cl_2(i\text{-}PrNC_2H_4NPr\text{-}i)}}$, containing an eight-membered P_2N_2 heterocycle rather than the expected C_1-symmetric phosphonous(dichloride–diamide) $C_5H_8(PCl_2)[PN(Pr\text{-}i)C_2H_4N(Pr\text{-}i)\text{-}c]$. Degradation of the eight-membered perhydro-1,6,2,5-diazaphosphocine ring with formation of the dissymmetric phosphine–phosphonous diamide $C_5H_8(PPh_2)[P(i\text{-}PrNCH_2\text{–})_2]$, $\mathbf{P^{Ph_2}P^{(i\text{-}PrNCH_2\text{—})_2}}$, was brought about by combination of $\mathbf{P_2^{Cl_2(i\text{-}PrNC_2H_4NPr\text{-}i)}}$ with 2 equiv. of phenyl magnesium bromide—probably as a result of nucleophile-induced ring contraction. Cleavage of the P–N bonds of $\mathbf{P^{Ph_2}P^{(i\text{-}PrNCH_2\text{—})_2}}$ with gaseous hydrogen chloride then afforded the phosphine–phosphonous dichloride $\mathbf{P^{Ph_2}P^{Cl_2}}$, which was converted to $C_5H_8(PPh_2)[P(OPh)_2]$, $\mathbf{P^{Ph_2}P^{(OPh)_2}}$, by reaction with phenol [23b,c].

2.4. *Characterizing optical rotations and selected X-ray structural data*

Optical rotations $[\alpha]_\lambda$ measured for the enantiopure ligands are collected in Table 1. X-ray data are available for ligands *rac*-, (*R*,*R*)- and (*S*,*S*)-$\mathbf{P_2^{Ph_4}}$,

Table 1
Optical rotations $[\alpha]_\lambda$ of $C_5H_8(PX_2)_2$ and $C_5H_8(PX_2)(PY_2)$ enantiomers[a,b]

Compound	$[\alpha]_{589}$	$[\alpha]_{578}$	$[\alpha]_{546}$	$[\alpha]_{436}$	$[\alpha]_{365}$	Solvent, temperature	Ref.
C_2-Symmetric bis(phosphines)							
(*S*,*S*)-**P$_2^{(C_6H_{11}\text{-}c)_4}$**	+35	+37	+42	+66	+92	$CHCl_3$, 20 °C	[23a]
(*S*,*S*)-**P$_2^{(CH_2OH)_4}$**	+52	+54	+61	+101	+154	H_2O, 22 °C	[22a]
(*R*,*R*)-**P$_2^{Ph_4}$**	+173, +185	+182, +196	+210, +227	+398, +430	+728, +786	$CHCl_3$, amb., $CHCl_3$, 20 °C	[21b], [23b]
(*S*,*S*)-**P$_2^{Ph_4}$**	−171	−180	−208	−394	−721	$CHCl_3$, amb.	[21b]
(*S*,*S*)-**P$_2^{(C_6F_5)_4}$**	−200	−210	−239	−406		$CHCl_3$, 20 °C	[23b]
(*S*,*S*)-**P$_2^{[C_6H_4CH(OMe)_2\text{-}(2)]_4}$**	−294	−310	−358	−678		CH_2Cl_2, 24 °C	[22a]
(*S*,*S*)-**P$_2^{[C_6H_3\{CH(OMe)_2\}_2\text{-}(3,5)]_4}$**	−60	−63	−73	−149	−298	CH_2Cl_2, 22 °C	[22a]
(*S*,*S*)-**P$_2^{[C_6H_4CHO\text{-}(2)]_4}$**	+83	+102	+198			CH_2Cl_2, 24 °C	[22a]
(*S*,*S*)-**P$_2^{[C_6H_3(CHO)_2\text{-}(3,5)]_4}$**	−170	−176	−200	−305		CH_2Cl_2, 22 °C	[22a]
(*S*,*S*)-**P$_2^{[C_6H_4CH=NR\text{-}(2)]_4}$**							
R = (*R*)-**CH(CH$_2$OH)Pr-*i***	+15	+16	+21	+117		CH_2Cl_2, 22 °C	[22a]
R = (*S*)-**CH(CH$_2$OH)Pr-*i***	−16	−17	−22	−9	−51	CH_2Cl_2, 22 °C	[22a]
(*S*,*S*)-**P$_2^{[C_6H_3(CH=NR)_2\text{-}(3,5)]_4}$**							
R = (*R*)-**CH(CH$_2$OH)Pr-*i***	−156	−165	−192	−357	−697	CH_2Cl_2, 22 °C	[22a]
R = (*S*)-**CH(CH$_2$OH)Pr-*i***	−28	−29	−35	−86	−185	CH_2Cl_2, 22 °C	[22a]
R = (*S*)-**CH(CH$_2$OH)Bu-*t***	−28	−29	−33	−82	−206	CH_2Cl_2, 21 °C	[22a]
R = (*R*)-**CH(Me)C$_6$H$_{11}$-*c***	−180	−189	−222	−443	−953	CH_2Cl_2, 22 °C	[22a]
(*R*,*R*)-**P$_2^{[C_6H_3\{CH_2Obornyl\text{-}(1S)\}_2-3,5]_4}$**	−28	−30	−31			CH_2Cl_2, 22 °C	[22a]
(*S*,*S*)-**P$_2^{[C_6H_3\{CH_2Obornyl\text{-}(1S)\}_2\text{-}3,5]_4}$**	−101	−105	−121			CH_2Cl_2, 22 °C	[22a]
(*S*,*S*)-**P$_2^{[H(O)OH]_2}$**	+52	+54	+61	+101	+154	H_2O, 22 °C	[22a]
(*R*,*R*)-**P$_2^{(OPh)_4}$**	−50	−52	−60	−102	−160	$CHCl_3$, amb.	[21b]
(*S*,*S*)-**P$_2^{(OPh)_4}$**	+50	+52	+59	+101	+160	$CHCl_3$, amb.	[21b]
(*S*,*S*)-**P$_2^{[OC_6H_3(CF_3)_2\text{-}(3,5)]_4}$**	+35	+36	+42	+73	+119	$CHCl_3$, 20 °C	[23b]
(*S*,*S*)-**P$_2^{[OC_6H_3F_2\text{-}(2,6)]_4}$**	+67	+69	+80	+150	+213	$CHCl_3$, 20 °C	[23b]
(*S*,*S*)-**P$_2^{[OC_6H_3F_2\text{-}(3,5)]_4}$**	+48	+50	+57	+97	+149	$CHCl_3$, 20 °C	[23b]
(*S*,*S*)-**P$_2^{[OC_6H_2F_3\text{-}(2,4,6)]_4}$**	+64	+68	+79	+92	+130	$CHCl_3$, 20 °C	[23b]
(*S*,*S*)-**P$_2^{(OC_6F_5)_4}$**	+48	+50	+57	+102	+170	$CHCl_3$, 20 °C	[23b]
(*R*,*R*)-**P$_2^{[(R)\text{-BINOLATE}]_2}$**	−76	−81	−140	−274	−577	Acetone, 20 °C	[25]
(*S*,*S*)-**P$_2^{[(S)\text{-BINOLATE}]_2}$**	+73	+78	+137	+270	+570	Acetone, 20 °C	[25]
(*R*,*R*)-**P$_2^{[(S)\text{-BINOLATE}]_2}$**	−44	−49	−72	−132	−473	Acetone, 20 °C	[25]
(*S*,*S*)-**P$_2^{[(S)\text{-BINOLATE}]_2}$**	+40	+45	+67	+124	+464	Acetone, 20 °C	[25]
(*S*,*S*)-**P$_2^{Cl_4}$**	+104	+109	+124			CH_2Cl_2, 22 °C	[22a]
(*R*,*R*)-**P$_2^{Cl_2(i\text{-}PrNC_2H_4NPr\text{-}i)}$**	+78	+85	+95	+176	+299	$CHCl_3$, 20 °C	[23c]
(*S*,*S*)-**P$_2^{Cl_2(i\text{-}PrNC_2H_4NPr\text{-}i)}$**	−96	−107	−124	−220	−355	$CHCl_3$, 20 °C	[23c]
C_1-symmetric bis(phosphines)							
(*R*,*R*)-**P^{Ph_2}P$^{(i\text{-}PrNCH_2\text{—})_2}$**	+164	+171	+199	+383	+724	$CHCl_3$, 20 °C	[23c]
(*R*,*R*)-**P^{Ph_2}P$^{(i\text{-}PrNCH_2\text{—})_2}$**	−130	−138	−159	−307	−682	$CHCl_3$, 20 °C	[23c]
(*R*,*R*)-**P^{Ph_2}P$^{(OPh)_2}$**	+6	+7	+8	+20	+44	$CHCl_3$, 20 °C	[23c]
(*S*,*S*)-**P^{Ph_2}P$^{(OPh)_2}$**	−9	−10	−12	−26	−57	$CHCl_3$, 20 °C	[23c]
(*R*,*R*)-**P^{Ph_2}P^{Cl_2}**	−16	−17	−19	−31	+45	$CHCl_3$, 20 °C	[23c]
(*S*,*S*)-**P^{Ph_2}P^{Cl_2}**	+15	+17	+18	+30	−45	$CHCl_3$, 20 °C	[23c]

[a] For structures and abbreviations, see Schemes 1–3, 5, 6, and 8.
[b] All $c = 1$.

(*S*,*S*)-**P$_2^{[C_6H_4CH(OMe)_2\text{-}(2)]_4}$**, (*S*,*S*)-**P$_2^{[C_6H_4CHO\text{-}(2)]_4}$**, *rac*-**P$_2^{[C_6H_4NMe_2\text{-}(2)]_4}$**, *rac*-**P$_2^{[C_5H_4N\text{-}(2)]_4}$**, *rac*-**P$_2^{(NC_5H_{10}\text{-}c)_4}$** as well as (*R*,*R*)-**P$_2^{\{[OCH(CO_2Pr\text{-}i)\text{-}(S)\text{—}]_2\}_2}$** and (*S*,*S*)-**P$_2^{\{[OCH(CO_2Pr\text{-}i)\text{-}(R)\text{—}]_2\}_2}$** (Table 2). All structural characterized bis(tertiary phosphines) bearing aromatic or heteroaromatic substituents on phosphorus show torsion angles P–C–C–P ≥ 160° and P···P distances in the range 4.4–4.5 Å, so that at first it appears that these compounds are not suitable disposed to act as chelate ligands. However, in metal complexes of these phosphines the P–C–C–P angles have closed to 40–50° and the P···P distances are only slightly above 3 Å, so that the familiar structural features of five-membered chelate systems are encountered (Section 3.7).

3. Coordination chemistry

3.1. Titanium complexes

Treatment of the binuclear cycloheptatrienyl complex $[\{Ti(\mu\text{-}Cl)(\eta^7\text{-}C_7H_7)(OC_4H_8)\}_2]$ with 1 equiv. of *rac*-**P$_2^{Me_4}$**

Table 2
Selected X-ray structural data for racemic and enantiopure *trans*-1,2-$C_5H_8(PR_2)_2$ bis(phosphines)[a]

Compound[b]	Space group	*d*(P—C) (Å)	P—C—C—P (°)	P···P (Å)	Ref.
rac-$\mathbf{P_2^{Ph_4}}$	*P*-1	1.858(2), 1.867(2)	161.8	4.45	[9b]
rac-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$	?	1.862(2), 1.863(2)	164.3	4.46	[34]
rac-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$	*Pbca*	1.870(6), 1.875(6)	153.9	4.39	[35a]
(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$	$P2_12_12_1$	1.866(4), 1.873(4)	−159.9	4.47	[25]
(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$	$P2_12_12_1$	1.862(4), 1.864(4)	+159.9	4.47	[25]
(*S*,*S*)-$\mathbf{P_2^{[C_6H_4CH(OMe)_2\text{-}(2)]_4}}$ [c]	$P2_1$	1.839, 1.865	+161.4	4.45	[22a]
(*S*,*S*)-$\mathbf{P_2^{[C_6H_4CHO\text{-}(2)]_4}}$	$P2_1$	1.864(2), 1.866(2)	+160.2	4.42	[22a]
(*S*,*S*)-$\mathbf{P_2^{[C_6H_4NMe_2\text{-}(2)]_4}}$ [d]	$P2_12_12_1$	1.879(2), 1.882(2)	+168.2	4.51	[26c]
(*R*,*R*)-$\mathbf{P_2^{[[OCH(CO_2Pr\text{-}i)\text{-}(S)\text{—}]_2]_2}}$	$P2_1$	1.828(3), 1.829(3)	−125.9	4.12	[19a]
(*S*,*S*)-$\mathbf{P_2^{[[OCH(CO_2Pr\text{-}i)\text{-}(R)\text{—}]_2]_2}}$	$P2_1$	1.793(6), 1.821(6)	+125.6	4.13	[18a]

[a] Crystallographic data of previously unpublished structure determinations (ligands *rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$, (*R*,*R*)-$\mathbf{P_2^{Ph_4}}$, and (*S*,*S*)-$\mathbf{P_2^{Ph_4}}$) have been deposited as 'Supplementary material' (Appendix A).
[b] For structures and abbreviations, cf. legend to Table 1.
[c] E.S.D. of P—C distances not available.
[d] Obtained by crystallization and spontaneous resolution of the racemate.

gave [Ti(Cl)(η^7-C_7H_7)(*rac*-$\mathbf{P_2^{Me_4}}$)] (**Ia**), which reacted with excess CH_3MgBr to furnish [Ti(CH_3)(η^7-C_7H_7)(*rac*-$\mathbf{P_2^{Me_4}}$)] (**Ib**). The tetrahydro- and tetradeuterioborato derivatives [Ti(BX_4)(η^7-C_7H_7)(*rac*-$\mathbf{P_2^{Me_4}}$)] (**Ic**) featuring single-bridged Ti—X—BX_3 groups (X = H, D) were similarly obtained from the chloro complex using Na[BH_4] and Na[BD_4], respectively [9c].

3.2. Molybdenum complexes

The highly photosensitive tetracarbonyl [Mo(CO)$_4$(*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$] was obtained by refluxing [Mo(CO)$_6$] with an equimolar quantity of the bis(phosphine) in light petroleum in the dark for several days [9a].

Racemic $\mathbf{P_2^{Ph_4}}$ reacted with $K_2[Mo_2Cl_8]$ in boiling methanol producing [Mo_2Cl_4(μ-*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$] (**IIa**) and with a mixture of [Mo_2(μ-O_2CCF_3)$_4$] and Me_3SiX (X = Br, I) in THF to give [Mo_2X_4(μ-*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$] (**IIb**, **IIc**). THF solvates of the three complexes form isotypic crystals in space group *C*2/*c* with two molecules in the unit cell that have bridging ligands with (*R*,*R*) chirality and Δ conformation of the metallaheterocycles and two others with opposite chirality. The twist angles P—Mo—Mo—P away from the eclipsed conformation are about the same for **IIa**–**IIc**, with an average of 22°. The Mo—P distances increase in the order of X = Cl < Br < I from 2.552(4) to 2.626(6) Å, whereas the lengths of the metal–metal quadruple bond (average value, 2.155 Å) remain essentially unaffected by the nature of the halo ligands. The three observed UV/vis absorption bands were assigned, in the order of increasing energies, to $d_{xy} \rightarrow d^*_{xy}$, (forbidden) $\delta_{xy} \rightarrow \delta_{x^2}$, and $\pi_{yz} \rightarrow \delta^*_{xy}$ transitions and were found to display marked sensitivities to the nature of X, being red-shifted in the order Cl < Br < I [36a].

Treatment of [Mo_2Cl_4(μ-*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$] with hot (*S*)-(−)-2-methyl-1-butanol resulted in partial resolution of the optical isomers by preferential dissolution of the Δ conformer bearing two ligands of (*R*,*R*) configuration [36a].

3.3. Rhenium complexes

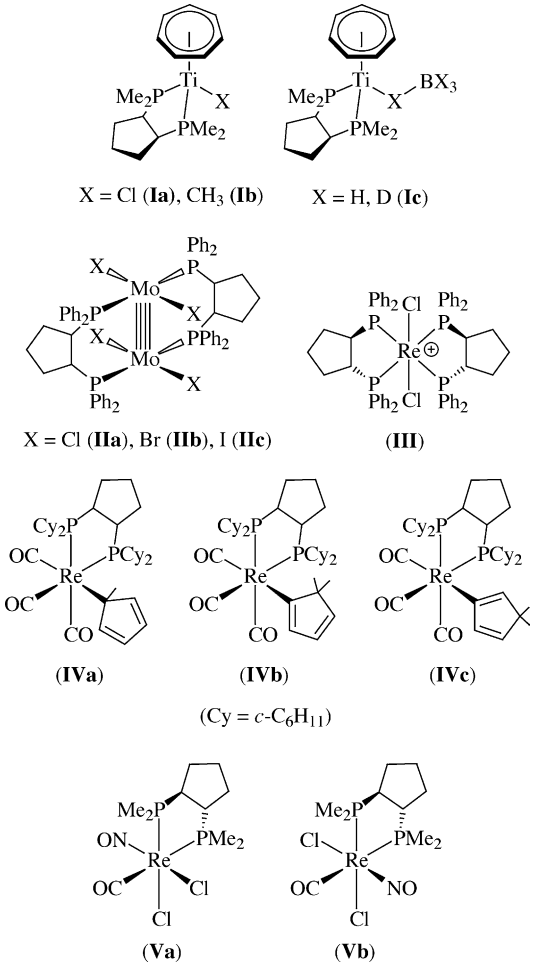
[$ReCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$][Re_2Cl_6(μ-O_2CPh)$_2$] (**III**) arose in low yield from a reaction between the metal–metal quadruple-bonded dirhenium compound [Re_2Cl_2(μ-O_2CPh)$_4$] and *rac*-$\mathbf{P_2^{Ph_4}}$ in the presence of Me_3SiCl, which was intended to give [Re_2Cl_6(μ-*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$]. In crystals of the chloroform solvate [$ReCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$][Re_2(O_2CPh)$_2Cl_6$]·$CHCl_3$, both the cation and the anion reside on a center of inversion, meaning that there is one (*S*,*S*)-$\mathbf{P_2^{Ph_4}}$ and one (*R*,*R*)-$\mathbf{P_2^{Ph_4}}$ ligand bound to the central metal of cationic complex **III**, as shown in Scheme 9 [36b].

Treatment of [Re(Br)(CO)$_5$] with *rac*-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$ in THF yielded *fac*-[Re(Br)(CO)$_3${*rac*-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}], which in turn afforded *fac*-[Re(OSO_2CF_3)(CO)$_3${*rac*-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}] if combined with AgO_3SCF_3 in CH_2Cl_2. Reaction of the triflate complex with sodium cyclopentadienide in THF produced *fac*-[Re(η^1-C_5H_5)(CO)$_3${*rac*-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}] as a mixture of three isomers with the rhenium atom in the allylic position of a fluxional sp^3-bonded ring (**IVa**) or in the two vinylic sites of an sp^2-bonded rigid C_5H_5 system, where the CH_2 group is either α (**IVb**) or β (**IVc**) to the metallated carbon atom [37].

The reaction of [$ReCl_2$(CO)$_2$(NO)(OC_4H_8)] with *rac*-$\mathbf{P_2^{Me_4}}$ proceeded with loss of the THF molecule and of one CO ligand to afford [$ReCl_2$(CO)(NO)(*rac*-$\mathbf{P_2^{Me_4}}$)] as a mixture of two diastereomeric pairs of enantiomers **Va** and **Vb**, illustrating only the (*S*,*S*) isomers [38].

3.4. Iron and ruthenium complexes

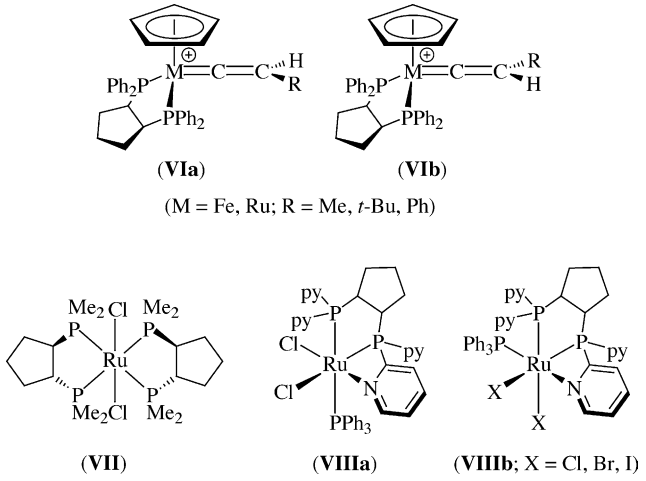
Irradiation of an equimolar mixture of [Fe(Br)(η^5-C_5H_5)(CO)$_2$] and *rac*-$\mathbf{P_2^{Ph_4}}$ in refluxing benzene gave [Fe(Br)(η^5-C_5H_5)(*rac*-$\mathbf{P_2^{Ph_4}}$)]. The ruthenium analogue [Ru(Cl)(η^5-C_5H_5)(*rac*-$\mathbf{P_2^{Ph_4}}$)] was prepared by treating [Ru(Cl)(η^5-C_5H_5)(PPh_3)$_2$] with a slight excess of the



Scheme 9. Titanium [9c], molybdenum [36a], and rhenium [36b,37,38] complexes **I–V**.

bis(phosphine) in boiling toluene [39b]. The alkylidenecarbene complexes $[M(\eta^5\text{-}C_5H_5)(=C=CHR)(rac\text{-}\mathbf{P_2^{Ph_4}})]PF_6$ (M = Fe, Ru; R = Me, *t*-Bu, Ph) were prepared through reactions of the two halo precursors with the required acetylene HC≡CR in methanol in the presence of KPF_6 or NH_4PF_6 as halide scavengers. In the preferred geometry of these compounds the plane of the =CHR moiety is perpendicular to the plane containing the C_5H_5 centroid, the metal atom, and the carbene carbon atom. The resulting two rotameric conformations of the alkylidenecarbene ligands give rise to two diastereomeric species, **VIa** and **VIb**, of which only one was recognizable in the low-temperature ^{31}P NMR spectra [39a–c].

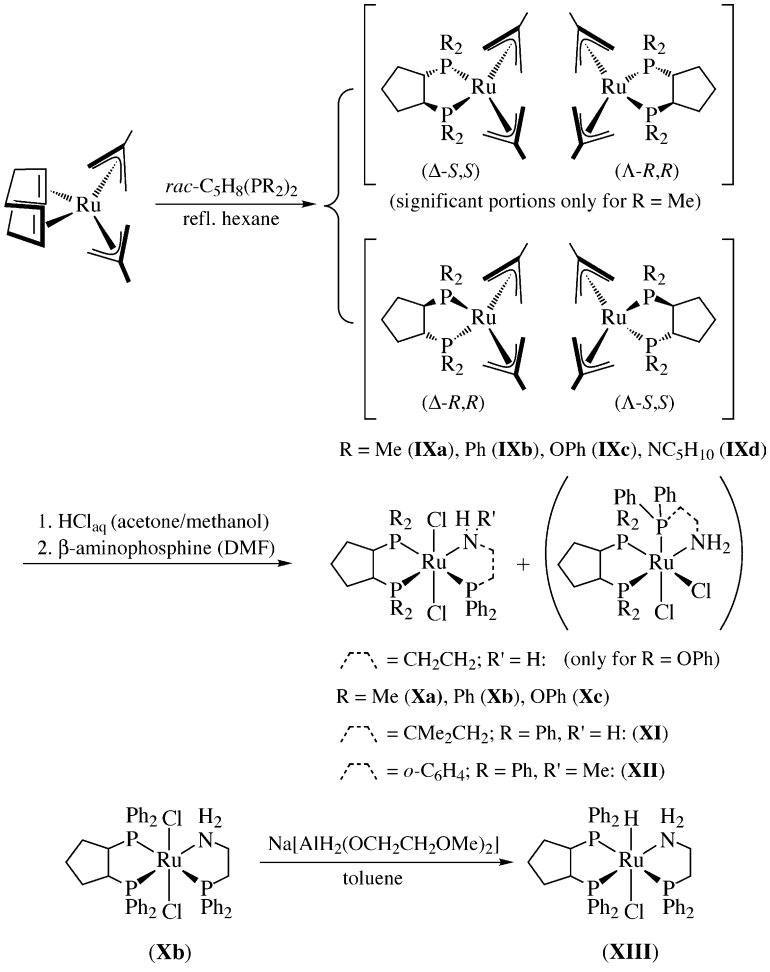
The indenyl and pentamethylcyclopentadienyl complexes $[Ru(Cl)(\eta^5\text{-}C_9H_7)\{(R,R)\text{-}\mathbf{P_2^{Ph_4}}\}]$ [39d] and $[Ru(Cl)(\eta^5\text{-}C_5Me_5)(rac\text{-}\mathbf{P_2^{Ph_4}})]$ [39e] were prepared from $[Ru(Cl)(\eta^5\text{-}C_9H_7)(\eta^4\text{-}C_8H_{12})]$ or $[Ru(Cl)(\eta^5\text{-}C_5Me_5)(PPh_3)_2]$ and the enantiopure or racemic P_2 ligand in toluene at reflux temperature. Subsequent reaction with 2e donors gave $[Ru(\eta^5\text{-}C_9H_7)\{(R,R)\text{-}\mathbf{P_2^{Ph_4}}\}L]Cl$ (L = CO, PMe_2Ph) [39d] and $[Ru(\eta^5\text{-}C_5Me_5)(rac\text{-}\mathbf{P_2^{Ph_4}})(NCMe)]PF_6$ [39e], respectively.



Scheme 10. Iron and ruthenium complexes **VI** [39a–c], **VII** [35b], and **VIII** [26b].

Reactions of the racemic ligands $\mathbf{P_2^{Me_4}}$ and $\mathbf{P_2^{Ph_4}}$ with $[RuCl_2(PPh_3)_3]$ in 1:1 stoichiometry resulted in the formation of *trans*-$[RuCl_2(rac\text{-}\mathbf{P_2^{Me_4}})_2]$ [35a,b] and *trans*-$[RuCl_2(rac\text{-}\mathbf{P_2^{Ph_4}})_2]$ [26b] rather than five-coordinate complexes $[RuCl_2(rac\text{-}\mathbf{P_2^{R_4}})(PPh_3)]$, which are preferred for mechanistic studies related to catalysis and have been described for, e.g., $Ph_2P(CH_2)_4PPh_2$, BINAP, DIOP, and 1,2-$C_6H_{10}(NHPPh_2)_2$ as bidentate ligands [40–42]. The lack of success in selectively replacing two of the three PPh_3 ligands of $[RuCl_2(PPh_3)_3]$ by the two cyclopentane-based bis(phosphines) is in accord with earlier findings that substitution by the shorter backbone bis(phosphines) $Ph_2P(CH_2)_nPPh_2$ (n = 1–3) yields only products of the type $[RuCl_2(P\cap P)_2]$ [40], while P_2 ligands that form seven-membered chelate rings such as $Ph_2P(CH_2)_4PPh_2$, BINAP, DIOP, and 1,2-$C_6H_{10}(NHPPh_2)_2$ give rise to $[RuCl_2(P\cap P)(PPh_3)]$ [41,42]. The failure to obtain coordinatively unsaturated complexes with five- and six-membered chelates has been attributed to the decrease of the chelate bite angle, which results in sterically less congested coordination spheres, accessible to further substitution with formation of the observed 18e products $[RuCl_2(P\cap P)_2]$ [40]. In a more straightforward fashion, the six-coordinate complexes *trans*-$[RuCl_2(rac\text{-}\mathbf{P_2^{R_4}})_2]$ (R = Me, Ph) were prepared by refluxing $RuCl_3\cdot xH_2O$ with 2 equiv. of the corresponding bis(phosphine) in ethanol, which gave the products as mixtures of the {(*R*,*R*/*R*,*R*)/(*S*,*S*/*S*,*S*)} racemates and the (*R*,*R*/*S*,*S*) *meso* forms, as expected [26b,35]. Single crystals of *trans*-$[RuCl_2(rac\text{-}\mathbf{P_2^{Me_4}})_2]$ contained the (*R*,*R*/*S*,*S*) stereoisomeric molecule **VII** located on a center of symmetry [35b].

The mixed-phosphine complex *trans*-$[RuCl_2(rac\text{-}\mathbf{P_2^{Ph_4}})\{Ph_2P(CH_2)_4PPh_2\}]$ was isolated from a 1:1 reaction between five-coordinate $[RuCl_2\{Ph_2P(CH_2)_4PPh_2\}(PPh_3)]$ (vide supra) and the P_2 ligand in benzene [26b]. In the reaction of $[RuCl_2(PPh_3)_3]$ with an equimolar quantity of the 2-pyridyl-substituted two-carbon backbone chelate ligand *rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$, the availability of the pyridyl nitrogen

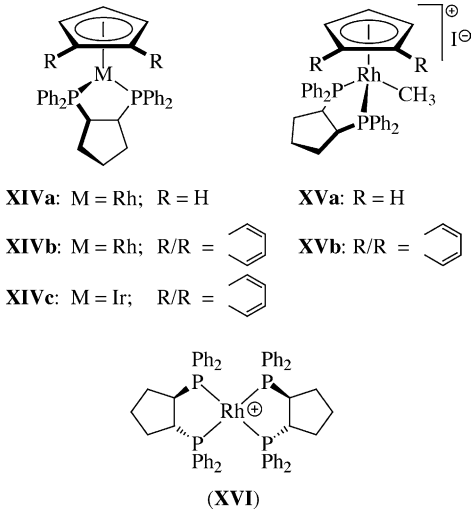


Scheme 11. Synthesis of ruthenium complexes **IX**–**XIII** [35].

atoms allowed for the coordination of only one *P*,*P*,*N*-bound chelate ligand with formation of hexacoordinate [$RuCl_2$(*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$-*P*,*P*,*N*)($PPh_3$)]·$H_2O$, which was obtained as a mixture of stereoisomers **VIIIa** and **VIIIb**. Treatment of the H_2O solvate of **VIIIb** with excess NaBr or NaI in acetone yielded [$RuBr_2$(*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$-*P*,*P*,*N*)($PPh_3$)]·$H_2O$ and [RuI_2(*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$-*P*,*P*,*N*)($PPh_3$)]·$H_2O$ with stereochemistry **VIIIb** [26b] (Scheme 10).

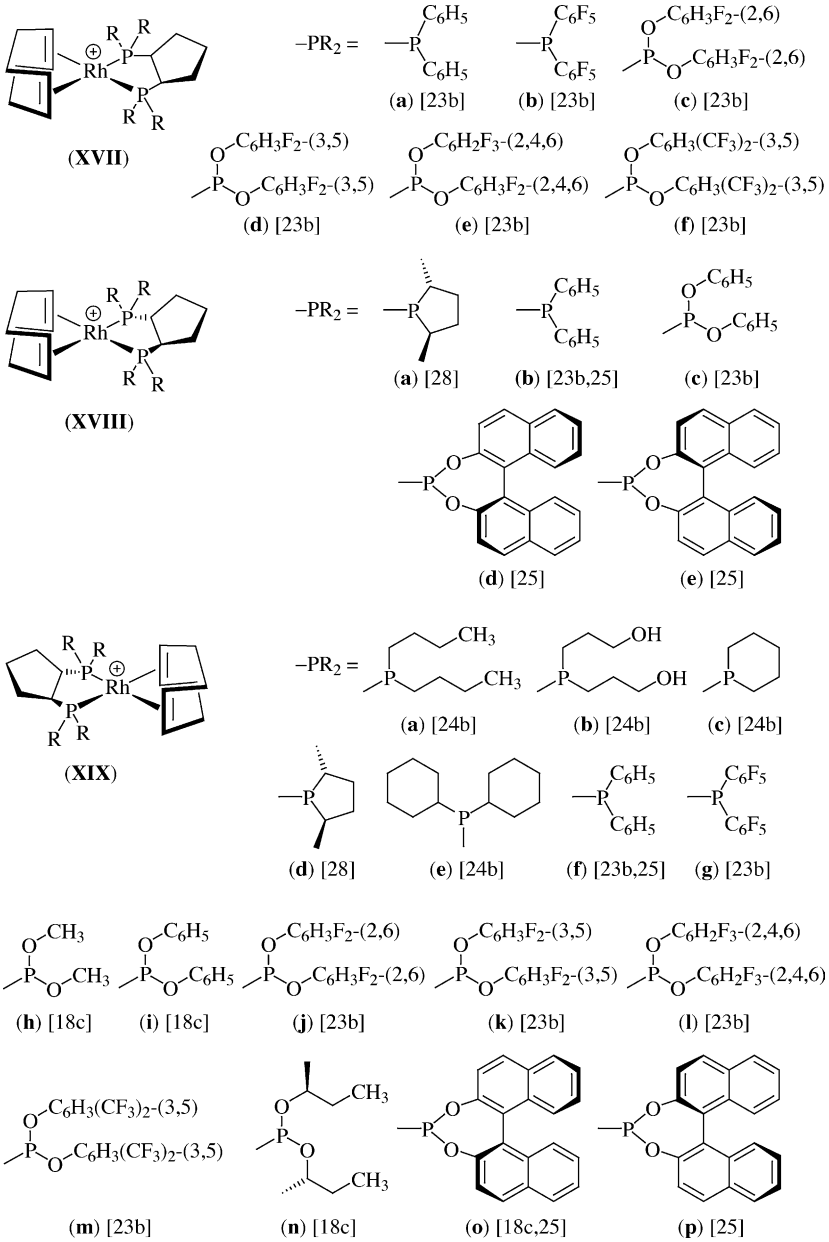
Trichloro-bridged mixed-valence complexes of the type [Ru_2Cl_2(μ-Cl)$_3$(*rac*-$\mathbf{P_2^{R_4}}$)$_2$] (R = *c*-C_6H_{11}, Ph) were synthesized by refluxing a hexane suspension of [$RuCl_2${P[C_6H_4Me-(4)]$_3$}$_3$] with an equimolar amount of the appropriate racemic bis(phosphine) [41a].

Bis(2-methylallyl)-substituted chelate complexes of the type [Ru{η^3-$(CH_2)_2$CMe}$_2$(*rac*-$\mathbf{P_2^{R_4}}$)] with R = Me (**IXa**), Ph (**IXb**), OPh (**IXc**), and NC_5H_{10}-*c* (**IXd**), respectively, were synthesized by the addition of 1 equiv. of the required P_2 chelate ligand to [Ru{η^3-$(CH_2)_2$CMe}$_2$(η^4-C_8H_{12})] in hexane at reflux temperature. Subsequently, bis(phosphine)/aminophosphine-coordinated complexes such as [$RuCl_2$(*rac*-$\mathbf{P_2^{R_4}}$){$Ph_2P(CH_2)_2NH_2$}], where R = Me (**Xa**), Ph (**Xb**), or OPh (**Xc**), [$RuCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$){$Ph_2PCH_2CMe_2NH_2$}] (**XI**), and [$RuCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)(*o*-



Scheme 12. Rhodium and iridium complexes **XIV** [43a,c,e], **XV** [43b,c], and **XVI** [36c].

$Ph_2PC_6H_4NHMe$)] (**XII**) were prepared by combining the bis(2-methylallyl) precursors first with 2 equiv. of aqueous HCl in methanol and then with equimolar amounts of the appropriate β-aminophosphine in DMF (Scheme 11) [35]. Because of the racemic nature of the different cyclopentane-based *P*,*P* ligands the diallyl bis(phosphine) complexes **IX** can exist as diastereomeric (*Λ*-*R*,*R*)/(*Δ*-*S*,*S*) and (*Δ*-*R*,*R*)/(*Λ*-*S*,*S*) pairs of enantiomers. For the Me_2P-substituted derivative **IXa**, the presence in solution of the two diastereomeric forms was indeed evident from their ^{31}P NMR spectra. In contrast, complexes **IXb**–**IXd** having sterically more demanding residues in their $–PR_2$ donor groups were shown by NMR spectroscopy to be formed with diastereoselectivities exceeding 98%. For complexes **IXb** and **IXd** the predominating stereoisomers could be assigned as (*Δ*-*R*,*R*)/(*Λ*-*S*,*S*) by X-ray structure analysis [35b]. While the reaction sequence outlined by Scheme 11 afforded the bis(phosphine)/aminophosphine complexes **Xa**, **Xb**, **XI**, and **XII** as pure *mer*-P_3 stereoisomers with *trans*-coordinated chloro ligands, the phenoxy-substituted derivative **Xc** was produced as an isomeric mixture containing the *fac*- and *mer*-P_3 forms in close to 3:2 molar ratio [35a,b]. The chloro hydrido complex [Ru(H)(Cl)(*rac*-$\mathbf{P_2^{Ph_4}}$){$Ph_2P(CH_2)_2NH_2$}] with stereochemistry **XIII** resulted from treatment of the dichloro precursor **Xb** with Na[AlH_2{$O(CH_2)_2OMe$}$_2$] in toluene [35c].



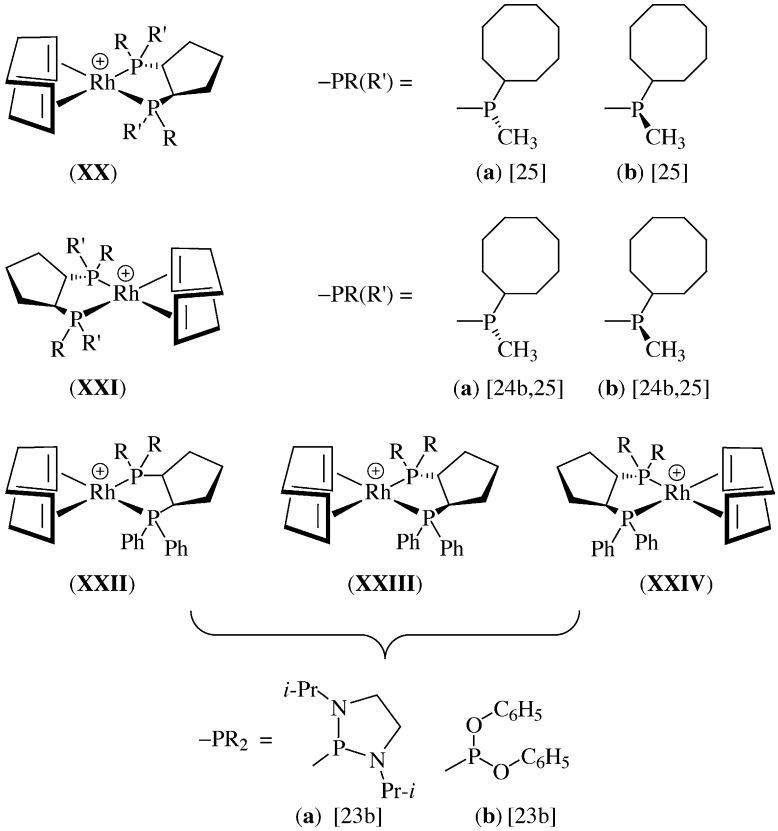
Scheme 13. Racemic and enantiopure rhodium complexes [Rh(η^4-C_8H_{12})(*rac*-$\mathbf{P_2^{R_4}}$)]$^+$ (**XVII**), [Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{R_4}}$}]$^+$ (**XVIII**), and [Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{R_4}}$}]$^+$ (**XIX**).

3.5. Rhodium and iridium complexes

The cyclopentadienyl complex [Rh(η^5-C_5H_5)(*rac*-$\mathbf{P_2^{Ph_4}}$)] (**XIVa**) was prepared by reacting [Rh(η^5-C_5H_5)(η^2-C_2H_4)$_2$] with an equimolar amount of the bis(phosphine) in toluene at reflux [43c]. The homologous indenyl derivatives [M(η^5-C_9H_7)(*rac*-$\mathbf{P_2^{Ph_4}}$)], where M = Rh (**XIVb**) [43a,c] or Ir (**XIVc**) [43e], resulted from treatment of the corresponding bis(ethylene) precursors [M(η^5-C_9H_7)(η^2-C_2H_4)$_2$] with the bidentate ligand in toluene at room temperature. The observed rate enhancement of the ligand exchange reaction was attributed to a facile ring slippage of the indenyl ligand from η^5- to η^3-coordination in the associative transition state [43a,c]. The indenyl complexes displayed a fluxional behavior in solution which was ascribed to either a rotation of the indenyl ligand or a displacement of the MP_2 moieties from the center of the five-membered ring towards a rapidly inverting η^3-coordinated pyramidal intermediate [43a,e]. Both **XIVa** and **XIVb** underwent rapid irreversible oxidative addition of methyl iodide giving [Rh(CH_3)(η^5-C_5H_5)(*rac*-$\mathbf{P_2^{Ph_4}}$)]I (**XVa**) [43c] and [Rh(CH_3)(η^5-C_9H_7)(*rac*-$\mathbf{P_2^{Ph_4}}$)]I (**XVb**), respectively [43b,c] (Scheme 12).

Reactions between [Ir(η^5-C_9H_7)(η^2-C_8H_{14})$_2$] or [Ir(η^5-C_9H_7)(η^4-C_8H_{12})] and *rac*-$\mathbf{P_2^{Ph_4}}$ or (*R*,*R*)-$\mathbf{P_2^{Ph_4}}$ led to complex reaction mixtures in which the cationic complexes [Ir(*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$]$^+$ and [Ir{(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}$_2$]$^+$ were identified as the major components. As chloride salts these compounds were obtained by treating [{Ir(μ-Cl)(η^2-C_2H_4)$_2$}$_2$] with the enantiopure or racemic P_2 ligand in toluene or dichloromethane at ambient temperature. No diastereoselectivity for the [Ir{(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}$_2$]$^+$/[Ir{(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$}$_2$]$^+$ racemate or the [Ir{(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}{(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$}]$^+$ *meso* form was observed in the reaction of *rac*-$\mathbf{P_2^{Ph_4}}$ with the chloro-bridged dimer [43d]. The analogous rhodium complex [Rh(*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$]BF_4 was prepared by combining [Rh$_2$(μ-O_2CMe)$_2$($NCMe$)$_6$][BF_4]$_2$ with an excess of the racemic bis(phosphine) in hot methanol. Crystallization of the product from CH_2Cl_2/hexane gave the compound as the solvate [Rh(*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$]BF_4·CH_2Cl_2 containing the *meso* isomeric cation **XVI** [36c]. The closely related optically pure complex salt [Rh{(*S*,*S*)-$\mathbf{P_2^{(OPh)_4}}$}$_2$]O_3SCF_3 resulted from the 1:2 reaction of [Rh(η^4-C_8H_{12})$_2$]O_3SCF_3 with the enantiopure ligand in acetone [18c].

1:1 reactions in THF, ethanol, or acetone between the bis(cyclooctadiene) precursors [Rh(η^4-C_8H_{12})$_2$]X (X = BF_4, O_3SCF_3) and the C_2- or C_1-symmetric bis(phosphines) $C_5H_8(PR_2)_2$, $C_5H_8[PR(R')]_2$, and $C_5H_8(PR_2)(PR'_2)$ led to a great variety of both racemic and enantiopure complexes containing cations of the types [Rh(η^4-C_8H_{12})(*rac*-$\mathbf{P_2^{R_4}}$)]$^+$ (**XVIIa–XVIIf**) [23b], [Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{R_4}}$}]$^+$ (**XVIIIa–XVIIIe**) [23b,25,28], [Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{R_4}}$}]$^+$ (**XIXa–XIXp**) [18c,23b,24b,25,28], [Rh(η^4-

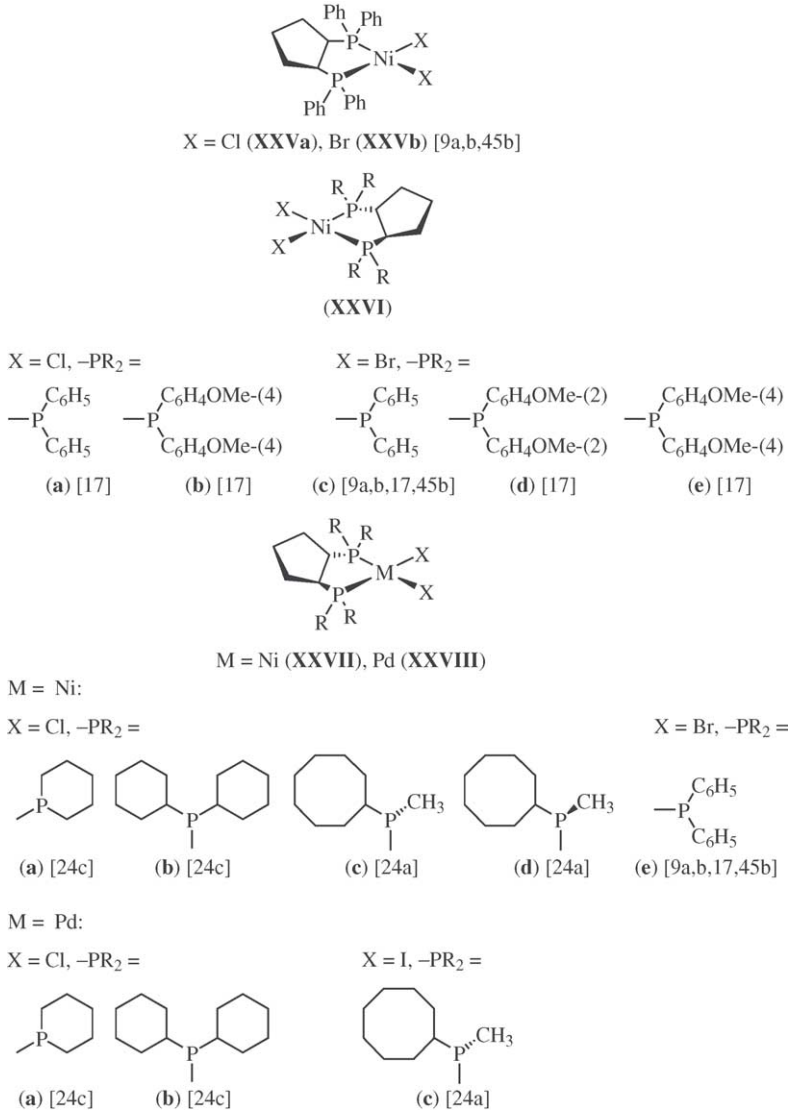


Scheme 14. Enantiopure rhodium complexes [Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{[R(R')]_2}}$}]$^+$ (**XX**) and [Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{[R(R')]_2}}$}]$^+$ (**XXI**) and C_1-symmetric rhodium complexes [Rh(η^4-C_8H_{12})(*rac*-$\mathbf{P^{Ph_2}P^{R_2}}$)]$^+$, [Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P^{Ph_2}P^{R_2}}$}]$^+$, and [Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P^{Ph_2}P^{R_2}}$}]$^+$ (**XXII–XXIV**).

C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{[R(R')]_2}}$}]$^+$ (**XXa**, **XXb**) [25], [Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{[R(R')]_2}}$}]$^+$ (**XXIa**, **XXIb**) [24b,25], [Rh(η^4-C_8H_{12})(*rac*-$\mathbf{P^{Ph_2}P^{R_2}}$)]$^+$ (**XXIIa**, **XXIIb**), [Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P^{Ph_2}P^{R_2}}$}]$^+$ (**XXIIIa**, **XXXIIIb**), and [Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P^{Ph_2}P^{R_2}}$}]$^+$ (**XXIVa**, **XXIVb**) [23b]; see Schemes 13 and 14 (see also Section 2.3.1.1; Scheme 4). Many of these compounds have been used as homogeneous catalysts, especially for >C=C< hydrogenation [18c,24b,25,28,44] and hydroformylation [23b]; see Sections 4.3 and 4.4.

3.6. Nickel, palladium, and platinum complexes

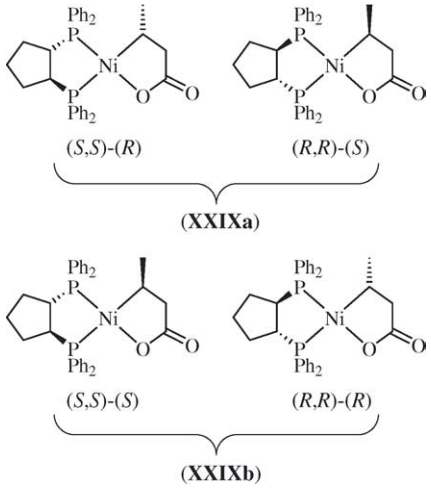
The dihalogeno nickel(II) complexes [NiX_2(*rac*-$\mathbf{P_2^{Ph_4}}$)], where X = Cl (**XXVa**) or Br (**XXVb**) were made by treating $NiCl_2{\cdot}6H_2O$, $NiBr_2{\cdot}3H_2O$, or anhydrous nickel(II) bromide with the pertinent racemic ligand in ethanol, ethanol/water, or ethanol/CH_2Cl_2 [9a,b,45b]. While the CH_2Cl_2 solvates of the optically active compounds (−)-[$NiBr_2${(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}] (**XXVIc**) and (+)-[$NiBr_2${(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$}] (**XXVIIe**) can be isolated by manual separation of the conglomerate of crystals formed by spontaneous resolution upon crystallization of the racemic mixture from dichloromethane [9a,b,45b] (Section 2.2), a more practicable method for obtaining larger amounts of such complexes makes use of stoichiometric reactions between nickel(II) halides and the corresponding enantiopure ligands. Complexes synthesized in this way include – in addition to **XXVIc** and **XXVIIe** [17] – the dichloro and dibromo derivatives (−)-[$NiCl_2${(*R*,*R*)-$\mathbf{P_2^{R_4}}$}], where R = C_6H_5 (**XXVIa**) or C_6H_4OMe-(4) (**XXVIb**), (−)-[$NiBr_2${(*R*,*R*)-$\mathbf{P_2^{R_4}}$}] with R = C_6H_4OMe-(2) (**XXVId**) or C_6H_4OMe-(4) (**XXVIe**) [17], as well as the phosphorinane- and dicyclohexylphosphino-substituted



Scheme 15. Racemic and enantiopure nickel and palladium complexes [NiX_2(*rac*-$\mathbf{P_2^{R_4}}$)] (**XXV**), [NiX_2{(*R*,*R*)-$\mathbf{P_2^{R_4}}$}] (**XXVI**), [NiX_2{(*S*,*S*)-$\mathbf{P_2^{R_4}}$}] (**XXVII**), and [PdX_2{(*S*,*S*)-$\mathbf{P_2^{R_4}}$}] (**XXVIII**).

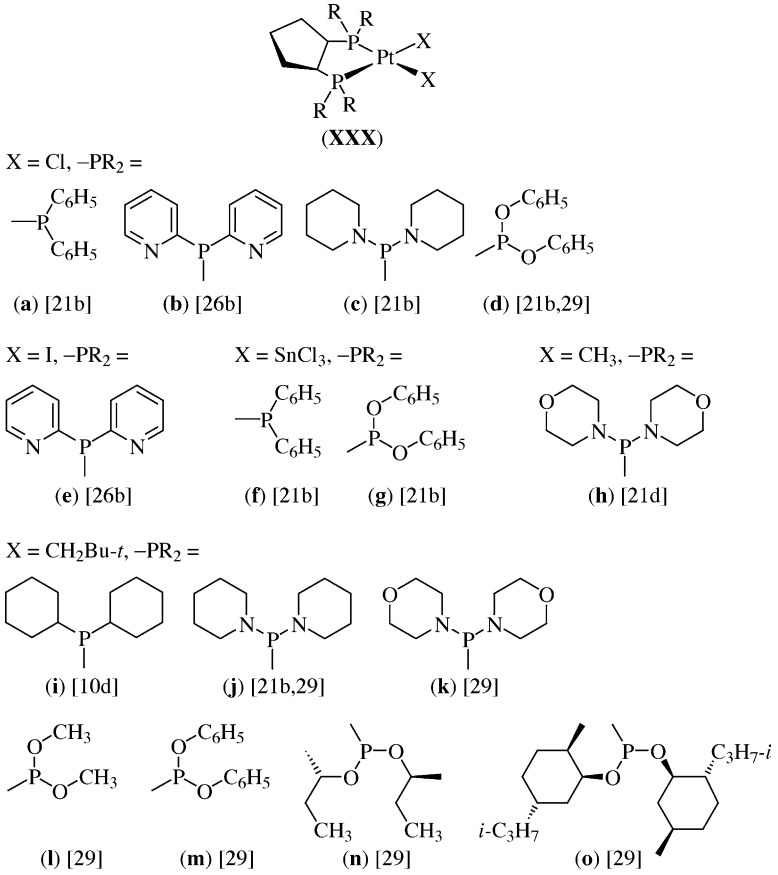
compounds [$NiCl_2${(*S*,*S*)-$\mathbf{P_2^{[(CH_2)_5\text{-}c]_2}}$}] (**XXVIIa**) and [$NiCl_2${(*S*,*S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}] (**XXVIIb**) [24c]. The diastereomers [$NiCl_2${(*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}] (**XXVIIc**) and [$NiCl_2${(*S*,*S*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}] (**XXVIId**) were found to co-crystallize from the mother liquors of the reaction between $NiCl_2{\cdot}6H_2O$ and an (1*S*,2*S*)-R_P,$R_{P'}$-, (1*S*,2*S*)-S_P,$S_{P'}$-, (1*S*,2*S*)-R_P,$S_{P'}$-isomeric mixture of the methyl(cyclohexyl)-substituted *C*,*P*-chirogenic bis(phosphine) (Scheme 15) [24a]; [Ni(*rac*-$\mathbf{P_2^{Me_4}}$)$_2$]Br_2 was briefly described as resulting from treatment of $NiBr_2$ with the permethylated P_2 ligand in ethanol [9a].

Addition of racemic $\mathbf{P_2^{Ph_4}}$ to the five-membered nickelacyclic complex [Ni{CH(Me)CH_2C(O)O}(bipy)] resulted in substitution of the bipyridyl ligands with formation of [Ni{CH(Me)CH_2C(O)O}(*rac*-$\mathbf{P_2^{Ph_4}}$)] (**XXIX**) as a mixture of two diastereomeric pairs of enantiomers, **XXIXa** and **XXIXb** (Scheme 16). The initially formed reaction mixture contained the thermodynamically less stable species **XXIXa** as the predominant stereoisomers, which underwent isomerization to their more stable forms **XXIXb** obeying first-order kinetics (d.e. after equilibration in methanol: 46%) [46].

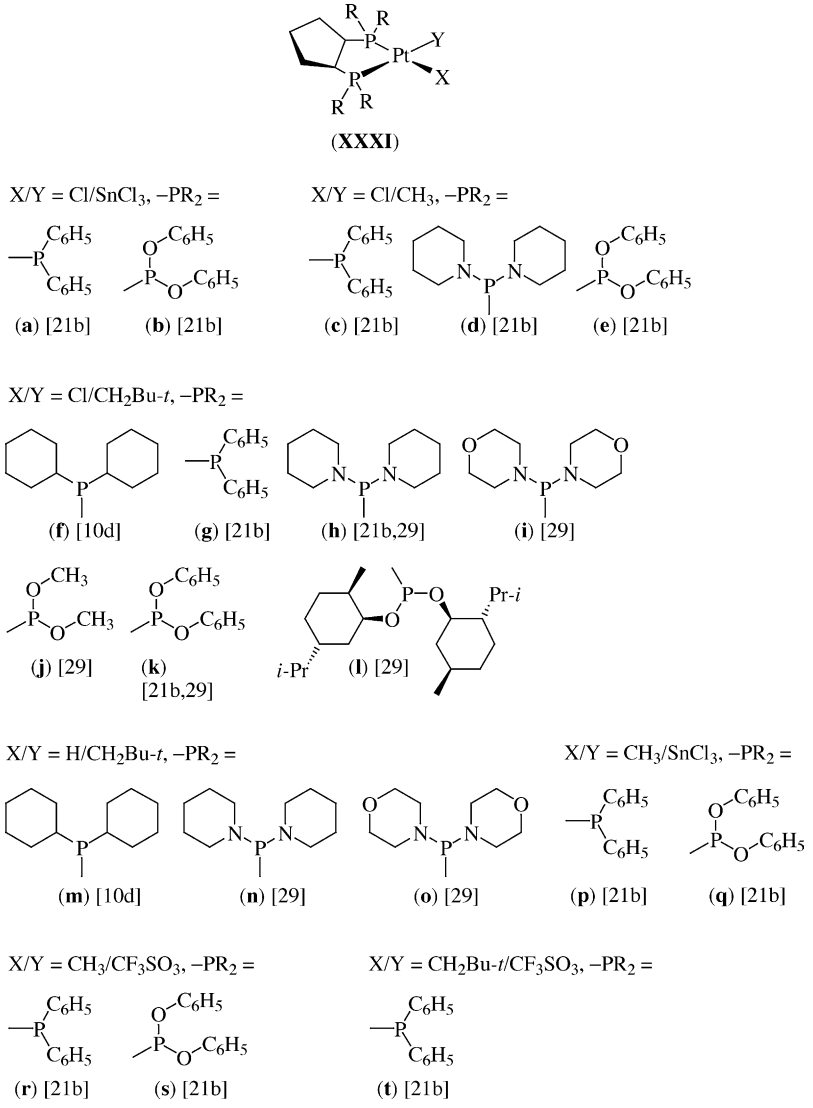


Scheme 16. Diastereomeric pairs of nickelacyclic enantiomers **XXIXa** (top) and **XXIXb** (bottom) [46].

Palladium complexes that have been described in the literature include [$PdCl_2${(*S*,*S*)-$\mathbf{P_2^{[(CH_2)_5\text{-}c]_2}}$}] (**XXVIIIa**), [$PdCl_2${(*S*,*S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}] (**XXVIIIb**), and [$PdI_2${(*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}] (**XXVIIIc**), made by combining [$PdX_2(\eta^4\text{-}C_8H_{12})$] (X = Cl, I) with the pertinent bis(phosphine) in dichloromethane (Scheme 15) [24a,c]. The 1,3-diphenylallyl compound [Pd(η^3-PhCHCHCHPh){(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}]PF_6 was prepared from [{Pd(η^3-PhCHCHCHPh)(μ-Cl)}$_2$] and the optically active bis(phosphine) in acetone containing added $TlPF_6$ [47].



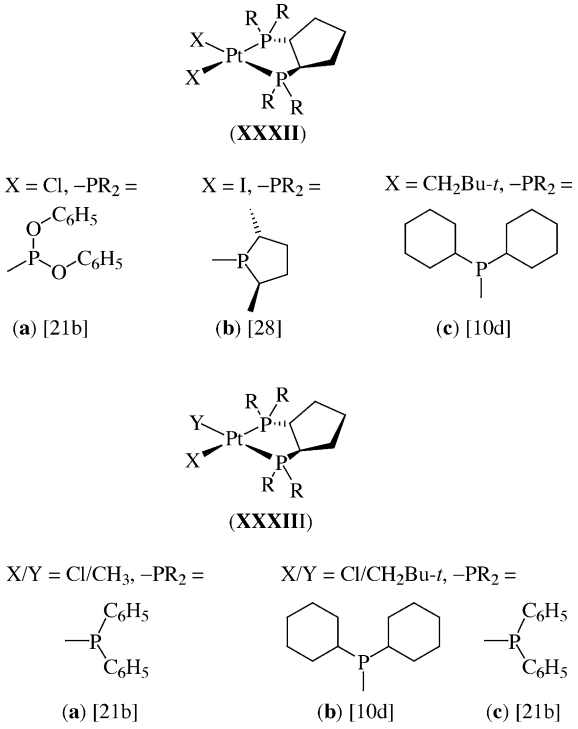
Scheme 17. Racemic platinum complexes [$PtX_2(\mathbf{P_2^{R_4}})$] (**XXX**).



Scheme 18. Racemic platinum complexes [Pt(X)(Y)($\mathbf{P_2^{R_4}}$)] (**XXXI**).

The majority of platinum complexes bearing $C_5H_8(PR_2)_2$ ligands in racemic or optically active form belong to the types [PtX_2($\mathbf{P_2^{R_4}}$)] and [Pt(X)(Y)($\mathbf{P_2^{R_4}}$)], where X, Y = halide, hydride, triflate, trichlorostannyl, and alkyl, respectively (Schemes 17–20).

Ligand exchange reactions between substitutionally labile cyclooctadiene precursors [PtX_2(η^4-C_8H_{12})] or [Pt(X)(Y)(η^4-C_8H_{12})] (X, Y = Cl, I, CH_3, CH_2But-*t*) and racemic or enantiopure $\mathbf{P_2^{R_4}}$ bis(phosphines) have been used to prepare the dihalo derivatives [PtX_2(*rac*-$\mathbf{P_2^{R_4}}$)] (**XXXa**–**XXXe**) [21b,26b,29], (+)-[$PtCl_2$\{(*R*,*R*)-$\mathbf{P_2^{(OPh)_4}}$\}] (**XXXIIa**), (−)-[$PtCl_2$\{(*S*,*S*)-$\mathbf{P_2^{(OPh)_4}}$\}] (**XXXIVc**) [21b], [PtI_2\{(*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$\}] (**XXXIIb**), [$PtI_2$\{(*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$\}] (**XXXIVd**) [28], and [PtI_2\{(*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$\}] (**XXXIVe**) [24a]; furthermore, the dialkyls [$Pt(CH_3)_2$\{*rac*-$\mathbf{P_2^{[N(C_2H_4)_2O\text{-}c]_4}}$\}] (**XXXh**) [21d], [$Pt(CH_2$Bu-*t*$)_2$(*rac*-$\mathbf{P_2^{R_4}}$)], **XXXi**–**XXXo** [10d,21b,29], (+)-[$Pt(CH_2$Bu-*t*$)_2$\{(*R*,*R*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$\}] (**XXXIIc**), (−)-[$Pt(CH_2$Bu-*t*$)_2$\{(*S*,*S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$\}] (**XXXIVf**) [10d], (−)-[$Pt(CH_2$Bu-*t*$)_2$\{(*S*,*S*)-$\mathbf{P_2^{[OCH(CO_2Pr\text{-}i)\text{-}(R)-]_2\}_2}}$\}] (**XXXIVg**), and [$Pt(CH_2$Bu-*t*$)_2$\{(*S*,*S*)-$\mathbf{P_2^{[Omenthyl\text{-}(1'R,2'S,5'R)]_4}}$\}] (**XXXIVh**) [29], as well as the mixed-anion compounds [Pt(Cl)(CH_3)(*rac*-$\mathbf{P_2^{R_4}}$)] (**XXXIc**–**XXXIe**) [21b], [Pt(Cl)(CH_2Bu-*t*)(*rac*-$\mathbf{P_2^{R_4}}$)], **XXXIg**–**XXXIi** [21b,29], [Pt(Cl)(CH_2Bu-*t*)\{*rac*-$\mathbf{P_2^{(OPh)_4}}$\}] (**XXXIk**) [21b,29], (−)-[Pt(Cl)(CH_3)\{(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$\}] (**XXXIIIa**), (+)-[Pt(Cl)-(CH_3)\{(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$\}] (**XXXVa**), (−)-[Pt(Cl)(CH_2Bu-*t*)\{(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$\}] (**XXXIIIc**), and (+)-[Pt(Cl)(CH_2Bu-*t*)\{(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$\}] (**XXXVc**) [21b]. The dichlorides [$PtCl_2$\{(*S*,*S*)-$\mathbf{P_2^{[(CH_2)_5\text{-}c]_2}}$\}] (**XXXIVa**) and [$PtCl_2$\{(*S*,*S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$\}] (**XXXIVb**) were similarly prepared by substituting the required bidentate phosphines for the dimethyl sulfoxide ligands of [$PtCl_2(OSMe_2)_2$] [24c]. An alternative method of synthesis for alkyl chloro complexes such as [Pt(Cl)(CH_2Bu-*t*)\{*rac*-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$\}] (**XXXIIf**) [10d], [Pt(Cl)(CH_2Bu-*t*)\{*rac*-$\mathbf{P_2^{(OR)_4}}$\}] (**XXXIIj**–**XXXXl**) [29], (+)-[Pt(Cl)(CH_2Bu-*t*)



Scheme 19. Enantiopure platinum complexes [PtX_2{(*R*,*R*)-$\mathbf{P_2^{R_4}}$}] (**XXXII**) and [Pt(X)(Y){(*R*,*R*)-$\mathbf{P_2^{R_4}}$}] (**XXXIII**).

{(*R*,*R*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}] (**XXXIIIb**), (−)-[Pt(Cl)(CH_2Bu-*t*){(*S*,*S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}] (**XXXVb**) [10d], [Pt(Cl)(CH_2Bu-*t*){(*S*,*S*)-$\mathbf{P_2^{[OCH(CO_2Pr\text{-}i)\text{-}(R)\text{—}]_2}}$}] (**XXXVd**), and [Pt(Cl)(CH_2Bu-*t*){(*S*,*S*)-$\mathbf{P_2^{[Omenthyl\text{-}(1'R,2'S,5'R)]_4}}$}] (**XXXVe**) [29] involves the controlled acidolysis of the corresponding dineopentyls with methanolic HCl.

The triflate derivatives [Pt(OSO_2CF_3)(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)], [Pt(OSO_2CF_3)(CH_3){*rac*-$\mathbf{P_2^{(OPh)_4}}$}], and [Pt(OSO_2CF_3)(CH_2Bu-*t*)(*rac*-$\mathbf{P_2^{Ph_4}}$)] (**XXXIr–XXXIt**) were made by treating their alkyl chloro precursors with AgO_3SCF_3 in CH_2Cl_2 at ambient conditions [21b], and alkyl hydrides [Pt(H)(CH_2Bu-*t*){*rac*-$\mathbf{P_2}^{(C_6H_{11}\text{-}c)_4}$}], [Pt(H)($CH_2$Bu-*t*){*rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$}], and [Pt(H)($CH_2$Bu-*t*){*rac*-$\mathbf{P_2^{[N(C_2H_4)_2O\text{-}c]_4}}$}] (**XXXIm–XXXIo**) were isolated from reactions of the required chloro neopentyls with Na[$BH(OMe)_3$] in THF [10d,29].

[$PtCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)] (**XXXa**) reacted with tin(II) chloride in 1:1 stoichiometry in CH_2Cl_2 at ambient conditions forming [Pt(Cl)($SnCl_3$)(*rac*-$\mathbf{P_2^{Ph_4}}$)] (**XXXIa**) together with the unreacted dichloro complex in 1:1 molar ratio. If [Pt(Cl)(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)] (**XXXIc**) or [Pt(Cl)(CH_3){*rac*-$\mathbf{P_2^{(OPh)_4}}$}] (**XXXIe**) were allowed to interact with equimolar $SnCl_2$ in acetone at room temperature, no pure trichlorostannato products [Pt($SnCl_3$)(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)] (**XXXIp**) or [Pt($SnCl_3$)(CH_3){*rac*-$\mathbf{P_2^{(OPh)_4}}$}] (**XXXIq**) were obtained, roughly 5:2:3 mixtures of **XXXIp**/**XXXIq**, [Pt(Cl)($SnCl_3$)(*rac*-$\mathbf{P_2^{Ph_4}}$)]/[Pt(Cl)($SnCl_3$){*rac*-$\mathbf{P_2^{(OPh)_4}}$}], and [$PtCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)]/[$PtCl_2${*rac*-$\mathbf{P_2^{(OPh)_4}}$}] being formed instead. Only if the reactants were combined at low temperature (−20 °C), tin(II) chloride was observed to cleanly insert into the Pt–Cl bond of **XXXIe**, giving the methyl trichlorostannyl derivative **XXXIq** as the exclusive complex, which at room temperature, however, underwent rapid degradation to [Pt(Cl)($SnCl_3$){*rac*-$\mathbf{P_2^{(OPh)_4}}$}] and [$PtCl_2${*rac*-$\mathbf{P_2^{(OPh)_4}}$}]. If the reactions between chloro methyl complex **XXXIc** or its phenoxy analogue **XXXIe** and $SnCl_2$ were carried out in toluene at 80 °C, the product mixtures were dominated by dichloro and bis(trichlorostannato) complexes [$PtCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)]/[Pt($SnCl_3$)$_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)] (**XXXa**/**XXXf**) and [$PtCl_2${*rac*-$\mathbf{P_2^{(OPh)_4}}$}]/Pt($SnCl_3$)$_2${*rac*-$\mathbf{P_2^{(OPh)_4}}$}] (**XXXd**/**XXXg**), the corresponding mono-trichlorostannates [Pt($SnCl_3$)(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)]/[Pt(Cl)($SnCl_3$)(*rac*-$\mathbf{P_2^{Ph_4}}$)] and [Pt($SnCl_3$)(CH_3){*rac*-$\mathbf{P_2^{(OPh)_4}}$}]/[Pt(Cl)($SnCl_3$){*rac*-$\mathbf{P_2^{(OPh)_4}}$}] representing only minor constituents of the product mixtures [21b].

[Pt{*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$}$_2$][$PF_6$]$_2$ resulted from a 1:2 reaction between [$PtCl_2$(η^4-C_8H_{12})] and the P_2 ligand in the presence of NH_4PF_6 [26b].

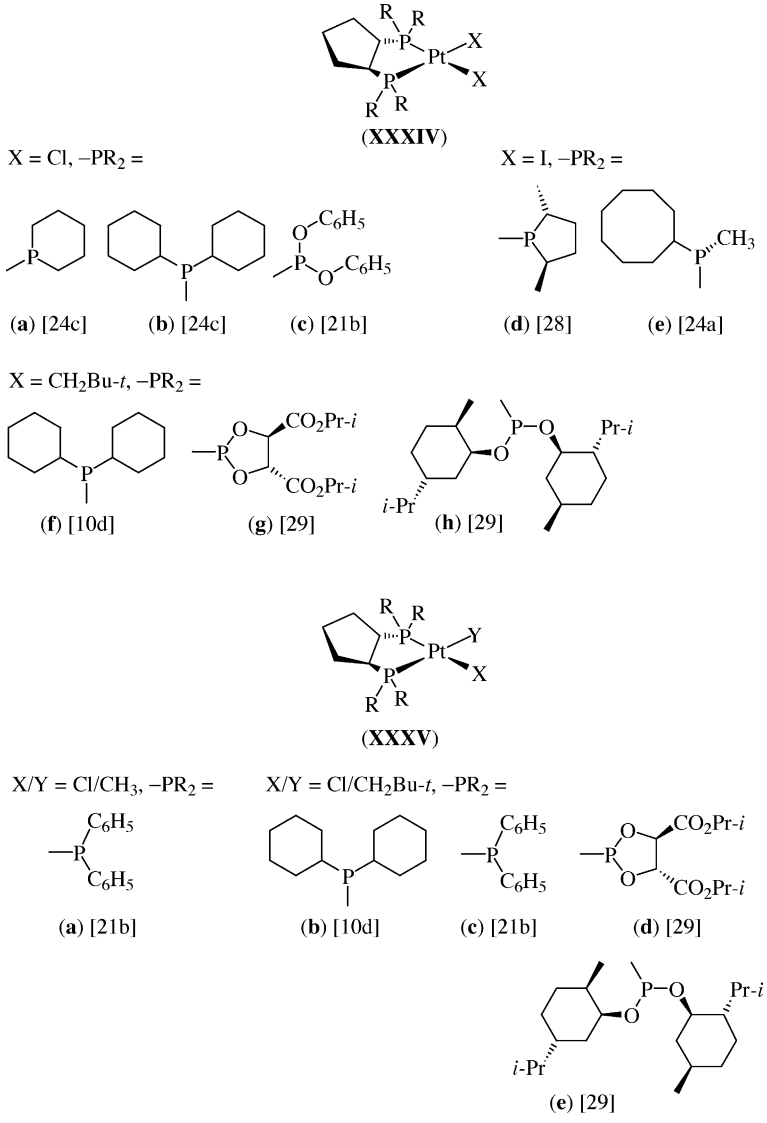
While mononuclear [Pt(OSO_2CF_3)(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)] was prepared by the addition, at room temperature, of [Pt(Cl)(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)] to a solution-suspension of AgO_3SCF_3 in CH_2Cl_2 (vide supra), the combination of the reactants in the reversed order at low temperature (−60 °C) led to the displacement of the $CF_3SO_3^-$ ligand from the already formed triflate product by unchanged starting complex, producing chloro-bridged [{Pt(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)}$_2$(μ-Cl)]O_3SCF_3 (**XXXVI**) [21b].

[Pt(Cl)(CH_2Bu-*t*){*rac*-$\mathbf{P^{(NC_5H_{10}\text{-}c)_2}P^{Cl(NC_5H_{10}\text{-}c)}}$}] (**XXXVII**) with one bis(piperidino)- and one chloro(piperidino)-substituted phosphorus atom was isolated from a 1:1 reaction between [Pt(Cl)(CH_2Bu-*t*)(η^4-C_8H_{12})] and an ethereal solution containing *rac*-C_5H_8[P(NC_5H_{10}-*c*)$_2$][P$Cl(NC_5H_{10}$-*c*)] and *rac*-C_5H_8[P(NC_5H_{10}-*c*)$_2$]$_2$ in approximately equimolar quantities [21c].

The coordination polymer [Pt_2{*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$}$_2$ $Ag_6(NO_3)_{10}$]$_n$ (**XXXVIII**), featuring a Pt_2{*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$}$_2$ core with each chelate ligand *P*,*N*-bridging two platinum atoms resulted from treatment of [PtI_2{*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$}] with excess silver nitrate in acetic acid/ethanol (Scheme 21) [26a].

3.7. X-ray structural data and chiroptical properties

Table 3 lists selected crystallographic and structural data for altogether 59 racemic and enantiopure complexes that have been studied by single crystal diffractometry. Particularly worthy of comment is the conformative flexibility of the 1,2-disubstituted cyclopentane backbone of the various P_2 ligands: with only few exceptions, the torsion angles P–C–C–P of the uncoordinated bis(phosphines) are found in the range 150–170°, which leads to distances between the two phosphorus atoms of 4.4–4.5 Å (Section 2.4; Table 2) and seems to indicate that these compounds will not act as good chelating ligands. However, in the mononuclear complexes collected in Table 3, the torsion angles P–C–C–P



Scheme 20. Enantiopure platinum complexes [PtX_2\{(*S*,*S*)-$\mathbf{P_2^{R_4}}$\}] (**XXXIV**) and [Pt(X)(Y)\{(*R*,*R*)-$\mathbf{P_2^{R_4}}$\}] (**XXXV**).

are normally close to 40–50°, values of ∼34° (measured for [$RuCl_2$(*rac*-$\mathbf{P_2^{Me_4}}$)$_2$]) and ∼65° (observed for the cation [$ReCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)]$^+$) marking a lower and an upper limit. As a consequence of the shrinking of the dihedral angle between the two PCC planes upon coordination, the phosphorus atoms move towards each other until they span, at the central metal, chelate P–M–P bite angles typically amounting to 85 ± 3°. In the cases of the three metal–metal-bonded dimolybdenum complexes [Mo_2Cl_4(μ-*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$] (X = Cl, Br, I), the P–C–C–P torsion angles are close to 85° and the distances between the two phosphorus atoms are shortened, with respect to the free $\mathbf{P_2^{Ph_4}}$ ligand, from ∼4.45 to ∼3.65 Å [36a].

The footnotes given in Table 3 to entries (−)-[Rh(η^4-C_8H_{12})\{(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$\}]O_3SCF_3, (+)-[Rh(η^4-C_8H_{12})\{(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$\}]O_3SCF_3, (+)-[Rh(η^4-C_8H_{12})\{(*R*,*R*)-$\mathbf{P_2^{(OPh)_4}}$\}]O_3SCF_3, (−)-[Rh(η^4-C_8H_{12})\{(*S*,*S*)-$\mathbf{P_2^{(OPh)_4}}$\}]O_3SCF_3, (−)-[Rh(η^4-C_8H_{12})\{(*S*,*S*)-$\mathbf{P_2^{[OC_6H_3F_2\text{-}(3,5)]_4}}$\}]$O_3SCF_3$, (−)-[Rh(η^4-$C_8H_{12}$)\{(*S*,*S*)-$\mathbf{P_2^{[OC_6H_2F_3\text{-}(2,4,6)]_4}}$\}]$O_3SCF_3$, (−)-[Rh(η^4-$C_8H_{12}$)\{(*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$\}]$O_3SCF_3$, (−)-[$NiBr_2$\{(*R*,*R*)-$\mathbf{P_2}^{Ph_4}$\}$_2$], (+)-[$PtCl_2$\{(*R*,*R*)-$\mathbf{P_2^{(OPh)_4}}$\}], and (−)-[$PtCl_2$\{(*S*,*S*)-$\mathbf{P_2^{(OPh)_4}}$\}] list the optical rotations measured at different wave lengths for these compounds and also for two additional enantiomers, (+)-[Rh(η^4-C_8H_{12})\{(*R*,*R*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$\}]$O_3SCF_3$ and (+)-[$NiBr_2$\{(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$\}$_2$]. Further complexes for which specific rotations $[\alpha]_\lambda$ have been measured include (+)-[Rh(η^4-C_8H_{12})\{(*S*,*S*)-$\mathbf{P_2^{(C_6F_5)_4}}$\}]$O_3SCF_3$, $[\alpha]_D^{20} = +36$; (−)-[Rh(η^4-C_8H_{12})\{(*S*,*S*)-$\mathbf{P_2^{[OC_6H_3F_2\text{-}(2,6)]_4}}$\}]$O_3SCF_3$, $[\alpha]_D^{20} = -46$ (both $c = 0.2$, acetone [23b]); (+)-[Pt(CH_2Bu-*t*)$_2$\{(*R*,*R*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$\}], $[\alpha]_D = +63$ ($c = 1$, THF) [10d]; (+)-[Pt(Cl)(CH_2Bu-*t*)$_2$\{(*R*,*R*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$\}], $[\alpha]_D = +71$ ($c = 1$, $CHCl_3$) [10d]; (−)-[Pt(CH_2Bu-*t*)$_2$\{(*S*,*S*)-$\mathbf{P_2^{[[OCH(CO_2Pr\text{-}i)\text{-}(R)\text{—}]_2]_2}}$\}], $[\alpha]_D = -31$ ($c = 0.3$, THF) [29];

Table 3
Selected X-ray structural data for transition metal complexes containing racemic and enantiopure *trans*-1,2-$C_5H_8(PR_2)_2$ or *trans*-$C_5H_8(PR_2)(PR'_2)$ bis(phosphines)[a]

Compound[b]	Space group	*d*(M—P) (Å)	P—M—P (°)	P—C—C—P (°)	Ref.
Mononuclear complexes with racemic C_2-symmetric ligands					
[$ReCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)][$Re_2(\mu\text{-}O_2CPh)_2Cl_6$][c] **(III)**	*P*-1	2.501(6), 2.515(7)	82.6(2)	64.7	[36b]
[$ReCl_2(CO)(NO)$(*rac*-$\mathbf{P_2^{Me_4}}$)] **(Va)**	*Fdd*2	2.392(2)[d], 2.459(2)[e]	83.3(1)	56.1	[38]
[$RuCl_2$(*rac*-$\mathbf{P_2^{Me_4}}$)$_2$][c] **(VII)**	$P2_1/n$	2.328(1), 2.331(1)	84.80(5)	34.4	[35b]
[$RuCl_2$(*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$-*P,P,N*)($PPh_3$)] **(VIIIa)**	*P*-1	2.269(1)[f], 2.364(1)[g]	82.26(4)	46.5	[26b]
[$RuCl_2$(*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$-*P,P,N*)($PPh_3$)][h] **(VIIIb)**	*P*-1	2.271(1)[f], 2.291(1)[i], 2.286(1)[f], 2.287(1)[I]	84.40(5), 83.94(5)	49.2, 51.0	[26b]
[Ru{η^3-$(CH_2)_2CMe$}$_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)][j] **(IXb)**	*C*2/*c*	2.3094(7), 2.3094(7)	86.92(4)	51.0	[35b]
[Ru{η^3-$(CH_2)_2CMe$}$_2$(*rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$}][j] **(IXd)**	*P*-1	2.3245(5), 2.3321(8)	87.42(2)	52.8	[35b]
[$RuCl_2$(*rac*-$\mathbf{P_2^{Me_4}}$){$Ph_2P(CH_2)_2NH_2$}] **(Xa)**	*P*-1	2.248(2)[k], 2.327(3)[l]	85.63(9)	35.9	[35b]
[$RuCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$){$Ph_2P(CH_2)_2NH_2$}] **(Xb)**	*P*-1	2.288(5)[k], 2.366(5)[l]	85.1(2)	50.4	[35b]
[$RuCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$){$Ph_2PCH_2CMe_2NH_2$}] **(XI)**	*P*-1	2.302(1)[k], 2.340(1)[l]	83.15(4)	50.8	[35b]
[$RuCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)(*o*-$Ph_2PC_6H_4NHMe$)] **(XII)**	*C*2/*c*	2.298(3)[k], 2.378(4)[l]	84.8(1)	60.3	[35c]
[Ru(H)(Cl)(*rac*-$\mathbf{P_2^{Ph_4}}$){$Ph_2P(CH_2)_2NH_2$}] **(XIII)**	*C*2/*c*	2.267(1)[k], 2.322(1)[l]	85.22(4)	52.3	[35c]
[Rh(*rac*-$\mathbf{P_2^{Ph_4}}$)$_2$]BF_4[c] **(XVI)**	*C*2/*c*	2.309(1), 2.320(1)	84.67(4)	52.6	[36c]
[Rh(η^4-C_8H_{12}){*rac*-$\mathbf{P_2^{[OC_6H_3F_2\text{-}(2,6)]_4}}$}]$O_3SCF_3$[h] **(XVIIc)**	*P*-1	2.208(2), 2.218(2), 2.211(3), 2.215(3)	83.0(1), 82.6(1)	49.7, 49.1	[23b]
[Rh(η^4-C_8H_{12}){*rac*-$\mathbf{P_2^{[OC_6H_3F_2\text{-}(3,5)]_4}}$}]$O_3SCF_3$ **(XVIId)**	$P2_1/c$	2.216(3), 2.227(4)	82.5(1)	44.3	[23b]
[Rh(η^4-C_8H_{12}){*rac*-$\mathbf{P_2^{[OC_6H_2F_3\text{-}(2,4,6)]_4}}$}]$O_3SCF_3$ **(XVIIe)**	*P*-1	2.219(2), 2.229(1)	82.90(6)	49.2	[23b]
[Rh(η^4-C_8H_{12}){(*R,R*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}]$O_3SCF_3$ [Rh(η^4- C_8H_{12}){(*S,S*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}]$O_3SCF_3$ **(XXIa)**/**(XXIb)**	$P2_1/c$	2.312(2), 2.323(2)	85.20(6)	44.7	[44]
[PtI_2){*rac*-$\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}$}][h] **(XXXb)**	$P2_1/c$	2.243(2), 2.248(2), 2.244(2), 2.247(2)	87.75(7), 87.05(7)	52.7, 53.5	[26b]
[$PtCl_2$){*rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$}] **(XXXc)**	*I*-42*d*	2.226(1), 2.226(1)	87.90(8)	55.2	[21b]
[$PtCl_2$){*rac*-$\mathbf{P_2^{(OPh)_4}}$}] **(XXXd)**	$P2_1/n$	2.199(2), 2.203(2)	86.24(8)	54.6	[29]
[$Pt(CH_3)_2$){*rac*-$\mathbf{P_2^{[N(C_2H_4)_2O\text{-}c]_4}}$}] **(XXXh)**	$P2_1/c$	2.268(2), 2.282(2)	85.81(6)	53.6	[21d]
[$Pt(CH_2Bu\text{-}t)_2$){*rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$}] **(XXXj)**	*Pbcn*	2.285(1), 2.285(1)	86.38(7)	58.8	[21b]
[$Pt(CH_2Bu\text{-}t)_2$){*rac*-$\mathbf{P_2^{[N(C_2H_4)_2O\text{-}c]_4}}$}] **(XXXk)**	$P2_1/n$	2.293(3), 2.307(3)	86.1(1)	56.6	[29]
[Pt(Cl)($SnCl_3$)(*rac*-$\mathbf{P_2^{Ph_4}}$)][h] **(XXXIa)**	$P2_1/c$	2.274(5)[m], 2.282(5)[n], 2.286(6)[m], 2.283(5)[n]	87.0(2), 86.9(2)	55.7, 52.6	[21b]
[Pt(Cl)(CH_3){*rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$}] **(XXXId)**	$P2_1/c$	2.213(6)[m], 2.276(6)[o]	87.8(2)	60.1	[21b]
[Pt(Cl)($CH_2Bu\text{-}t$)(*rac*-$\mathbf{P_2^{Ph_4}}$)] **(XXXIg)**	$P2_1/n$	2.208(1)[m], 2.344(1)[o]	86.74(5)	56.4	[21b]
[Pt(Cl)($CH_2Bu\text{-}t$){*rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$}] **(XXXIh)**	$P2_1/c$	2.206(1)[m], 2.327(2)[o]	86.94(5)	57.4	[21b]
[Pt(Cl)($CH_2Bu\text{-}t$){*rac*-$\mathbf{P_2^{(OPh)_4}}$}] **(XXXIk)**	$P2_1/c$	2.181(1)[m], 2.277(1)[o]	85.26(5)	50.1	[21b]
[Pt(OSO_2CF_3)($CH_2Bu\text{-}t$)(*rac*-$\mathbf{P_2^{Ph_4}}$)] **(XXXIt)**	$P2_1/c$	2.189(2)[p], 2.346(2)[o]	86.28(8)	52.5	[21b]
Mononuclear complexes with enantiopure C_2-symmetric ligands					
(−)-[Rh(η^4-C_8H_{12}){(*R,R*)-$\mathbf{P_2^{Ph_4}}$}]O_3SCF_3[q,r] **(XVIIIb)**	$P2_1$	2.328(4), 2.328(4)	84.2(1)	−49.5	[44]
(−)-[Rh(η^4-C_8H_{12}){(*R,R*)-$\mathbf{P_2^{Ph_4}}$}]O_3SCF_3[r,s] **(XVIIIb)**	$P2_1$	2.293(2), 2.309(2)	84.08(6)	−57.7	[44]
(+)-[Rh(η^4-C_8H_{12}){(*R,R*)-$\mathbf{P_2^{(OPh)_4}}$}]O_3SCF_3[h,t] **(XVIIIc)**	$P2_1$	2.207(1), 2.268(1), 2.225(1), 2.261(1)	82.94(5), 82.67(5)	−49.4, −51.1	[23b]
[Rh(η^4-C_8H_{12}){(*S,S*)-$\mathbf{P_2^{(Bu\text{-}n)_4}}$}]$O_3SCF_3$[h] **(XIXa)**	$P2_1$	2.308(2), 2.311(1), 2.303(2), 2.313(2)	84.47(7), 84.64(8)	+47.4, +49.2	[24b]
[Rh(η^4-C_8H_{12}){(*S,S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}]$O_3SCF_3$[h] **(XIXe)**	$P2_1$	2.330(2), 2.332(1), 2.327(2), 2.331(2)	84.91(5), 86.16(5)	+53.1, +46.6	[24b]
(+)-[Rh(η^4-C_8H_{12}){(*S,S*)-$\mathbf{P_2^{Ph_4}}$}]O_3SCF_3[q,u] **(XIXf)**	$P2_1$	2.306(4), 2.315(4)	84.42(8)	+48.8	[44]
(−)-[Rh(η^4-C_8H_{12}){(*S,S*)-$\mathbf{P_2^{(OPh)_4}}$}]O_3SCF_3[h,v] **(XIXi)**	$P2_1$	2.207(1), 2.268(1), 2.227(1), 2.264(1)	82.88(6), 82.79(6)	+49.0, +51.1	[23b]
(−)-[Rh(η^4-C_8H_{12}){(*S,S*)-$\mathbf{P_2^{[OC_6H_3F_2\text{-}(3,5)]_4}}$}]$O_3SCF_3$[h,w] **(XIXk)**	$P2_1$	2.216(3), 2.245(4), 2.217(4), 2.246(4)	82.7(1), 82.6(1)	+49.1, +45.9	[23b]
(−)-[Rh(η^4-C_8H_{12}){(*S,S*)-$\mathbf{P_2^{[OC_6H_2F_3\text{-}(2,4,6)]_4}}$}]$O_3SCF_3$[x] **(XIXl)**	$P4_1$	2.228(1), 2.230(2)	83.20(8)	+50.6	[23b]
(−)-[Rh(η^4-C_8H_{12}){(*S,S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}]$O_3SCF_3$[y] **(XXIa)**	$P2_1$	2.305(1), 2.316(1)	84.33(3)	+52.7	[24b]
(−)-[$NiBr_2$){(*R,R*)-$\mathbf{P_2^{Ph_4}}$}$_2$][z] **(XXVIc)**	$P2_1$	2.158(1), 2.178(1)	88.33	−53.7	[9b]
[$NiCl_2$){(*S,S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}][h] **(XXVIIb)**	$P2_1$	2.174(3), 2.178(3), 2.174(3), 2.182(3)	89.8(1), 89.8(1)	44.9, 43.9	[24c]
[$NiCl_2$){(*S,S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}][A] **(XXVIIc)**	$P2_1$	2.158(3), 2.161(3)	88.4(1)	+50.8	[24a]
[$NiCl_2$){(*S,S*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}][A] **(XXVIId)**	$P2_1$	2.157(3), 2.166(3)	89.0(1)	+39.0	[24a]
[PdI_2){(*S,S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}] **(XXVIIIc)**	$P4_1$	2.256(2), 2.257(2)	87.22(7)	+50.4	[24a]
(+)-[$PtCl_2$){(*R,R*)-$\mathbf{P_2^{(OPh)_4}}$}][h,B] **(XXXIIa)**	$P2_1$	2.194(3), 2.204(3), 2.199(3), 2.200(3)	86.4(1), 86.1(1)	−52.3, −52.2	[21b]
[PtI_2){(*R,R*)-$\mathbf{P_2^{[(R)\text{-}CH(Me)CH_2^-]_2]_2}}$}]$BF_4$ **(XXXIIb)**	$P3_222_1$	2.237(2), 2.237(2)	88.2(1)	−46.3	[28]
(−)-[$PtCl_2$){(*S,S*)-$\mathbf{P_2^{(OPh)_4}}$}][h,C] **(XXXIVc)**	$P2_1$	2.196(4), 2.200(3), 2.205(3), 2.207(3)	86.4(1), 86.1(1)	+54.0, +52.4	[21b]
[PtI_2){(*S,S*)-$\mathbf{P_2^{[(R)\text{-}CH(Me)CH_2^-]_2]_2}}$}]$BF_4$ **(XXXIVd)**	$P2_1$	2.248(2), 2.258(2)	86.44(9)	+58.0	[28]

[PtI_2{(*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}] (**XXXIVe**)	$P4_1$	2.236(3), 2.237(3)	87.7(1)	+48.8	[24a]
[$Pt(CH_2Bu\text{-}t)_2${(*S*,*S*)-$\mathbf{P_2^{[Omenthyl\text{-}(1'R,2'S,5'R)]_4}}$}][h] (**XXXIVh**)	$P2_1$	2.253(4), 2.262(5), 2.261(4), 2.262(4)	84.8(2), 85.1(2)	+49.2, +50.3	[29]
[$Pt(Cl)(CH_2Bu\text{-}t)${(*S*,*S*)-$\mathbf{P_2^{[Omenthyl\text{-}(1'R,2'S,5'R)]_4}}$}] (**XXXVe**)	$P2_1$	2.185(2)[m], 2.295(2)[o]	86.56(7)	+52.6	[29]
Mononuclear complexes with C_1-symmetric ligands					
[$Rh(\eta^4\text{-}C_8H_{12})${*rac*-$\mathbf{P^{Ph_2}P^{(i\text{-}PrNCH_2)_2}}$}]$O_3SCF_3$[h] (**XXIIa**)	$P2_1/a$	2.292(2)[D], 2.296(2)[E], 2.330(2)[D], 2.261(2)[E]	85.59(6), 85.76(6)	56.0, 54.8	[23b]
[$Rh(\eta^4\text{-}C_8H_{12})${(*S*,*S*)-$\mathbf{P^{Ph_2}P^{(OPh)_2}}$}]$O_3SCF_3$ (**XXIVb**)	$P3_1$	2.178(2)[F], 2.273(2)[D]	85.35(8)	+53.2	[23b]
[$Pt(Cl)(CH_2Bu\text{-}t)${*rac*-$\mathbf{P^{(NC_5H_{10}\text{-}c)_2}P^{Cl}(NC_5H_{10}\text{-}c)}$}] (**XXXVII**)	$P2_1/n$	2.213(3)[m], 2.289(3)[o]	85.4(1)	51.8	[21c]
Di- and oligonuclear complexes					
[$Mo_2Cl_4(\mu\text{-}rac\text{-}\mathbf{P_2^{Ph_4}})_2$] (**IIa**)	$C2/c$	2.552(4), 2.596(4)	[G]	84.8	[36a]
[$Mo_2Br_4(\mu\text{-}rac\text{-}\mathbf{P_2^{Ph_4}})_2$] (**IIb**)	$C2/c$	2.564(7), 2.609(6)	[G]	85.9	[36a]
[$Mo_2I_4(\mu\text{-}rac\text{-}\mathbf{P_2^{Ph_4}})_2$] (**IIc**)	$C2/c$	2.580(6), 2.626(6)	[G]	85.7	[36a]
[{$Pt(CH_3)(rac\text{-}\mathbf{P_2^{Ph_4}})$}$_2$(μ-Cl)]$O_3SCF_3$[c] (**XXXVI**)	$P\text{-}1$	2.190(3)[m], 2.312(3)[o], 2.192(3)[m], 2.325(2)[o]	88.0(1), 88.2(1)	49.4, 57.2	[21b]
[Pt_2{*rac*-$\mathbf{P_2^{[C_5H_4\tilde{N}\text{-}(2)]_4}}$}$_2Ag_6(NO_3)_{10}]_n$[c] (**XXXVIII**)	$P2_1/n$	2.241(2), 2.255(2)	86.0(1)	36.6	[26a]

[a] Crystallographic data of previously unpublished structure determinations (complexes **XII**, **XIII**, **XVIIc**, **XVIId**, **XVIIe**, **XVIIIc**, **XIXi**, **XIXk**, **XIXl**, **XXIIa**, **XXIVb**) have been deposited as 'Supplementary material' (Appendix A).

[b] For numbering of complexes, see Sections 3.2–3.7.

[c] (*R*,*R*/*S*,*S*) *meso* forms.

[d] Re—P bond *trans* to Cl.

[e] Re—P bond *trans* to CO.

[f] Bichelating Ru—P bonds trans to Cl.

[g] Ru—P bond *trans* to PPh_3.

[h] Two crystallographically independent molecules in unit cell.

[i] Monochelating Ru—P bonds *trans* to Cl.

[j] (*Δ*-*R*,*R*)/(*Λ*-*S*,*S*) enantiomeric pairs.

[k] Ru—P bonds *trans* to —NH_2 or —NHMe.

[l] Ru—P bonds *trans* to —PPh_2.

[m] Pt—P bonds *trans* to Cl.

[n] Pt—P bonds *trans* to $SnCl_3$.

[o] Pt—P bonds *trans* to alkyl.

[p] Pt—P bond *trans* to triflate.

[q] Specimens taken from recrystallized samples of the enantiopure complexes [25].

[r] $[\alpha]_D^{20}$ ($c = 0.2$, acetone): −119 [25], −120 [23b].

[s] Specimen picked from a conglomerate of [$Rh(\eta^4\text{-}C_8H_{12})$(*rac*-$\mathbf{P_2^{Ph_4}}$)]$O_3SCF_3$, which underwent spontaneous resolution upon crystallization from THF/*n*-pentane [23b].

[t] $[\alpha]_D^{20}$ ($c = 0.2$, acetone): +4 [23b].

[u] $[\alpha]_D^{20}$ ($c = 0.2$, acetone): +117 [23b], +118 [25].

[v] $[\alpha]_D^{20}$ ($c = 0.2$, acetone): −3 [23b].

[w] $[\alpha]_D^{20}$ ($c = 0.2$, acetone): −39 [23b].

[x] $[\alpha]_D^{20}$ (c = 0.2, acetone): −49 [23b].

[y] $[\alpha]_D^{20}$ ($c = 0.2$, acetone): −56; for (+)-[$Rh(\eta^4\text{-}C_8H_{12})${(*R*,*R*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}]$O_3SCF_3$ enantiomer: +63 [25].

[z] $[\alpha]_D^{20}$ (CH_2Cl_2): -325 ± 8; for (+)-[$NiBr_2${(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$}$_2$] enantiomer: $+319 \pm 13$ [9b].

[A] The two stereoisomers co-crystallized, forming [$NiCl_2${(*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}]·[$NiCl_2${(*S*,*S*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}].

[B] $[\alpha]_\lambda$ ($c = 1$, CH_2Cl_2, ambient): +165(589 nm), +174(578 nm), +201(546 nm), +384(436 nm) [23b].

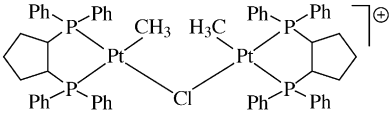
[C] $[\alpha]_\lambda$ ($c = 1$, CH_2Cl_2, ambient): −166(589 nm), −175(578 nm), −202(546 nm), −383(436 nm), −717(365 nm) [23b].

[D] Rh—PPh_2 bonds.

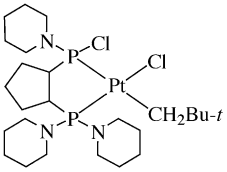
[E] Rh—P(N<)$_2$ bonds.

[F] Rh—$P(OPh)_2$ bond.

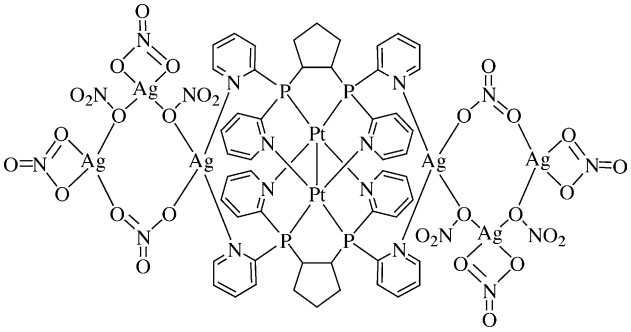
[G] Distances between the two phosphorus atoms of the bridging $\mathbf{P_2^{Ph_4}}$ ligand: 3.635 Å for X = Cl, 3.646 Å for X = Br, and 3.678 Å for X = I.



(**XXXVI**)



(**XXXVII**)



(**XXXVIII**)

Scheme 21. Platinum complexes **XXXVI** [21b], **XXXVII** [21c], and **XXXVIII** [26c].

(−)-[Pt(Cl)(CH$_3$){(*R*,*R*)-**P$_2^{Ph_4}$**}], $[\alpha]_\lambda = -187$ (589 nm), −196 (578 nm), −224 (546 nm), −401 (436 nm), −701 (365 nm); (+)-[Pt(Cl)(CH$_3$){(*S*,*S*)-**P$_2^{Ph_4}$**}], $[\alpha]_\lambda = +186$ (589 nm), +194 (578 nm), +222 (546 nm), +396 (436 nm), +682 (365 nm), (−)-[Pt(Cl)(CH$_2$Bu-*t*){(*R*,*R*)-**P$_2^{Ph_4}$**}], $[\alpha]_\lambda = -146$ (589 nm), −153 (578 nm), −175 (546 nm), −323 (436 nm); (+)-[Pt(Cl)(CH$_2$Bu-*t*){(*S*,*S*)-**P$_2^{Ph_4}$**}], $[\alpha]_\lambda = +137$ (589 nm), +144 (578 nm), +167 (546 nm), +305 (436 nm), +581 (365 nm) (all $c = 1$, CHCl$_3$ [21b]). Comparison with the data compiled for the free (tertiary phosphine)- and phosphonite-type ligands (*R*,*R*)-**P$_2^{R_4}$**/(*S*,*S*)-**P$_2^{R_4}$** and (*R*,*R*)-**P$_2^{(OR)_4}$**/(*S*,*S*)-**P$_2^{(OR)_4}$** in Section 2.4 (Table 1), shows that their coordination induces the sense of the optical rotation to change sign irrespective of the nature of the central metal and the additional ligands.

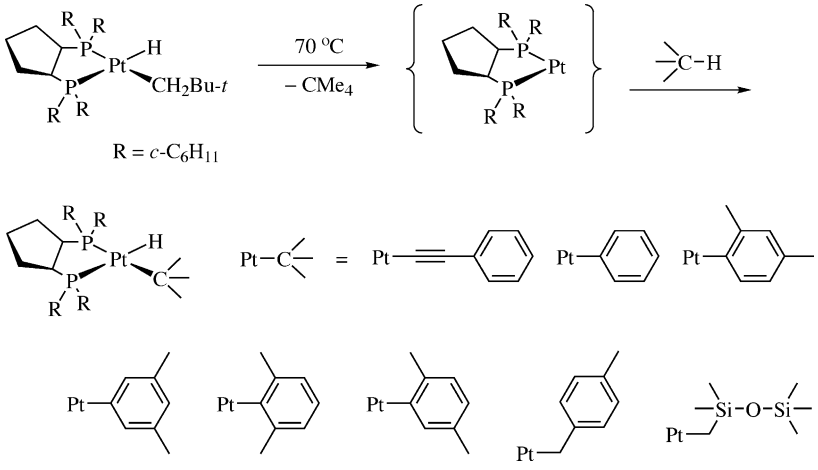
In the CD spectra of partially resolved [Mo$_2$Cl$_4$(μ-*rac*-**P$_2^{Ph_4}$**)$_2$] (twist angle P–Mo–Mo–P, ∼22°), the most drastic changes were observed in the range where the $\pi_{xy} \rightarrow \delta_{xy}$, $\pi_{xz} \rightarrow \delta_{xy}$, and $\pi_{yz} \rightarrow \delta_{x^2-y^2}$ transitions occur. On the basis of a (verified) CD sign rule predicting negative and positive CD bands, respectively, for the $\delta_{xy} \rightarrow \delta^*_{xy}$ transitions of *Λ*- and *Δ*-conformer dinuclear metal−metal-bonded complexes [M$_2$X$_4$(μ-P∩P)$_2$] with P–M–M–P torsional angles between 0° and 45° and the observation of opposite signs for the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ and $\delta_{xy} \rightarrow \delta^*_{xy}$ transitions [48], it was concluded that this partially resolved dimolybdenum complex was dominated by the *Δ* conformer with ligands of (*R*,*R*) chirality, since the sign for the CD band attributed to the $\delta_{xy} \rightarrow \delta_{x^2-y^2}$ transition was negative [36a].

4. Application to synthesis and catalysis

4.1. C–H bond activation

Given the extensive C–H activation chemistry displayed by the angular carbene-like d^{10}-ML$_2$ equivalent {Pt^0(*c*-C$_6$H$_{11}$)$_2$P(CH$_2$)$_2$P(C$_6$H$_{11}$-*c*)$_2$} established by Whitesides and Hackett in the mid 1980s [16], it was not surprising to see that the 14e species {Pt^0[*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**]}, generated in situ from [Pt(H)(CH$_2$Bu-*t*){*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] under mild thermal conditions, also oxidatively added to a wide range of sp^3, sp^2, and sp C–H bonds. Thus, thermolysis of the racemic hydrido neopentyl complex in cyclohexane solutions of phenylacetylene produced the alkynyl hydride [Pt(H)(C$_2$Ph){*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] in addition to the coordination compound [Pt(η^2-HC≡CPh)({*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}]. Thermolysis in benzene proceeded to quantitatively afford [Pt(H)(C$_6$H$_5$){*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}]. If the {Pt^0[*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**]} species was generated in *meta*-xylene, three platinum aryl hydrides were formed as expected: [Pt(H){C$_6$H$_3$Me$_2$-(2,4)}{*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}], [Pt(H){C$_6H_3Me_2$-(3,5)}{*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}], and [Pt(H){C$_6H_3Me_2$-(2,6)}{*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}]. Thermolysis of the neopentyl hydride in *para*-xylene afforded mixtures of products resulting from aryl and benzyl C–H activation, [Pt(H){C$_6$H$_3$Me$_2$-(2,5)}{*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] and [Pt(H){CH$_2C_6H_4$Me-(4)}{*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}], respectively. Finally, heating of [Pt(H)(CH$_2$Bu-*t*){*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] in the presence of hexamethyldisiloxane led to oxidative addition of methyl C–H bonds giving [Pt(H)(CH$_2$SiMe$_2$OSiMe$_3$){*rac*-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] (Scheme 22) [10].

Thermolyses of the enantiomerically pure starting materials [Pt(H)(CH$_2$Bu-*t*){(*R*,*R*)-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] and [Pt(H)(CH$_2$Bu-*t*){(*S*,*S*)}-**P$_2$**$^{(C_6H_{11}-c)_4}$}] were performed at 68 °C in cyclohexane containing precisely 2 equiv. of (±)-2,2′-dimethyl-1,1′-binaphthyl or (±)-2,2′-di-*t*-butyl-1,1′-biphenyl. Monitoring the decomposition of the two neopentyl hydrides and the formation of products by ^{31}P and ^{1}H NMR spectroscopy indicated the expected biaryl hydrides [Pt(H)(biaryl){(*R*,*R*)-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] and [Pt(H)(biaryl){(*S*,*S*)-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] to be produced as mixtures of isomers in quantitative yields. The degree of optical resolution achieved during (±)-biaryl–H oxidative addition was subsequently estimated from the enrichment of the (*R*)- and (*S*)-enantiomers remaining in the unreacted biaryls. For both substrates the optical inductions were low (3–6%) but clearly above the level of confidence as it could be shown that the enantiodiscrimination that was achieved during the attempted resolution of the two biaryls is controlled by the chirality of the bis(phosphine) ligand. Thus, with [Pt(H)(CH$_2$Bu-*t*){(*R*,*R*)-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] as a source for the reactive intermediate {Pt^0[(*R*,*R*)-**P$_2^{(C_6H_{11}\text{-}c)_4}$**]}, the (*S*)-(+)-2,2′-dimethyl-1,1′-binaphthyl was found to be slightly enriched in the biaryl sample recovered from the C–H cleavage reaction and thermolysis of [Pt(H)(CH$_2$Bu-*t*){(*S*,*S*)-**P$_2^{(C_6H_{11}\text{-}c)_4}$**}] correspondingly resulted in slight



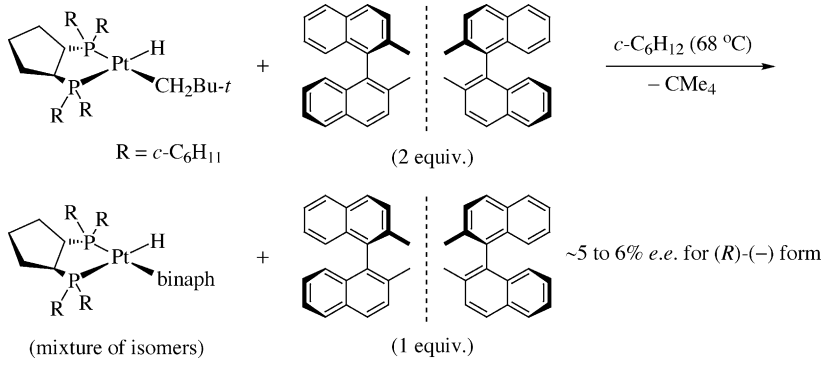
Scheme 22. C—H activation chemistry displayed by [Pt(H)(CH_2Bu-*t*){*rac*-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}] [10].

enrichment of the (*R*)-(−)-2,2′-dimethyl-1,1′-binaphthyl in the unreacted biaryl (Scheme 23) [10].

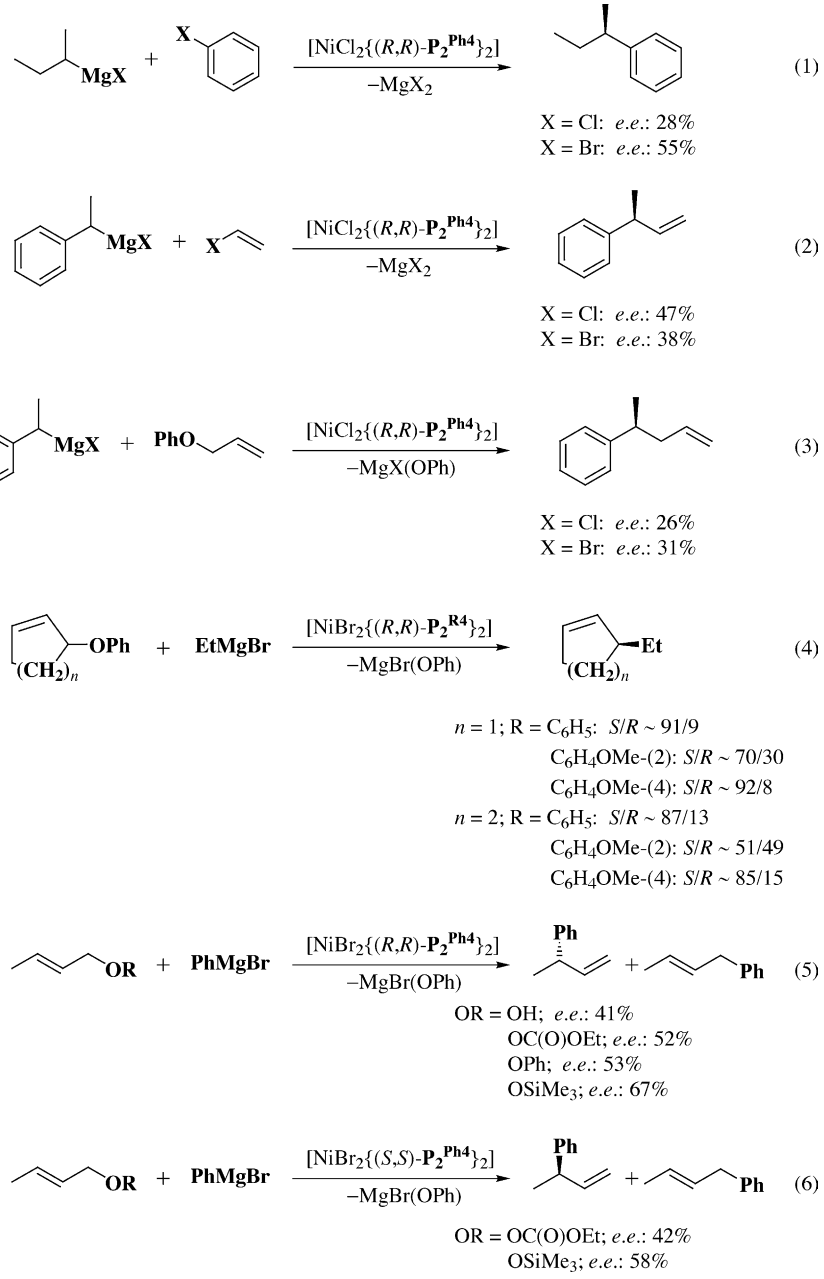
For improving the optical yields of the resolution procedure outlined before, alternative routes allowing a reactive chiral (chelate phosphine)platinum(0) fragment to be generated at lower temperatures were investigated. As it had been demonstrated that the introduction of oxygen and nitrogen substituents onto the phosphorus atoms of neopentyl hydrides [Pt(H)(CH_2Bu-*t*)(P∩P)] results in more facile reductive elimination of neopentane and oxidative addition of unactivated hydrocarbons [49], the reactivities towards C–H elimination and addition of the piperidino- and morpholino-substituted complexes [Pt(H)(CH_2Bu-*t*){*rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}c)_4}}$}] and [Pt(H)($CH_2$Bu-*t*){*rac*-$\mathbf{P_2^{[N(C_2H_4)_2O\text{-}c]_4}}$}] were studied. However, the two compounds exhibited similar inertness towards thermal release of neopentane as did the racemic or enantiopure complexes [Pt(H)(CH_2Bu-*t*){$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}], giving C–H insertion products such as the phenyl hydrides [Pt(H)(C_6H_5){*rac*-$\mathbf{P_2}^{(NC_5H_{10}-c)_4}$}] and [Pt(H)($C_6H_5$){*rac*-$\mathbf{P_2^{[N(C_2H_4)_2O\text{-}c]_4}}$}] only upon prolonged thermolysis at 60 °C [29].

4.2. Grignard cross-coupling

A study of the [$NiCl_2${(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}]- or [$NiCl_2${(*R*,*R*)-$\mathbf{P_2^{[C_6H_4OMe\text{-}(4)]_4}}$}]-catalyzed cross-coupling of some aryl, vinyl, and allyl electrophiles RX with α-*C*-chiral Grignard reagents R′CH(Me)MgX (R′ = Et, Ph) showed that use of the phenyl-substituted catalyst gave higher e.e. (up to 55%, depending on the nature of X) for the product isomers indicated in Scheme 24 (Eqs. (1)–(3)), than the *p*-anisyl-substituted one. The reactions proceeded with high chemoselectivity, the extent of formation of isomeric coupling products (1-phenylbutane, 4-phenyl-1-butene, and 5-phenyl-1-pentene, respectively) generally being <1–2% [17a]. In cross-coupling reactions between 1-phenylethyl magnesium bromide and vinyl chloride which used $NiBr_2$–(*R*,*R*)-$\mathbf{P_2^{R_4}}$ in situ catalysts with R = C_6H_5, C_6H_4OMe-(2), or C_6H_4OMe-(4) instead of the preformed dichloro complexes of Scheme 24 (Eq. (2)), the degree of asymmetric induction was found to decrease in the order of the *P*-substituents R = C_6H_4OMe-(2) (best e.e. ∼ 44%) > C_6H_4OMe-(4) (17%) > C_6H_5 (11%). Furthermore, the enantioselectivities changed with the extent of



Scheme 23. Reaction of [Pt(H)(CH_2Bu-*t*){(*S*,*S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}] with 2 equiv. of (±)-2,2′-dimethyl-1,1′-binaphthyl [10].

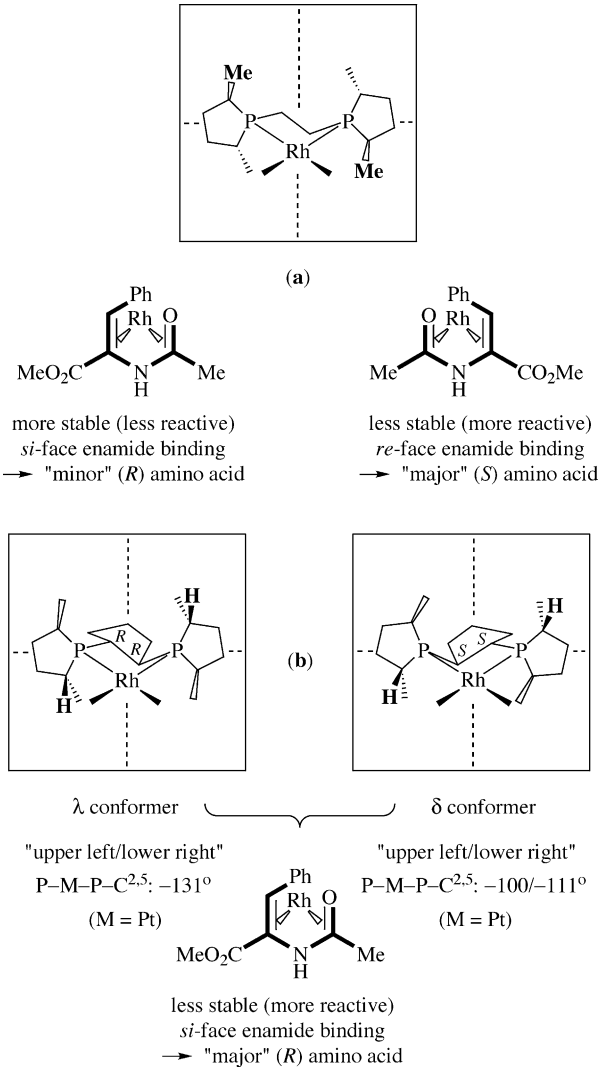


Scheme 24. NiX_2—(*R*,*R*)-$\mathbf{P_2^{R_4}}$- and NiX_2—(*S*,*S*)-$\mathbf{P_2^{R_4}}$-catalyzed Grignard cross-coupling reactions [17,45b].

conversion and were substantially affected by the method used to prepare the reaction mixtures [17d].

Cross-coupling reactions of 2-cyclopentenyl phenyl ether and 2-cyclohexenyl phenyl ether with ethyl magnesium bromide, which were carried out in the presence of the dibromo complexes [$NiBr_2${(*R*,*R*)-$\mathbf{P_2^{R_4}}$}], where R = C_6H_5, C_6H_4OMe-(2), or C_6H_4OMe-(4), gave the best enantioselectivities with [$NiBr_2${(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}] and [$NiBr_2${(*R*,*R*)-$\mathbf{P_2^{[C_6H_4OMe\text{-}(4)]_4}}$}] as (pre)catalysts (Scheme 24, Eq. (4)) [17b]. In cross-coupling reactions between two cycloalkenyl phenyl ethers and different alkyl magnesium bromides RMgX (R = Me, Et, *n*-Pr, *i*-Pr) which used [$NiCl_2${(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}] as the catalyst precursor, the enantioselectivities for the (*S*) products were in general lower in the alkylation of 2-cyclohexenyl phenyl ether than in that of 2-cyclopentenyl phenyl ether. With both substrates, maximum e.e. of ~74 and ~83%, respectively, were observed for the ethylation reaction [17e].

The enantioselectivities of cross-coupling reactions between crotyl alcohol derivatives $CH_3CH{-}CHCH_2OR$ (OR = OH, OC(O)OEt, OPh, $OSiMe_3$) and phenyl magnesium bromide which used both [$NiBr_2${(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}] and [$NiBr_2${(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$}] as catalyst complexes were found to depend on the size of the leaving group OR: the larger their volume, the higher the enantiomeric excesses (Scheme 25, Eqs. (5) and (6)). Monitoring the different reaction mixtures



Scheme 25. (a) Quadrant-blocking in Rh-(*R*,*R*)-Me-BPE catalysts by equatorially aligned phospholane methyl substituents and favored (less favored) *si*-face (*re*-face) binding of the substrate as proposed by Burk [5e] and (b) quadrant-blocking in λ- and δ-shaped Rh-(*R*,*R*)-$\mathbf{P_2^{[[(R)\text{-}CH(Me)CH_2^-]_2]_2}}$ and Rh-(*S*,*S*)-$\mathbf{P_2^{[[(R)\text{-}CH(Me)CH_2^-]_2]_2}}$ catalysts by axially oriented phospholane hydrogen atoms and (in either case) less favored enamide *si*-face binding as suggested by Pringle [28].

by circular dichroism and ^{31}P NMR spectroscopy revealed the presence of [Ni(Br)(C_6H_5)($\mathbf{P_2^{Ph_4}}$)], [Ni(C_6H_5)$_2$($\mathbf{P_2^{Ph_4}}$)], and [Ni($\mathbf{P_2^{Ph_4}}$)] intermediates. [Ni(OR)(η^3-crotyl)($\mathbf{P_2^{Ph_4}}$)] species, believed to be involved in the catalysis at low concentrations, remained undetected. A stereochemical model was set up in order to explain the observed relationship between product configuration and chelate conformation [45b].

Cross-coupling reactions between 1-bromo-2-methylnaphthalene with its derived Grignard reagent, which were carried out in the presence of nickel and palladium complexes of the types [MCl_2{(*S*,*S*)-$\mathbf{P_2^{[(CH_2)_5\text{-}c]_2}}$}] and [$MCl_2${(*S*,*S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}], generally suffered from low conversions. With [$NiCl_2${(*S*,*S*)-$\mathbf{P_2^{(C_6H_{11}\text{-}c)_4}}$}] as catalyst precursor, the coupling product (*R*)-(−)-2,2′dimethyl-1,1′-binaphthyl was obtained in modest enantiomeric excess (26%) [24c].

4.3. >C=C< hydrogenation

Many of the optically active (1*R*,2*R*)- and (1*S*,2*S*)-$C_5H_8(PR_2)_2$ ligands have been investigated for their efficacy in Rh-catalyzed asymmetric hydrogenations of standard enamide substrates such as *N*-acetylamino acrylic (Ac-acrH) and cinnamic (Ac-cinH) acid and their methyl esters, Ac-acrMe and Ac-cinMe, respectively [9a,b,18c,22a,b,24b,25,28]. One important purpose of these studies was to elucidate possible correlations between the results of the hydrogenation reactions and structural properties of the metal complexes in order to understand the factors governing the stereoselectivity of the catalysts. Some particularly illuminating results of such studies are collected in Table 4.

One first conclusion to be drawn for hydrogenations using either the unsubstituted (*R*,*R*)-$\mathbf{P_2^{Ph_4}}$ or (*S*,*S*)-$\mathbf{P_2^{Ph_4}}$ ligands (nos. **1a** and **1b**) or their dendritically expanded homologues with different multiple homochiral units in the periphery (nos. **2a**–**2d**) is that the generally high enantioselectivity for the (*S*)- or (*R*)-products displayed by the *P*-phenylated rhodium catalysts summarized under entries **1** and **2** 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 [22a,b]. The rhodium chelate complexes of these ligands thus follow an empirical λ/δ rule which predicts that a λ chelate will give the (*S*) enantiomer while a δ chelate will produce the (*R*) enantiomer [45a]. While this is the case for all ligands bearing two aryl substituents, the 1,1′-bi(2-naphthol)-derived bis(phosphonites) of entries **5a**–**5d** reveal such a strong influence of the axially chiral substituents on the orientation of the optical induction that their sense of chirality can supersede the contribution of the ligand core. Thus, rhodium(I) catalyst complexes possessing (*R*,*R*)-$\mathbf{P_2^{[(R)\text{-}BINOLATE]_2}}$ or (*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}BINOLATE]_2}}$ ligands always gave rise to hydrogenation products with (*S*) configuration (entries **5a** and **5d**) whereas the (*R*) enantiomers predominated in the product mixtures formed with the two diastereomeric rhodium(I) catalysts bearing (*S*,*S*)-$\mathbf{P_2^{[(S)\text{-}BINOLATE]_2}}$ and (*R*,*R*)-$\mathbf{P_2^{[(S)\text{-}BINOLATE]_2}}$ ligands (nos. **5b** and **5c**). The optical yields achieved with the (*S*,*S*)-$\mathbf{P_2^{[(S)\text{-}BINOLATE]_2}}$ bis(phosphonite) are by far superior to those obtained with the catalytic system based on the (*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}BINOLATE]_2}}$ ligand and, correspondingly, the (*R*,*R*)-$\mathbf{P_2^{[(R)\text{-}BINOLATE]_2}}$ ligand is much more selective than its (*R*,*R*)-$\mathbf{P_2^{[(S)\text{-}BINOLATE]_2}}$ diastereomer. Obviously, the two enantiomers with like chirality of their backbone carbon atoms and phosphonite substitutents represent the beneficial matched combination of stereochemical elements while the forms with unlike configuration of the two-carbon backbone and the BINOL-derived phosphonite rings must be looked at as the disadvantageous mismatched counterparts.

Clear-cut matched–mismatched effects in enantioselective hydrogenation are also manifest for the >C=C<

Table 4
Enantioselective hydrogenation of standard enamide substrates with optically active [Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{R_4}}$}]X and [Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{R_4}}$}]X (pre)catalysts[a]

No.	Ligand	Substrate				
	$\mathbf{P_2^{R_4}}$	Ac-acrH e.e. (%)	Ac-acrMe e.e. (%)	Ac-cinH e.e. (%)	Ac-cinMe e.e. (%)	Ref.
1a	(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$	92 (*S*)	86 (*S*)	95 (*S*)	91 (*S*)	[25]
1b	(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$	91 (*R*)	85 (*R*)	93 (*R*)	91 (*R*)	[25]
2	(*S*,*S*)-$\mathbf{P_2^{[C_6H_3(CH{=}NR)_2\text{-}(3,5)]_4}}$ [b]					
2a	**R** = (*R*)-**CH(CH$_2$OH)Pr-*i***			96 (*R*)		[22a,b]
2b	**R** = (*S*)-**CH(CH$_2$OH)Pr-*i***			94 (*R*)		[22a,a]
2c	**R** = (*R*)-**CH(Me)C$_6$H$_{11}$-*c***			94 (*R*)		[22a,b]
2d	(*R*,*R*)-$\mathbf{P_2^{[C_6H_3\{CH_2Obornyl-(1S)\}_2\text{-}(3,5)]_4}}$ [b]			96 (*S*)		[22a,b]
2e	(*S*,*S*)-$\mathbf{P_2^{[C_6H_3\{CH_2Obornyl-(1S)\}_2\text{-}(3,5)]_4}}$ [b]			94 (*R*)		[22a]
3a	(*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$		73 (*R*)		77 (*R*)	[28]
3b	(*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$		95 (*R*)		98 (*R*)	[28]
4a	(*R*,*R*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$ [c]	23 (*R*)	28 (*R*)	28 (*R*)	34 (*R*)	[25]
4b	(*S*,*S*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$ [c]	21 (*S*)	29 (*S*)	26 (*S*)	35 (*S*)	[25]
4c	(*R*,*R*)-$\mathbf{P_2^{[(S)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$ [c]	90 (*S*)	83 (*S*)	73 (*S*)	86 (*S*)	[25]
4d	(*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$ [c]	90 (*R*)	82 (*R*)	74 (*R*)	86 (*R*)	[25]
5a	(*R*,*R*)-$\mathbf{P_2^{[(R)\text{-}BINOLATE]_2}}$	92 (*S*)	86 (*S*)	77 (*S*)	85 (*S*)	[25]
5b	(*S*,*S*)-$\mathbf{P_2^{[(S)\text{-}BINOLATE]_2}}$	96 (*R*)	89 (*R*)	78 (*R*)	85 (*R*)	[25]
5c	(*R*,*R*)-$\mathbf{P_2^{[(S)\text{-}BINOLATE]_2}}$	27 (*R*)	39 (*R*)	20 (*R*)	36 (*R*)	[25]
5d	(*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}BINOLATE]_2}}$	28 (*S*)	31 (*S*)	24 (*S*)	36 (*S*)	[25]

[a] $X^- = Cl^-$ (nos. **2a**–**2e**): in situ catalysts generated from [{Rh(μ-Cl)(η^4-C_8H_{12})}$_2$] and the corresponding chelate phosphine), BF_4^- (nos. **3a** and **3b**) or $F_3CSO_3^-$ (entries **1a**, **1b**, **4a**–**4d**, and **5a**–**5d**).
[b] See Section 2.3.1.2; Schemes 5 and 6.
[c] The configurations at the phosphorus atoms are given for the *free* ligands; they are inverted upon coordination to rhodium as a consequence of the CIP sequence rules.

reductions catalyzed by the more electron-rich rhodium complexes possessing either the diastereomeric (*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$ and (*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$ bis(phospholane) ligands **3a** and **3b** or the *C*,*P*-chirogenic methyl(cyclooctyl)-substituted bis(phosphines) of entries **4a**–**4d**.

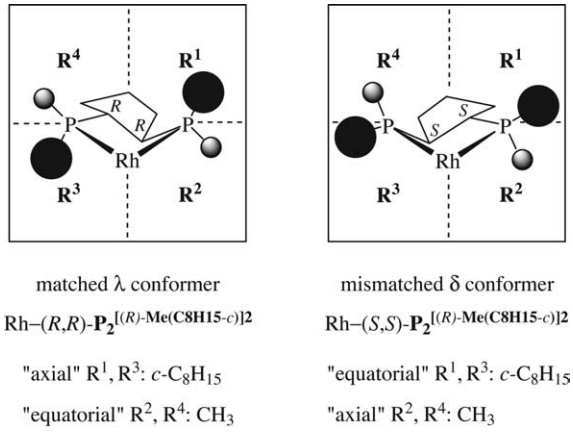
The bis(phospholane) (*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$ is clearly more enantiodiscriminative than its (*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$ diastereomer. The observation that the Rh-(*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$ catalyst, which has δ conformation of its chelate ring, proved to be much more selective for the (*R*) products than the corresponding λ conformer Rh-(*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$ was unexpected [28]: so far, the stereochemical model used for the understanding of the enantioselection by catalysts bearing chiral phospholane groups such as the DuPHOS- and BPE-type *o*-phenylene- or 1,2-ethylene-bis-(2*R*,5*R*)-dialkylphospholanes was based on the assumption that two of the four equatorially aligned alkyl ring substituents adjacent to the phosphorus atoms effectively block the "top left and bottom right coordination quadrants" [2c], as indicated by drawing (a) of Scheme 25 [5c,e]. In the *more stable* (less reactive) enamide adduct, the substrate should therefore be bonded through its *si*-face, the less favored (more reactive) adduct diastereomer being that in which the enamide is coordinated through its *re*-face. Since Rh-DuPHOS catalysts have been confirmed to follow the Halpern–Brown-type "anti-lock-and-key" mechanistic behavior [5d,50] in which the major product enantiomer is formed by hydrogenation of the less favorably bonded enantioface, both the high (*R*)-selectivity of the Rh–(*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$ complex and the somewhat lower (*R*)-discriminating properties of the Rh–(*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$ diastereomer are suggestive of *si*-face binding of the substrate in the *less stable* adducts (Scheme 25 (b)). In contrast to the original stereochemical model proposed for chelate complexes of bis(phospholane)-substituted ligands, it was therefore concluded that it is the top right and bottom left quadrants which are more effectively shielded in the ground-state geometries of the two diastereomers than the quadrants left side up and right side down—actually, to a higher extent in matched δ-[Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$}]$^+$ but to a lower degree in the less matched cation λ-[Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$}]$^+$ [28]. In fact, crystal structures analyses of two model complexes, δ-[PtI_2{(*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$}] and λ-[$PtI_2${(*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2-]_2\}_2}}$}], showed that the equatorial methyl substituents of the phospholane rings blocking the top left and bottom right quadrants are ∼0.5 Å closer to the iodo ligands in the λ than in the δ conformer, whereas the axial α-hydrogen atoms occupying the lower left and upper right quadrants are ∼0.3 Å closer to the other ligands in the δ than in the λ diastereomer. It was therefore concluded that it is the steric repulsion between the enamide substrate with

the axially aligned hydrogen atoms which substantially contributes to the enantiofacially discriminating abilities of the catalyst complexes (Scheme 25(b)) [28]. A different interpretation is given below.

With regard to the diastereomeric ligands featuring mixed methyl(cyclooctyl) substitution of their donor atoms, entries **4a**–**4d** of Table 4 make it clear that it is the two bis(phosphine) enantiomers with opposite configuration at carbon and phosphorus which make up the superior hydrogenation catalysts. Rhodium complexes derived from these four electron-rich bis(phosphines) resemble the complexes based on the more electron-poor bis(phosphonites) **5a**–**5d** in that the compounds showing the matched combination of stereoelements (nos. **4c**/**4d** and **5a**/**5b**) follow the λ/δ rule (vide supra), whereas the mismatched catalysts (entries **4a**/**4b** and **5c**/**5d**) do not. The catalytic results obtained with the complexes of the aforementioned two diastereomeric bis(phospholane) ligands are akin: the matched δ-conformer Rh–(*S*,*S*)-$\mathbf{P_2^{[(\mathit{R})\text{-}CH(Me)CH_2-]_2}}$ induces (*R*) stereoselection and thus obeys the rule; mismatched λ-shaped Rh–(*R*,*R*)-$\mathbf{P_2^{[(\mathit{R})\text{-}CH(Me)CH_2-]_2}}$ likewise favors the formation of products with (*R*) configuration and, hence, breaks the rule.

There exists substantial structural information on complexes of the four isomeric $\mathbf{P_2^{[Me(C_8H_{15}\text{-}\mathit{c})]_2}}$ ligands **4a**–**4d** (Section 3.7; Table 3), which strongly suggests that the very different enantioselectivities displayed by their rhodium catalysts with like or unlike stereochemistry at the donor and the backbone atoms is related to differences in the spatial alignment of the bulky cycloalkyl rings in the diastereomeric complex cations [24a,b,25,44]: Major structural differences between δ-shaped [Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{[(\mathit{R})\text{-}Me(C_8H_{15}\text{-}\mathit{c})]_2}}$}]$^+$ (which is characterized by the *mismatched* combination of its *C* and *P* stereogenic elements; see footnote 'c' to Table 4) and its *matched* counterpart λ-[Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{[(\mathit{R})\text{-}Me(C_8H_{15}\text{-}\mathit{c})]_2}}$}]$^+$ arise from the contrasting orientations of these sterically demanding groups with respect to the P–Rh–P coordination plane; in both cases they shield the bottom left and top right quadrants of the ligand sphere, but are equatorially aligned in the former (torsion angles P–Rh–P–C_8H_{15}-*c*, 137.2° and 131.5°), whereas they point towards a more axial direction in the latter (torsion angles P–Rh–P–C_8H_{15}-*c*, 114.3° and 113.8°) (Scheme 26) [44].

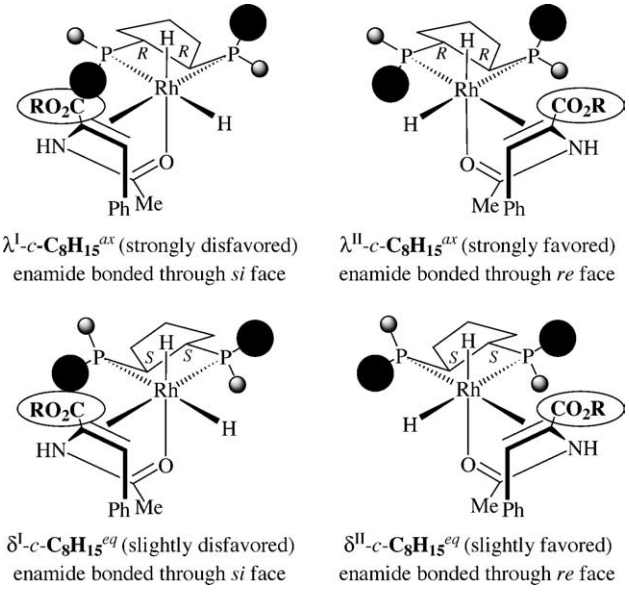
Following the quadrant model previously proposed by Knowles [2c], Gridnev and Imamoto [51] have recently presented evidence that any rhodium catalyst with *P*-chirogenic chelate phosphines, in which the difference in size between the terminal substituents is as distinct as in the $\mathbf{P_2^{[Me(C_8H_{15}\text{-}\mathit{c})]_2}}$ ligands, will favor the formation of (*R*) hydrogenation products *irrespective* of a λ or δ conformation of the backbone, if the more voluminous groups are located in the upper left and lower right quadrants, while opposite orientation, i.e., in the bottom left and top right quadrants will provoke (*S*) stereoselection, as observed for λ-[Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{[(\mathit{R})\text{-}Me(C_8H_{15}\text{-}\mathit{c})]_2}}$}]$^+$ and δ-[Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{[(\mathit{R})\text{-}Me(C_8H_{15}\text{-}\mathit{c})]_2}}$}]$^+$. This is because the migratory insertion of the enamide to form an alkyl hydride,



Scheme 26. Spatial orientation of cyclooctyl and methyl substituents in *C*,*P*-chirogenic matched λ-[Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{[(\mathit{R})\text{-}Me(C_8H_{15}\text{-}\mathit{c})]_2}}$}]$^+$ and mismatched δ-[Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{[(\mathit{R})\text{-}Me(C_8H_{15}\text{-}\mathit{c})]_2}}$}]$^+$ catalyst precursors [44].

which has been identified as the enantiodetermining irreversible step of asymmetric hydrogenation, is controlled in an enantiofacially discriminating fashion by repulsive interaction between the chelate ring of the substrate and the bulky *P*-substituents in short-lived diastereomeric dihydrido enamide intermediates [51] such as depicted in Scheme 27 for the RhH_2–substrate adducts of the two rhodium catalysts bearing the cyclooctyl(methyl)-substituted ligands with (1*R*,2*R*)-R_P,$R_{P'}$ and (1*S*,2*S*)-R_P,$R_{P'}$ configuration.

For δ-[Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{[(\mathit{R})\text{-}Me(C_8H_{15}\text{-}\mathit{c})]_2}}$}]$^+$, e.g., the diastereomer δ^{II}-*c*-$C_8H_{15}^{eq}$, containing the substrate



Scheme 27. Favored and disfavored cationic RhH_2–enamide intermediates derived from λ-[Rh(η^4-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{[(\mathit{R})\text{-}Me(C_8H_{15}\text{-}\mathit{c})]_2}}$}]$^+$ and δ-[Rh(η^4-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{[(\mathit{R})\text{-}Me(C_8H_{15}\text{-}\mathit{c})]_2}}$}]$^+$ precatalysts (after Gridnev and Imamoto [51]).

bonded through its *re*-face to give (*S*)-amino acids as observed, should be lower in energy than δ^{I}-*c*-$C_8H_{15}^{eq}$ because it is the smaller *P*-bound methyl group rather than the bulky cyclooctyl substituent that undergoes direct steric repulsion with the carboxyl residue of the enamide chelate ring. As a consequence of their pronounced equatorial alignment, however, the spatially expanded cyclooctyl rings of δ-[Rh(η⁴-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}]⁺ not only block the two down left and top right quadrants of the diastereomeric intermediates δ^{I} and δ^{II} but also 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; see Schemes 26 (right) and 27 (bottom) [24b,44]. This reduces the degree of favorable quadrant-blocking, thought to make diastereomer δ^{II}-*c*-$C_8H_{15}^{eq}$ more readily accessible than δ^{I}-*c*-$C_8H_{15}^{eq}$, and results in only little stereodiscriminating abilities of the complex. Matched catalyst λ-[Rh(η⁴-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{[(R)\text{-}Me(C_8H_{15}\text{-}c)]_2}}$}]⁺, on the other hand, differs in structure from its mismatched δ-shaped counterpart by a distinct axial arrangement of the cyclooctyl rings. This results in steric blocking of only the top right and bottom left quadrants, making λ^{II}-*c*-$C_8H_{15}^{ax}$ of Scheme 27 (top) definitely lower in energy than λ^{I}-*c*-$C_8H_{15}^{ax}$; see also Scheme 26 (left) [44].

The platinum complex δ-[PtI_2{(*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2\text{—}]_2\}_2}}$}], which served as a structural model of the matched catalyst δ-[Rh(η⁴-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2\text{—}]_2\}_2}}$}]⁺ (vide supra), possesses quadrant-blocking methyl groups at the 2,5 positions of the phospholane rings which show a decidedly axial alignment relative to the coordination plane in the upper left and lower right coordination quadrants (torsion angles P–Rh–P–$C^{2,5}$, −99.6°/−110.7°) [28]. According to the Gridnev/Imamoto rule, this arrangement should favor the formation of dihydride enamide intermediates which give high optical yields of the (*R*) hydrogenation products as observed. In contrast, the λ-[PtI_2{(*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2\text{—}]_2\}_2}}$}] diastereomer, which was used to model the structure of mismatched λ-[Rh(η⁴-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2\text{—}]_2\}_2}}$}]⁺, presents the same two methyl groups in the same two quadrants in equatorial orientation with respect to the coordination plane (torsion angles P–Rh–P–$C^{2,5}$, −131.1° each), which can safely be predicted to result in some unwanted deshielding of the top left and bottom right quadrants. As the location of the phospholane substituents in the coordination 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's top left and down right; small H's down left and top right) and as both rhodium analogues induce (*R*) stereoselection, it becomes clear that the two Rh–(*R*,*R*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2\text{—}]_2\}_2}}$ and Rh–(*S*,*S*)-$\mathbf{P_2^{\{[(R)\text{-}CH(Me)CH_2\text{—}]_2\}_2}}$ complexes also fit the aforementioned Gridnev/Imamoto rule for catalysts bearing *P*-chirogenic bis(phosphines) with substituents pairwise differing in size.

The observed enhancement of enantioselectivity achieved by changing the alignment of a large substituent from a more equatorial to a more axial orientation satisfies an early prediction formulated by Nagel as follows: "... to build a good catalyst for the hydrogenation of *N*-acylacrylic acid derivatives, it is necessary to have two large groups in the chelating diphosphine as axial as possible" [52].

4.4. Hydroformylation

In the presence of tin(II) chloride, the platinum complexes [$PtCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)], [$PtCl_2${*rac*-$\mathbf{P_2^{(OPh)_4}}$}], [Pt(Cl)(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)], [Pt(Cl)(CH_3){*rac*-$\mathbf{P_2^{(OPh)_4}}$}], [Pt(Cl)(CH_2Bu-*t*){*rac*-$\mathbf{P_2^{(OPh)_4}}$}], and [Pt(OSO_2CF_3)(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)] acted as catalysts for the hydroformylation of styrene, forming 2- and 3-phenylpropanal together with ethylbenzene. Except for [$PtCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)], they also catalyzed the consecutive hydrogenation of the primary propanals to alcohols. High regioselectivities towards 2-phenylpropanal (branched-to-normal ratios ≥91:9) were obtained in hydroformylations catalyzed by [$PtCl_2${*rac*-$\mathbf{P_2^{(OPh)_4}}$}] and [Pt(Cl)(CH_3)(*rac*-$\mathbf{P_2^{Ph_4}}$)], for which the influence of varied CO/H_2 partial pressures, catalyst-to-substrate ratios, and different reaction temperatures and times on the outcome of the catalytic reaction was studied. When tin-modified complexes (+)-[$PtCl_2${(*R*,*R*)-$\mathbf{P_2^{(OPh)_4}}$}], (−)-[$PtCl_2${(*S*,*S*)-$\mathbf{P_2^{(OPh)_4}}$}], and (+)-[Pt(Cl)(CH_3){(*S*,*S*)-$\mathbf{P_2^{Ph_4}}$}] were used as optically active catalysts, only low stereoselectivity for asymmetric hydroformylation (e.e. < 18%) was observed [21b].

Hydroformylations of styrene which were run in toluene at 40 °C under 50 bar of a 1:1 CO/H_2 synthesis gas mixture in the presence of 0.2 mol% of a rhodium complex of the type [Rh(η⁴-C_8H_{12})(*rac*-$\mathbf{P_2^{R_4}}$)]O_3SCF_3, where R = C_6H_5, C_6F_5, OC_6H_5, $OC_6H_3(CF_3)_2$-(3,5), $OC_6H_3F_2$-(2,6), $OC_6H_3F_2$-(3,5), or $OC_6H_2F_3$-(2,4,6), proceeded with extremely high chemoselectivity in that neither the formation of ethylbenzene nor the consecutive production of alcohols did occur. Regioselectivities for the branched aldehyde 2-phenylpropanal as high as 99:1 were achieved for the very electron-poor catalyst complexes with R = C_6F_5, $OC_6H_3F_2$-(2,6), or $OC_6H_3F_2$-(3,5). On the other hand, virtually no enantioselectivity for (*R*)- or (*S*)-PhCH(Me)CHO was observed if the enantiopure complexes [Rh(η⁴-C_8H_{12}){(*R*,*R*)-$\mathbf{P_2^{R_4}}$}]O_3SCF_3 with R = C_6H_5 or C_6F_5 and [Rh(η⁴-C_8H_{12}){(*S*,*S*)-$\mathbf{P_2^{R_4}}$}]O_3SCF_3 with R = C_6H_5, C_6F_5, OC_6H_5, $OC_6H_3(CF_3)_2$-(3,5), $OC_6H_3F_2$-(2,6), $OC_6H_3F_2$-(3,5), or $OC_6H_2F_3$-(2,4,6) were used as (pre)catalysts [23b].

4.5. Miscellaneous applications

In the presence of KOBu-*t* as activating base, the bis(phosphine)/aminophosphine-coordinated ruthenium complexes [$RuCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$){$Ph_2P(CH_2)_2NH_2$}] (Section 3.5; Scheme 11: **Xb**) and [$RuCl_2$(*rac*-$\mathbf{P_2^{Ph_4}}$)($Ph_2PCH_2CMe_2NH_2$)] (**XI**) were used as catalysts for the transfer hydrogenation of acetophenone with isopropanol as the hydrogen source. In C_6H_6/*i*-PrOH (1:1) at 50 °C, at substrate/catalyst/base ratios of 200:1:5, the conversions of

PhC(Me)=O to PhCH(Me)OH after 3 h were 97% for **Xb** and 53% for **XI**. The clear-cut drop in activity observed for **XI** was ascribed to hindered accessibility of the Ru–NH_2 bond for the ketone owing to steric shielding of the amino functions by the adjacent methyl substituents [35b].

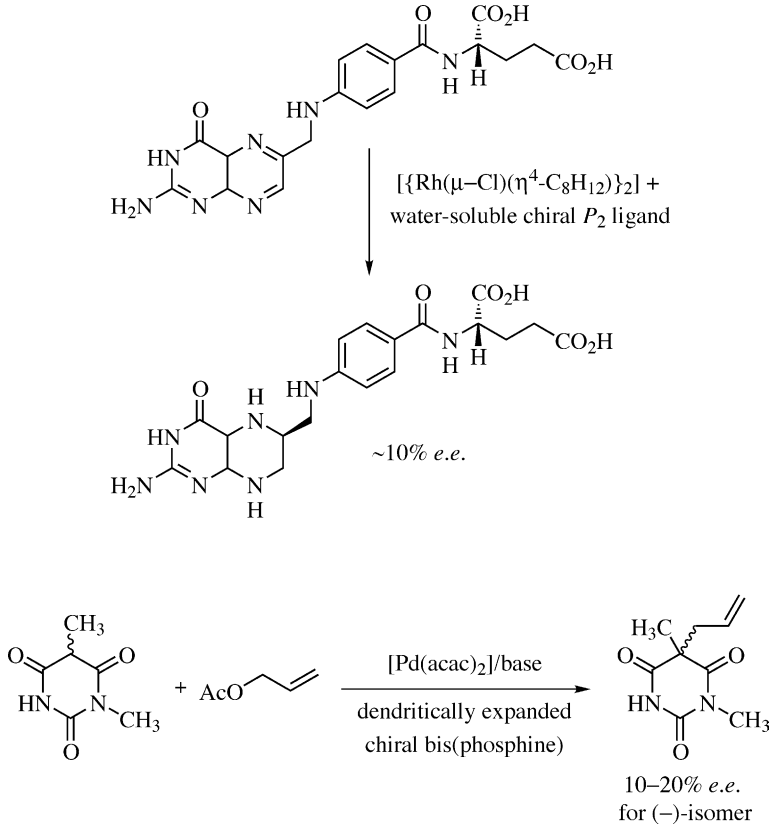
The complexes $[RuX_2(rac\text{-}\mathbf{P_2^{[C_5H_4N\text{-}(2)]_4}}\text{-}P,P,N)(PPh_3)]\cdot H_2O$, where X = Cl, Br, and I, respectively (Section 3.4; Scheme 10: **VIIIb**), effected the homogeneous catalytic hydrogenation of aldimines to amines. Under 1000 psi of H_2, in MeOH at ambient temperature and a substrate-to-catalyst ratio of 2000:1, the conversions of PhC(H)=NPh to $PhCH_2NHPh$ after 3 h were 80, 99, and 63% for the chloro, bromo, and iodo complexes, respectively. With the imine substrate $PhC(H)=NCH_2Ph$, under the conditions outlined before but for 1 h reaction time, the conversions to dibenzylamine were as low as 5% (X = Cl), 10% (X = Br), and 28% (X = I) [26b].

Promoted by 18-crown-6 as a phase transfer reagent, two in situ catalytic systems made up in toluene of $[\{Rh(\mu\text{-}Cl)(\eta^4\text{-}C_8H_{12})\}_2]$ and either of the two "octaborneol-bis(phosphines)" (*R*,*R*)- and (*S*,*S*)-$\mathbf{P_2^{[C_6H_3\{CH_2Obornyl\text{-}(1S)\}_2\text{-}(3,5)]_4}}$ (Section 2.3.1.2; Scheme 6), catalyzed the two-phase hydrogenation of an aqueous solution of sodium (*Z*)-α-acetamidocinnamate with e.e. of 60–80% for the (*S*) and (*R*) products, respectively, showing that the dendritically expanded ligands maintained a great deal of their high enantioselectivities known from monophasic hydrogenations (Section 4.3; Table 4). Conventional ligands such as (*R*,*R*)- and (*S*,*S*)-$\mathbf{P_2^{Ph_4}}$ suffered a great loss of their selectivities under biphasic conditions, giving the hydrogenation products only with 23% e.e. [22a,b].

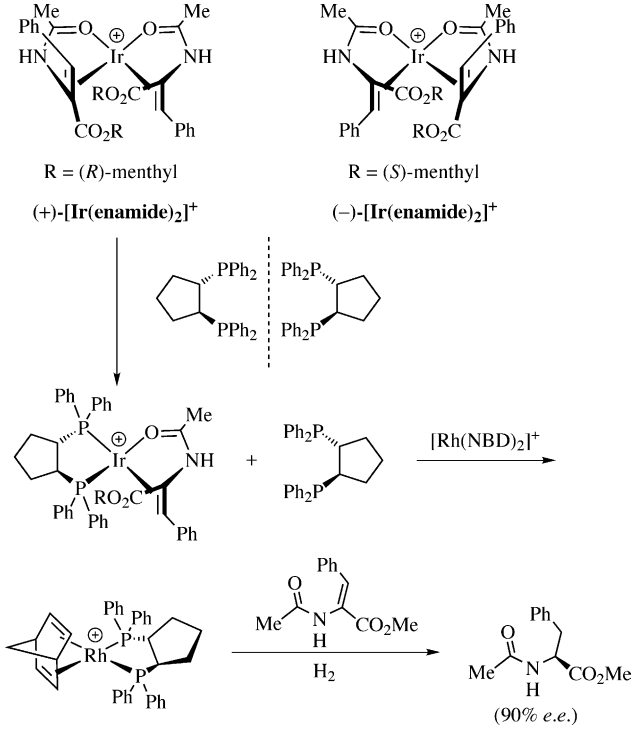
A water-soluble in situ catalyst prepared from $[\{Rh(\mu\text{-}Cl)(\eta^4\text{-}C_8H_{12})\}_2]$ and the hydroxymethyl-substituted ligand (*S*,*S*)-$\mathbf{P_2^{(CH_2OH)_4}}$ assisted the homogeneous hydrogenation of sodium (*Z*)-α-acetamidocinnamate in aqueous solution with 22% e.e. for the (*R*)-product [22a,b].

Water-soluble in situ catalysts composed of $[\{Rh(\mu\text{-}Cl)(\eta^4\text{-}C_8H_{12})\}_2]$ and (*S*,*S*)-$\mathbf{P_2^{(CH_2OH)_4}}$ or (*S*,*S*)-$\mathbf{P_2^{\{C_6H_3[CH(OH)(SO_3^-Na^+)]_2\text{-}(3,5)\}_4}}$ (the sulfite adduct of (*S*,*S*)-$\mathbf{P_2^{[C_6H_3(CHO)_2\text{-}(3,5)]_4}}$) were also used for the homogeneous hydrogenation in aqueous solution of the C=N double bonds of the pyrazine ring of folic acid to 5,6,7,8-tetrahydrofolic acid, where a new stereogenic center is formed at C-6 of the pteridine system (Scheme 28, top). The reactions proceeded rather slowly, producing diastereomeric excesses for the (6*S*,*S*) stereoisomer of ~10% [22c].

Reactions of the resolved bis(menthyl (*Z*)-α-acetamidocinnamate) iridium(I) complexes (+)-$[Ir\{O{=}C(Me)NHC[CO_2menthyl\text{-}(R)]{=}CHC_6H_5\}_2]BF_4$ and (−)-$[Ir\{O{=}C(Me)NHC[CO_2menthyl\text{-}(S)]{=}CHC_6H_5\}_2]BF_4$ with 2 equiv. of the racemic $\mathbf{P_2^{Ph_4}}$ bis(phosphine) in CH_2Cl_2 proceeded with high enantioselectivity giving $[Ir\{O{=}C(Me)NHC[CO_2menthyl\text{-}(R)]{=}CHC_6H_5\}\{(S,S)\text{-}\mathbf{P_2^{Ph_4}}\}]BF_4$ and $[Ir\{O{=}C(Me)NHC[CO_2menthyl\text{-}(S)]{=}CHC_6H_5\}\{(R,R)\text{-}\mathbf{P_2^{Ph_4}}\}]BF_4$



Scheme 28. Rh-catalyzed enantioselective hydrogenation of folic acid (top) [22c] and Pd-catalyzed enantioselective allylation of 1,5-dimethyl barituric acid (bottom) [22a,b].



Scheme 29. Iridium–bis(enamide)-induced in situ resolution of *rac*-$\mathbf{P_2^{Ph_4}}$ for enantioselective homogeneous hydrogenation [53].

and leaving 1 equiv. of the enantiomers (*R*,*R*)- and (*S*,*S*)-$\mathbf{P_2^{Ph_4}}$ as free ligands in solution. Adding [Rh(norbornadiene)$_2$]BF_4 (0.8 equiv.) and methyl (*Z*)-α-acetamidocinnamate (50–100 equiv.) followed by stirring under H_2 thus gave the methyl ester of *N*-acetyl-(*S*)-phenylalanine in 90% e.e. starting with the dextrorotatory bis(enamide) compound and the (*R*) hydrogenation product in 91% e.e. starting with the laevorotatory precursor complex (Scheme 29) [53].

A number of experiments aiming at the enantioselective hydrosilylation of acetophenone with diphenylsilane were run in the neat substrate using in situ catalytic systems composed of [{Rh(μ-Cl)(η^4-C_8H_{12})}$_2$] and an tetra- or octaimine type ligand (*S*,*S*)-$\mathbf{P_2^{[C_6H_4CH{=}NR\text{-}(2)]_4}}$ and (*S*,*S*)-$\mathbf{P_2^{[C_6H_3(CH{=}NR)_2\text{-}(3,5)]_4}}$ (Section 2.3.1.2; Scheme 5). At a substrate-to-catalyst ratio of 400:1, the "octaimine-bis(phosphine)" bearing eight aldimine groups derived from D-(−)-valinol (R = (*R*)-CH(CH$_2$OH)Pr-*i*) afforded the highest e.e. of 23% (*S*). The diastereomer with eight L-(+)-valinol-derived substituents (R = (*S*)-CH(CH$_2$OH)Pr-*i*) furnished the same (*S*)-enantiomeric reduction product in only 12% e.e., indicating a rather strong influence of the peripheral groups on the outcome of the catalysis. With eight (*R*)-CH(Me)C_6H_{11}-*c* residues R in the periphery of the "octaimine-bis(phosphine)", an e.e. of 19% (*S*) was obtained. The "tetraimine-bis(phosphine)" ligands (*S*,*S*)-$\mathbf{P_2^{[C_6H_4CH{=}NR\text{-}(2)]_4}}$, where R = (*R*)- or (*S*)-CH(CH$_2$OH)Pr-*i*, induced only low optical yields (3–6%) of (*R*)-PhCH(Me)OH [22a,b].

The 1,3-diphenylallyl complex [Pd(η^3-PhCHCHCHPh){(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$}]PF_6 was used as a catalyst for the Pd-assisted alkylation of the racemic allylic acetate PhCH=CHCH(OAc)Ph with dimethyl malonate as a soft carbon nucleophile, which gave the substitution product (*S*)-PhCH=CHCH{CH(CO$_2$Me)$_2$}Ph in 85% e.e. [47].

The Pd-catalyzed enantioselective allylation of 1,5-dimethyl barbituric acid with allyl acetate according to Scheme 28 (bottom) was studied using several in situ catalysts made up of palladium acetylacetonate and different dendritically expanded P_2 ligands of the "tetra- or octaimine-bis(phosphine)" and "octaborneol-bis(phosphine)" types (*S*,*S*)-$\mathbf{P_2^{[C_6H_4CH{=}NR\text{-}(2)]_4}}$, (*S*,*S*)-$\mathbf{P_2^{[C_6H_3(CH{=}NR)_2\text{-}(3,5)]_4}}$, and (*R*,*R*)- or (*S*,*S*)-$\mathbf{P_2^{[C_6H_3\{CH_2Obornyl\text{-}(1S)\}_2\text{-}(3,5)]_4}}$, respectively. The "octaimines" with R = (*R*)-CH(CH$_2$OH)Pr-*i*, (*S*)-CH(CH$_2$OH)Pr-*i*, and (*S*)-CH(CH$_2$OH)Bu-*t* induced e.e. in the range of 10–20% for the laevorotatory allylation product, showing that the direction of optical induction was exclusively determined by the (1*S*,2*S*) architecture of the chelate backbone. Only marginal enantioselectivities were displayed by the two diastereomeric "octaborneols", the (*R*)- and (*S*)-valinol-derived "tetraimines", and the "octaimine bis(phosphine)" with R = (*R*)-CH(Me)C_6H_{11}-*c* [22a,b].

The enantioselective extrusion of carbon dioxide from the linear or branched allyl phenyl carbonates MeCH=CHCH$_2$OCO$_2$Ph and H$_2$C=CHCH(Me)OCO$_2$Ph, respectively, produced the allyl phenyl ethers MeCH=CHCH$_2$OPh and H$_2$C=CHCH(Me)OPh in a close to 4:1 molar ratio with ∼10–14 e.e. for the (*S*) enantiomer of the branched decarboxylation product, if catalyzed by [Pd$_2$(PhCH=CHC(O)CH=CHPh)$_3$]/(*R*,*R*)-$\mathbf{P_2^{Ph_4}}$ [54].

5. Concluding remarks

Since the first synthesis and resolution of *rac*-$C_5H_8(PPh_2)_2$ by Green and co-workers a broad spectrum of bis(phosphines) based on the 1,2-*trans*-disubstituted cyclopentane backbone has become available. The convenient structural modification of the compounds by a modular approach allows diverse $C_5H_8(PR_2)_2$ ligands with widespread substitution patterns to be readily isolated in optically active form. There exists a large number of mono-, di-, and oligonuclear metal complexes bearing the bidentates either as racemates or as resolved enantiomers in chelating or bridging coordination. Successful applications of the ligands to homogeneous catalysis so far include Ni-assisted enantioselective Grignard cross-coupling reactions, regio-selective (but not enantioselective) hydroformylations of styrene with rhodium catalysts and, particularly, Rh-catalyzed asymmetric ⩾C=C⩽ hydrogenations.

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for all previously unpublished structures collected in Tables 2 and 3 of this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 256731 (*rac*-$\mathbf{P_2^{(NC_5H_{10}\text{-}\mathit{c})_4}}$), 256721 ((*R*,*R*)-$\mathbf{P_2^{Ph_4}}$), 256722 ((*S*,*S*)-$\mathbf{P_2^{Ph_4}}$), 256720 (**XII**), 237811 (**XIII**), 256724 (**XVIIc**), 256725 (**XVIId**), 256723 (**XVIIe**), 256729 (**XVIIIc**), 256726 (**XIXi**), 256727 (**XIXk**), 256728 (**XIXl**), 256719 (**XXIIa**), and 256730 (**XXIVb**). Copies of the data may be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: (intern.)+44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).

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