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New Enantiopure P,P-Bidentate Bis(diamidophosphite) Ligands. Application in Asymmetric Rhodium-Catalyzed Hydrogenation

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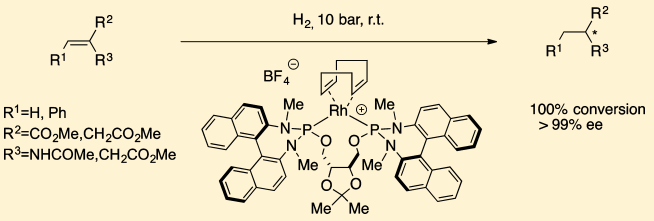
Supporting Information

ABSTRACT: Two series of new enantiopure bidentate bis(diamidophosphite) ligands with diazaphospholidine and diazaphosphepine heterocyclic backbones were prepared. The ligands have a highly modular structure, which is well suited to the synthesis of a small library of compounds. Preparation was accomplished by the successive addition of enantiomerically pure substituted diamines (*N*,*N*′-dibenzylcyclohexane-1,2-diamine (**1**), *N*,*N*′-dimethylcyclohexane-1,2-diamine (**2**), and *N*,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine (**3**)) and enantiomerically pure diols (butanediol (**a**), cyclohexanediol (**b**), di-*O*-isopropylidenethreitol (**c**), and binaphthol (**d**)) to phosphorus trichloride. The corresponding bis(diamidophosphite) selenides were prepared, and the $^{1}J_{PSe}$ values were calculated in order to evaluate the σ-donor ability of the new ligands. The cationic Rh(I) complexes [Rh(COD)(P,P)]BF_4 were synthesized with 8 of the 12 new bis(diamidophosphite) ligands. The complexes were used as catalytic precursors for the asymmetric hydrogenation of benchmark substrates, namely methyl α-acetamidoacrylate (**4**), methyl (*Z*)-α-acetamidocinnamate (**5**), and dimethyl itaconate (**6**). The influence of the nature of both the terminal and bridging fragments of the bis(diamidophosphite) ligands on the asymmetric induction is discussed. Most proved to be effective catalysts for the process, attaining total conversion and excellent enantioselectivity (>99% ee) with the complex containing the (*R*;R_{al},R_{al};*R*)-**3c** ligand in the hydrogenation of the three substrates. The best performing catalytic precursor [Rh(COD)-((*R*;R_{al},R_{al};*R*)-**3c**)]BF_4 was tested in the hydrogenation of selected cyclic enamides (**7**−**9**) and β-acetamidoacrylate (**10**).



INTRODUCTION

The design and synthesis of efficient chiral phosphorus ligands has played an important role in the development of transition-metal-catalyzed asymmetric reactions.[1] Although phosphines with either alkyl or aryl groups were the first effective phosphorus donor ligands reported, nowadays a great variety of P−O and P−N bond-containing ligands have been demonstrated to have the capacity to accelerate and enantioselectively catalyze a number of pivotal organic processes. This class of ligands has the advantage of being highly modular in nature and readily accessible via simple condensation reactions. The vast majority of such ligands contain a cyclic structure in which the phosphorus atom is a component of a heterocyclic ring; a feature that contributes to their stability and simplifies their preparation.[2]

Phosphonite (2P−O/1P−C), phosphite (3P−O), and phosphoramidite (2P−O/1P−N) ligands containing a heterocyclic ring derived from enantiopure chiral diols (i.e., BINOL, TADDOL) and a P−C, P−O, or P−N exocyclic bond have been found to have a wide scope in metal-catalyzed asymmetric transformations. Among them, the ones that stand out the most are conjugate addition reactions,[3−5] Ir-catalyzed allylation,[6−8] Pd-allylic alkylation,[9,10] asymmetric hydrovinylation of vinylarenes,[11,12] and Rh-catalyzed asymmetric hydrogenation.[13−18] Less research has been done on the synthesis and application of chiral diamidophosphite ligands (2P−N/1P−O) containing heterocyclic rings derived from enantiopure chiral diamines. Such compounds are expected to have different activities and/or enantioselectivities in comparison to phosphonites, phosphoramidites, or phosphites when applied as ligands in asymmetric catalysis. The substitution of oxygen atoms by nitrogen should increase the electron density at the phosphorus atom, and the presence of different substituents on the nitrogen will create more steric bulk around the phosphorus.

Only a few chiral diamines have been used as scaffolds in the synthesis of the diamidophosphite ligands (Figure 1). The in

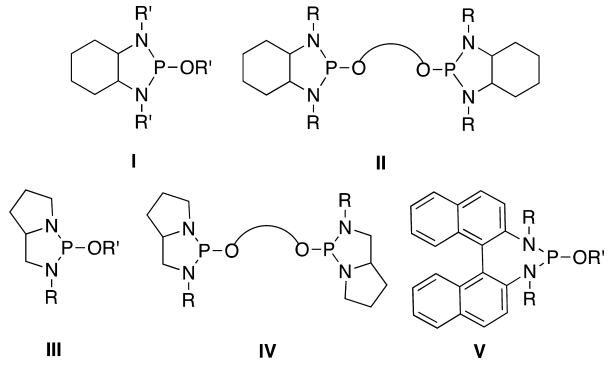


Figure 1. General structures of reported diamidophosphite ligands.

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situ formation of diamidophosphites (**I** and **II** in Figure 1) derived from enantiopure 1,2-cyclohexyldiamine and racemic chiral alcohols has long been reported as a method for analyzing the enantiomeric composition of chiral alcohols by ^{1}H and ^{31}P NMR spectroscopy,[19] but the coordination chemistry of these kinds of ligands has only scarcely been reported in the literature. Similar enantiopure ligands have been applied to a limited range of asymmetric catalyzed transformations, such as the hydrovinylation of styrene,[20] Pd-allylic substitution,[21] and more recently vinyl-substituted trimethylenemethane [3 + 2] cycloaddition.[22]

A family of P-chiral monodentate and bidentate diamidophosphite ligands, containing diazaphospholidine rings based on 2-(anilinomethyl)pyrrolidine as the heterocyclic fragment and several alcohols and diols such as BINOL, benzyltartarimide, and 1,4:3,6-dianhydromannitol have previously been synthesized (**III** and **IV** in Figure 1). The corresponding organometallic precursors have been prepared and tested in asymmetric Pd-catalyzed allylic substitution and Rh-catalyzed hydrogenation.[23,24] It should be mentioned that, unlike phosphoramidite ligands based on BINOL, monodentate diamidophosphites are worse stereoselectors than bidentate chelating agents in Rh-catalyzed hydrogenation.

A limited number of ligands with a P-containing heterocyclic ring derived from an axially chiral 1,1′-binaphthyl-2,2′-diamine have previously been described (**V** in Figure 1). Reetz reported the corresponding monodentate diamidophosphite ligand with a methoxy exocyclic fragment that was tested in the Rh-catalyzed hydrogenation of the itaconic acid dimethyl ester. Low conversion and enantioselectivity were achieved.[25] Recently, we reported the synthesis of a new monodiamidophosphite ligand based on the same backbone and a chiral bornyloxy group that was tested in hydrovinylation reactions with encouraging results.[20] A set of closely related chiral phosphorus triamides based on the 1,1′-binaphthyl-2,2′-diamine backbone and their application in the copper-catalyzed conjugate addition of diethylzinc to cyclohex-2-enone and the nickel-catalyzed hydrovinylation of styrene that yield good activities and chemoselectivities and moderate enantioselectivities in both reactions have also previously been described.[26]

On the basis of the observation that chiral bidentate diamidophosphites are effective ligands for the Rh-asymmetric hydrogenation,[23] we describe here the synthesis of a series of modular chiral bis(diamidophosphite) compounds with the general formula shown in Figure 2, which have been designed to ensure systematic modifications of the ligands. Their corresponding cationic rhodium(I) complexes were prepared and fully characterized. They were tested in asymmetric hydrogenation of the benchmark substrates: methyl α-acetamidoacrylate, methyl (*Z*)-α-acetamidocinnamate, and dimethyl itaconate. The best catalytic precursor was tested in the hydrogenation of some challenging prochiral cyclic enamides.

Enantiomerically pure dimethyl-1,1′-binaphthyldiamine and disubstituted cyclohexyldiamine were used to form the heterocyclic rings (diazaphosphepine and diazaphospholidine, respectively) as the terminal fragments, and different enantiopure diols were used as the bridging fragments. For the same terminal heterocyclic ring, the different bridging fragments allowed us to study the effect of rigidity and length of the bridge on the activity and enantioselectivity of the catalytic process. Ligands with different substituents on the nitrogen and identical bridging fragments were prepared to study the influence of the steric bulk close to the phosphorus atom. Bis(diamidophosphites) with an identical bridging fragment and different heterocycles were prepared with the aim of studying the influence of the terminal fragment. Furthermore, both the terminal and bridging units with different absolute configurations were combined in order to study the matching–mismatching effects on the sense and extent of the asymmetric induction of the catalyzed reactions.

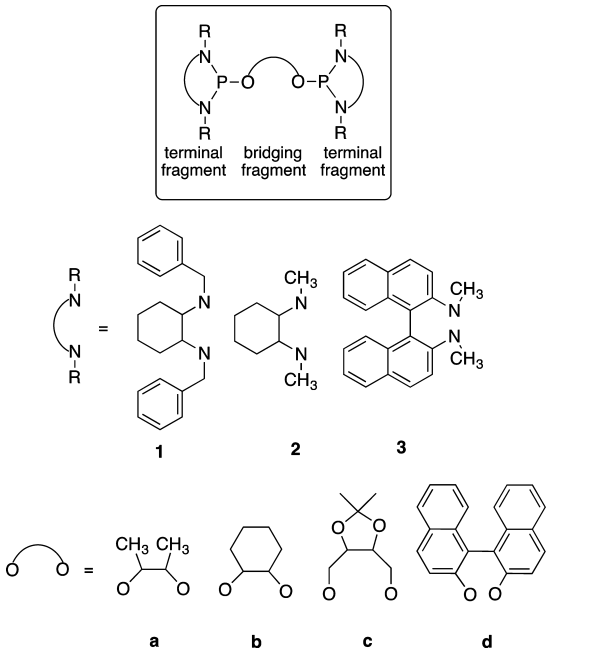

Figure 2. Building blocks for the synthesis of the new bis(diamidophosphite) ligands and numbering of the terminal and bridging fragments.

RESULTS AND DISCUSSION

Synthesis of Bis(diamidophosphite) Ligands. The new homochiral bidentate diamidophosphite (P,P) ligands were prepared via two consecutive condensation reactions from enantiomerically pure diamines and diols in the presence of a base, following procedures reported in the literature with slight modifications.[20,22] The first step in the synthesis is the formation of the heterocyclic terminal fragment [N_2P] by the reaction of the diamine with PCl_3 (Scheme 1). This process is accompanied by a favorable entropy change and is favored in the presence of a base acting as an HCl acceptor.

Reaction conditions such as reaction time, molar ratio, the length of the addition of the reagents, and the nature of the HCl scavenger were appropriately chosen to ensure the formation of the desired products with high yields. Different reaction conditions were used for bis(diamidophosphites) with terminal rings derived from cyclohexyldiamine and those derived from binaphthyldiamine. The reaction of phosphorus trichloride with the enantiomerically pure disubstituted cyclohexyldiamine (*R*,*R*)-**1** or (*R*,*R*)-**2** in the presence of an excess of Et_3N led to the formation of the chlorodiazaphospholidine derivatives ((*R*,*R*)-**1Cl** or (*R*,*R*)-**2Cl**) after 2 h of stirring. The condensation reaction between PCl_3 and the diamine *N*,*N*′-dimethylbinaphthyldiamine ((*R*)-**3** or (*S*)-**3**) required a longer reaction time (20 h) and *i*-Pr_2EtN as the hydrogen chloride acceptor to ensure complete formation of the chlorodiazaphosphepine species (*R*)-**3Cl** or (*S*)-**3Cl**. The synthesis of chloride

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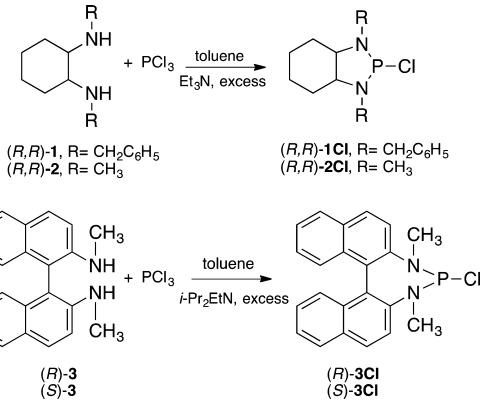
Scheme 1. Synthesis of Chloride Derivatives

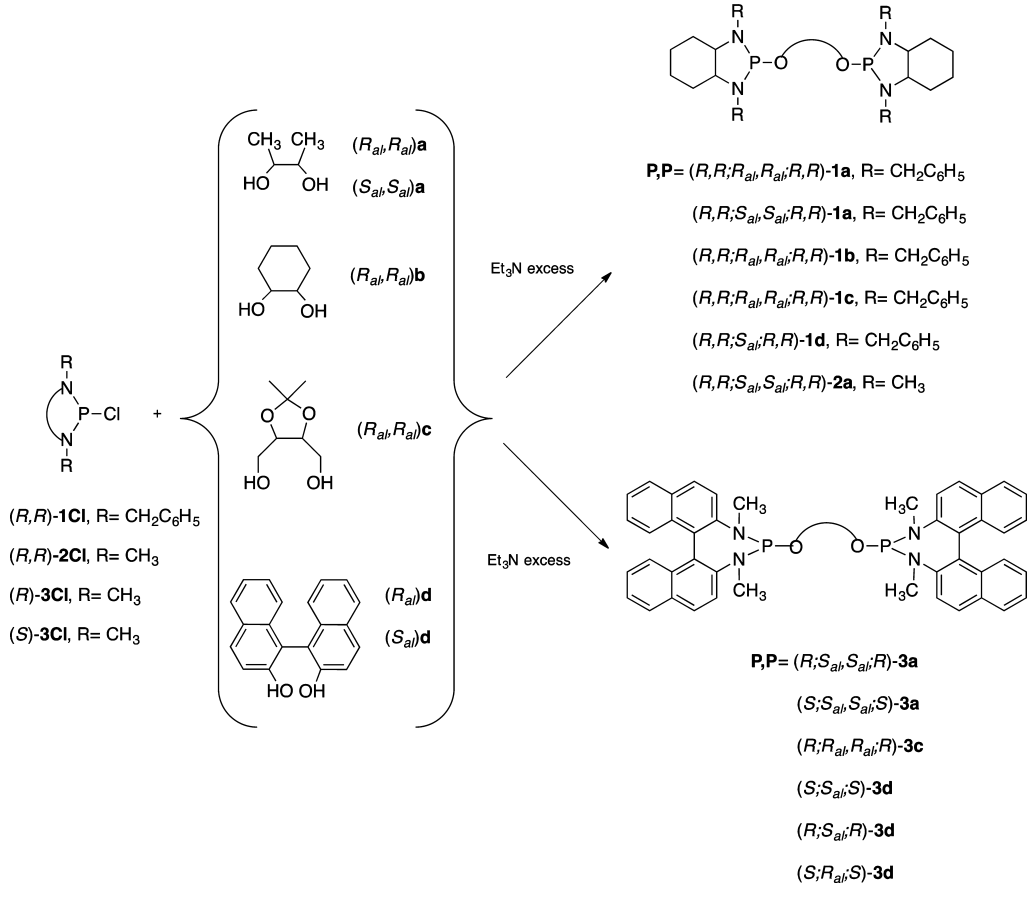


derivatives **1Cl**, **2Cl**, and **3Cl** was monitored by phosphorus NMR spectroscopy, and they were used immediately because of their sensitivity to oxygen and moisture.[20−28]

The second step is the formation of the [POC_nOP] bridge between the two terminal rings by condensation of the heterocyclic chloride derivative and the corresponding enantiomerically pure chiral diol in the presence of a base (Scheme 2).

To a solution of 2 equiv of the chlorophospholidine **1Cl** and excess Et_3N was added 1 equiv of the corresponding chiral alcohol ((R_{al},R_{al})-**a**, (S_{al},S_{al})-**a**, (R_{al},R_{al})-**b**, (R_{al},R_{al})-**c**, or (S_{al})-**d**). After 4 h of stirring at room temperature, bis(diamidophosphite) ligands with a diazaphospholidine backbone $(R,R;R_{a1},R_{a1};R,R)$-**1a**, $(R,R;S_{a1},S_{a1};R,R)$-**1a**, $(R,R;R_{al},R_{al};R,R)$-**1b**, $(R,R;R_{al},R_{al};R,R)$-**1c**, and $(R,R;S_{al};R,R)$-**1d** were obtained. Slightly different conditions had to be applied for the synthesis of bis(diamidophosphite) $(R,R;S_{al},S_{al};R,R)$-**2a** and ligands with a diazaphosphepine backbone $(R;S_{al},S_{al};R)$-**3a**, $(S;S_{al},S_{al};S)$-**3a**, $(R;R_{al},R_{al};R)$-**3c**, $(S;S_{al};S)$-**3d**, $(R;S_{al};R)$-**3d**, and $(S;R_{al};S)$-**3d**. The reaction of (R,R)-**2Cl**, (R)-**3Cl**, and (S)-**3Cl** with the stoichiometric amount of the corresponding chiral alcohol requires the addition of DMAP[8] as a catalyst and excess of Et_3N as the HCl scavenger. In this case, the use of DMAP proved to be advantageous, as it decreased the reaction time and also reduced the amount of byproducts, as reported previously.[29,30] Moreover, slow addition of the diol in three portions led to better yields. These conditions were particularly important in the synthesis of diamidophosphite **3a**, as 1,3-butanediol (**a**) tends to cyclize into a dioxaphospholidine derivative with the consequent cleavage of the diazaphospholidine ring.[19c] Bis(diamidophosphite) ligands were obtained as viscous oils for **1a−d** and **2a** and as yellow solids for **3a,c,d**. The new compounds were found to be easily hydrolyzed and oxidized in open air but could be stored under inert conditions at room temperature for at least a few months with little degradation. The products from hydrolysis or oxidation appeared in the δ ∼17−25 ppm range in the ^{31}P NMR spectra. As extensive manipulation led to ligand decomposition, they were used without further purification both in the formation of the corresponding rhodium cationic complexes and in asymmetric hydrogenation reactions, when they were carried

Scheme 2. Synthesis of New Bis(diamidophosphite) Ligands



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out in situ. The progress of the reactions and the purity of the ligands were easily monitored by ^{31}P NMR spectroscopy.

The new ligands were characterized by mass spectrometry and ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. ^{31}P NMR data are shown in Table 1. The ^{31}P chemical shift values are in the same range as those reported for analogous monodentate diamidophosphites[20,25] and mainly depend on the diamine scaffold. With a cyclohexyldiamine terminal fragment (**1a−d**, **2a**), the δ values were in the δ ~136−139 ppm range; while for ligands containing binaphthyldiamine (**3a,c,d**), a deshielding effect occurs around the phosphorus, bringing the δ values downfield to the δ ~168−178 ppm region. A small influence of the bisalkoxy bridge was also observed. Slightly different chemical shifts were found for the diastereoisomers of the same ligand, (*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)-**1a** and (*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)-**1a**, (*R;S*$_{al}$,*S*$_{al}$;*R*)-**3a** and (*S;S*$_{al}$,*S*$_{al}$;*S*)-**3a**, and (*S;S*$_{al}$;*S*)-**3d** and (*R;S*$_{al}$;*R*)-**3d**, showing that the phosphorus atom experiences different environments in each diastereoisomer.[19b,d]

Table 1. ^{31}P NMR Data[a] for P,P Ligands and Cationic Rhodium(I) Complexes

P,P	δ(P,P)[b]	δ((P,P)-Se$_2$)[c]	$^{1}J_{PSe}$((P,P)-Se$_2$)	δ([Rh(COD)(P,P)]BF$_4$)[d] ($^{1}J_{PRh}$)
(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)-**1a**	138.2	86.6	888.9	136.8[b] (d, 216.2)
(*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)-**1a**	137.6	87.3	887.7	139.8[b] (d, 228.3)
(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)-**1b**	136.5	85.6	893.8	134.8 (d, 216.2)
(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)-**1c**	136.3	88.2	890.6	125.0 (d, 227.1)
(*R,R;S*$_{al}$;*R,R*)-**1d**	139.3	81.5	920.5	
(*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)-**2a**	139.1	87.0	889.0	134.0 (d, 228.3)
(*R;S*$_{al}$,*S*$_{al}$;*R*)-**3a**	178.3	91.4	882.4	130.7 (d, 228.3)
(*S;S*$_{al}$,*S*$_{al}$;*S*)-**3a**	176.6	89.9	887.3	
(*R;R*$_{al}$,*R*$_{al}$;*R*)-**3c**	168.9	91.5	892.0	129.4 (d, 227.1)
(*S;S*$_{al}$;*S*)-**3d**	173.6	82.6	913.6	
(*R;S*$_{al}$;*R*)-**3d**	174.6	85.2	919.0	132.0 (d, 222.2)

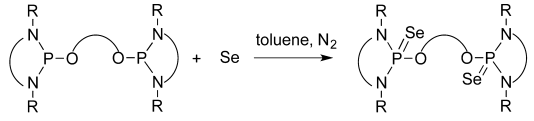
[a]Conditions for $^{31}P\{^{1}H\}$ NMR: 298 K, 101.2 MHz, δ in ppm, coupling constants in Hz. [b]$CDCl_3$. [c]Toluene. [d]CH_2Cl_2/toluene.

In order to unequivocally assign ^{1}H NMR spectra, it was necessary to undertake a two-dimensional HSQC experiment. Those ligands derived from benzylcyclohexyldiamine, **1a−d**, exhibited four signals corresponding to the diastereotopic benzylic protons, each of them coupled to the other geminal proton and to the phosphorus atom. Consequently, they appeared as four different signals with a triplet, doublet of doublet, or overlapped multiplet structure depending on the relative values of J_{HH} and J_{PH}, although usually $J_{HH} > J_{PH}$ as reported for other similar ligands.[20,27] Protons bonded to the cyclohexyl chiral carbon atoms always appeared as two multiplets, in contrast to one multiplet in the parent free amine. In bis(diamidophosphite) ligands with *N,N′*-dimethylcyclohexyldiamine and *N,N′*-dimethylbinaphthyldiamine, the *N*-methyl substituents appeared as two different doublets, showing coupling with the phosphorus atom. All these data suggest that the new bidentate diamidophosphite ligands show C_2 symmetry and that the local C_2 symmetry of the free diamine is lost. ^{13}C NMR spectra of the new compounds showed very different coupling constants $^{2}J_{CP}$ (~40, ~20 Hz) for the two carbon atoms of the diamine substituents NCH_3 and $NCH_2C_6H_5$. These data show that the amino substituents of the heterocyclic ring adopt different orientations with respect to the phosphorus lone pair, as reported.[23]

Selenide Derivatives. Since both reactivity and selectivity in catalytic processes are controlled by steric and electronic factors, it is expected that phosphorus ligands with different basicities and different steric requirements will give rise to different results. A simple way to evaluate the electron-donating ability of phosphorus toward metal acceptors is based on the magnitude of the $^{1}J(^{77}Se-^{31}P)$ coupling of selenide derivatives. It is known that the respective coupling constants increase as the groups attached to the phosphorus become more electron withdrawing, indicating an increased σ character of the phosphorus lone pair and forming an apparently weaker donor to metals.[31]

The bis(diamidophosphite)diselenides (**1a−d**)-Se$_2$, **2a**-Se$_2$, and (**3a,c,d**)-Se$_2$, were prepared by simply stirring the phosphorus compounds with an excess of elemental selenium in toluene at room temperature for 24 h (Scheme 3).

Scheme 3. Synthesis of Selenide Derivatives



P,P= 1(a - d), 2a, 3(a, c, d) (P,P)-Se$_2$= 1(a - d)-Se$_2$, 2a-Se$_2$, 3(a, c, d)-Se$_2$

The diselenide compounds were characterized in situ by ^{31}P NMR spectroscopy. In each case a single new resonance that exhibited coupling to ^{77}Se, at fields higher than those for free bis(diamidophosphites), was observed (Table 1). The ^{31}P NMR chemical shift of all the bis(diamidophosphite) selenides occurs in a narrow range around δ 80−90 ppm. In contrast, free bis(diamidophosphite) ligands with a diazaphospholidine backbone (**1a−d**, **2a**) showed δ values at around 140 ppm, while for those with a diazaphosphepine backbone (**3a,c,d**) it was approximately 170 ppm.

The coupling constant values, $^{1}J_{SeP}$, for the new selenide are close to those reported for similar monodentate diamidophosphites[20] showing a σ-donor character between phosphines and phosphites (reported values[31d] for PPh_3 phosphine and $P(OPh)_3$ phosphite are $^{1}J_{SeP}$ = 745 Hz and $^{1}J_{SeP}$ = 1039 Hz, respectively). From the magnitude of $^{1}J_{SeP}$ values it can be seen that there are no significant differences between the selenides containing different terminal rings and the same bridging fragment. Within compounds with an identical heterocycle, the highest $^{1}J_{SeP}$ value was observed when the binaphthol group was acting as the bridging fragment. Presumably the electron-withdrawing character and the stereochemical requirements of the binaphthol fragment reduce the σ-donor ability of the ligands **1d** and **3d**. The $^{1}J_{SeP}$ values also had interesting stereochemical dependencies; thus, different diastereoisomers showed different values for $^{1}J_{SeP}$, especially between selenides with terminal fragments derived from binaphthyldiamine: (*R;S*$_{al}$,*S*$_{al}$;*R*)-**3a**, (*S;S*$_{al}$,*S*$_{al}$;*S*)-**3a** and (*S;S*$_{al}$;*S*)-**3d**, (*R;S*$_{al}$;*R*)-**3d**.

Synthesis of Rhodium(I) Complexes. Rhodium complexes, [Rh(COD)(P,P)]BF$_4$, with 8 of the 12 novel bis(diamidophosphites) (P,P = (*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)-**1a**, (*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)-**1a**, (*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)-**1b**, (*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)-**1c**, (*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)-**2a**, (*R;S*$_{al}$,*S*$_{al}$;*R*)-**3a**, (*R;R*$_{al}$,*R*$_{al}$;*R*)-**3c**, and (*R;S*$_{al}$;*R*)-**3d**) were prepared. The complexes were synthesized by reaction at room temperature of a dichloromethane solution of the cationic complex [Rh(COD)$_2$]BF$_4$ and a stoichiometric

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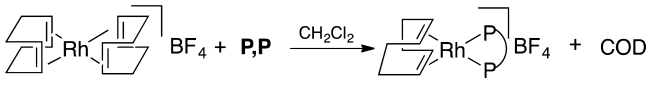
amount of the corresponding diamidophosphite ligand. Free COD was added in order to dissolve the $[Rh(COD)_2]BF_4$ complex in CH_2Cl_2 when it was not freshly prepared (Scheme 4).

Scheme 4. Synthesis of Cationic Rhodium(I) Complexes



P,P= (*R*,*R*;S_{al},S_{al};*R*,*R*)-**1a**
(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1a**
(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1b**
(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1c**
(*R*,*R*;S_{al},S_{al};*R*,*R*)-**2a**
(*R*;S_{al},S_{al};*R*)-**3a**
(*R*;R_{al},R_{al};*R*)-**3c**
(*R*;S_{al};*R*)-**3d**

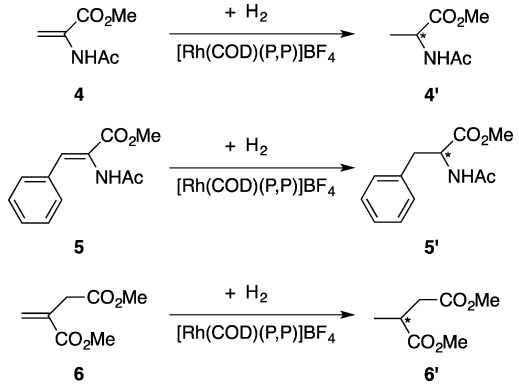
The new compounds are yellow solids that were found to be stable under an inert atmosphere at room temperature and soluble in common organic solvents. They were characterized in the solid state by elemental analysis and/or mass spectrometry. The mononuclear character of the complexes was confirmed by HRMS/ESI spectrometry, which in all cases showed molecular ions corresponding to the $[Rh(COD)(P,P)]^+$ and $[Rh(P,P)]^+$ cations. ^1H and ^{31}P NMR spectroscopy allowed us to characterize these complexes in solution. The ^{31}P NMR spectral data are summarized in Table 1. The spectra show one doublet with a $^1J_{PRh}$ value of between 219 and 228 Hz, similar to those reported in the literature[24,25,32,33] for cationic rhodium complexes with a cis arrangement of two phosphorus atoms. The phosphorus chemical shifts of complexes with diamidophosphite ligands containing a diazaphospholidine terminal fragment (**1a−c**, **2a**) were at values similar to that of the free ligand, but for complexes with diazaphosphepine terminal fragment (**3a,c,d**) the signal lay upfield.

Two-dimensional NMR heterocorrelation $^1H-^{13}C$ experiments were important to assign the different signals of the ^1H spectra, in particular for the complexes $[Rh(COD)((R,R;S_{al},S_{al};R,R)$-**1a**$)]BF_4$, $[Rh(COD)((R,R;R_{al},R_{al};R,R)$-**1c**$)]BF_4$, and $[Rh(COD)((R;S_{al},S_{al};R)$-**3a**$)]BF_4$. Complexes with ligands containing the dibenzylcyclohexyldiamine terminal fragment, **1a−c**, showed four signals for the benzylic protons, usually overlapped. Complexes with the dimethylbinaphthyldiamine terminal fragment, **3a,c,d**, showed all the proton signals shifted to fields lower than those of the free ligand. For the methyl substituents of the heterocycle, two different doublets ($^1J_{HP}$ = 8 and $^1J_{HP}$ = 12 Hz) were observed. All the Rh(I) complexes showed two groups of signals between 5.79 and 4.59 ppm and between 2.45 and 1.86 ppm for the methynic and methylenic groups, respectively, of the 1,5-cyclooctadiene ligand. All these data confirm that the complexes with the new diamidophosphite ligands retain the C_2 symmetry of the free bidentate ligand in solution.

No stable cationic rhodium complex with the (*R*,*R*;S_{al};*R*,*R*)-**1d** ligand could be isolated under the described conditions. The reaction was monitored by ^{31}P NMR spectroscopy. A $CDCl_3$ (10 mL) solution of (*R*,*R*;S_{al};*R*,*R*)-**1d** with $[Rh(COD)_2]BF_4$ (1 equiv) showed a predominant doublet centered at δ 118.2 ppm with a coupling constant $^1J_{PRh}$ of 234 Hz and a minor singlet at 20 ppm assigned to oxidized bis(diamidophosphite). Any attempt to isolate the rhodium complex resulted in the rapid disappearance of the doublet signal and the formation of bis(diamidophosphite) oxide, showing the high instability of the rhodium complex. The same behavior has been reported for cationic rhodium(I) complexes bearing related ligands.[34] The poor σ-donor ability of bis(diamidophosphite) **1d** reflected in its high coupling constants ($^1J_{PSe}$ = 920 Hz and $^1J_{RhP}$ = 234 Hz) would explain the low stability of the complex.

Rhodium-Catalyzed Asymmetric Hydrogenation. The novel bis(diamidophosphite) ligands were initially tested in the Rh-catalytic hydrogenation of benchmark substrates in order to explore their scope and limitations (Scheme 5).

Scheme 5. Rh-Catalyzed Asymmetric Hydrogenation Reaction



The results for the asymmetric hydrogenation of methyl α-acetamidoacrylate (**4**), methyl (*Z*)- α-acetamidocinnamate (**5**), and dimethyl itaconate (**6**) catalyzed with the $[Rh(COD)(P,P)]BF_4$ (P,P = **1a−c**, **2a**, **3a,c,d**) complexes are given in Tables 2 and 3. All the reactions were conducted under 10 bar of H_2 in CH_2Cl_2 at room temperature for 6 h, with a substrate:

Table 2. Asymmetric Hydrogenation[a] of Substrates 4−6 with $[Rh(COD)(P,P)]BF_4$ (P,P = 1a−c, 2a)

entry	P,P	substrate	conversion (%)	ee (%)[b]
1	(*R*,*R*;S_{al},S_{al};*R*,*R*)-**1a**	**4**	100	>**99** (*R*)
2	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1a**	**4**	100	70 (*R*)
3	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1b**	**4**	100	70 (*R*)
4	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1c**	**4**	100	26 (*S*)
5	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1c**[c]	**4**	100	23 (*S*)
6	(*R*,*R*;S_{al};*R*,*R*)-**1d**[c]	**4**	0	
7	(*R*,*R*;S_{al},S_{al};*R*,*R*)-**2a**	**4**	100	74 (*R*)
8	(*R*,*R*;S_{al},S_{al};*R*,*R*)-**1a**	**5**	100	95 (*R*)
9	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1a**	**5**	100	75 (*R*)
10	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1b**	**5**	100	76 (*R*)
11	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1c**	**5**	100	Racemic
12	(*R*,*R*;S_{al},S_{al};*R*,*R*)-**2a**	**5**	100	52 (*R*)
13	(*R*,*R*;S_{al},S_{al};*R*,*R*)-**1a**	**6**	70	**97** (*S*)
14	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1a**	**6**	18	72 (*S*)
15	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1b**	**6**	88	74 (*S*)
16	(*R*,*R*;R_{al},R_{al};*R*,*R*)-**1c**	**6**	100	Racemic
17	(*R*,*R*;S_{al};*R*,*R*)-**1d**[c]	**6**	0	-
18	(*R*,*R*;S_{al},S_{al};*R*,*R*)-**2a**	**6**	100	90 (*S*)

[a]Standard reaction conditions: 25 mL of CH_2Cl_2, 1.00 mmol of substrate, 0.01 mmol of $[Rh(COD)(P,P)]BF_4$, 10 bar of H_2, 6 h, room temperature. Conversion and ee values were determined by GC. [b]The absolute configuration was determined by comparison with the known sign of specific rotation. [c]Catalyst formed in situ from 0.01 mmol of $[Rh(COD)_2]BF_4$ and 0.011 mmol of (P,P).

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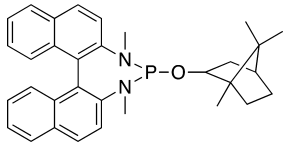
Table 3. Asymmetric Hydrogenation[a] of Substrates 4−6 with [Rh(COD)(P,P)]BF_4 (P,P = 3a,c−e)

entry	P,P	substrate	conversion (%)	ee (%)[b]
1	(R;S_{al},S_{al};R)-**3a**	**4**	100	28 (*R*)
2	(S;S_{al},S_{al};S)-**3a**[c]	**4**	100	98 (*R*)
3	(R;R_{al},R_{al};R)-**3c**	**4**	100	>**99** (*R*)
4	(R;S_{al};R)-**3d**	**4**	100	>**99** (*S*)
5	(R;S_{al};R)-**3d**[c]	**4**	100	>**99** (*S*)
6	(S;S_{al};S)-**3d**[c]	**4**	100	10 (*R*)
7	(S;R_{al};S)-**3d**[c]	**4**	100	>**99** (*R*)
8	(S;R_{al};S)-**3d**[c]	**4**	100	>**99** (*R*)
9	(R;S_{al})-**3e**[d]	**4**	100	53 (*R*)
10	(R;S_{al},S_{al};R)-**3a**	**5**	100	29 (*R*)
11	(S;S_{al},S_{al};S)-**3a**[c]	**5**	100	92 (*S*)
12	(R;R_{al},R_{al};R)-**3c**	**5**	100	>**99** (*S*)
13	(R;S_{al};R)-**3d**	**5**	100	96 (*S*)
14	(S;S_{al};S)-**3d**[c]	**5**	90	75 (*S*)
15	(R;S_{al})-**3e**[d]	**5**	100	79 (*R*)
16	(R;S_{al},S_{al};R)-**3a**	**6**	100	9 (*S*)
17	(S;S_{al},S_{al};S)-**3a**[c]	**6**	100	98 (*S*)
18	(R;R_{al},R_{al};R)-**3c**	**6**	100	>**99** (*R*)
19	(R;S_{al};R)-**3d**	**6**	92	75 (*R*)
20	(S;S_{al};S)-**3d**[c]	**6**	53	38 (*S*)
21	(R;S_{al})-**3e**[d]	**6**	100	78 (*S*)

[a]Standard reaction conditions: 25 mL of CH_2Cl_2, 1.00 mmol of substrate, 0.01 mmol of [Rh(COD)(P,P)]BF_4, 10 bar of H_2, 6 h, room temperature. Conversion and ee values were determined by GC. [b]The absolute configuration was determined by comparison with the known sign of specific rotation. [c]Catalyst formed in situ from 0.01 mmol of [Rh(COD)$_2$]BF_4 and 0.011 mmol of (P,P). [d]Catalyst formed in situ from 0.01 mmol of [Rh(COD)$_2$]BF_4 and 0.022 mmol of (R;S_{al})-**3e**.



(R,S_{al})-**3e**

[Rh] ratio of 100:1 and the preformed catalyst unless stated. Using the preformed catalyst ensured us that the catalytic precursor was accurately defined and that the exact catalyst loading was introduced in the reactor. Nevertheless, we tested for the ligand (R,R;R_{al},R_{al};R,R)-**1c** (Table 2, entries 4 and 5) and (R;S_{al};R)-**3d** (Table 3, entries 4 and 5) hydrogenation reactions with in situ conditions ([Rh(COD)$_2$]BF_4:P,P = 1:1.1) and obtained similar results.

Table 2 shows the results obtained with Rh(I) complexes containing ligands with disubstituted cyclohexyldiamine terminal fragments. With the ligands **1a−c** and **2a**, complete conversion of the dehydro amino acid methyl esters **4** and **5** was achieved in 6 h, showing a wide range of ee values. Lower activity was accomplished for the hydrogenation of dimethyl itaconate (**6**) with precursors containing the ligands **1a,b** ((R,R;S_{al},S_{al};R,R)-**1a**, 70%; (R,R;R_{al},R_{al};R,R)-**1a**, 18%; (R,R;R_{al},R_{al};R,R)-**1b**, 88%, entries 13−15). The highest ee values were obtained with the (R,R;S_{al},S_{al};R,R)-**1a** ligand (99% *R* for **4′**, 95% *R* for **5′**, 97% *S* for **6′**; entries 1, 8 and 13). A match−mismatch effect was seen for both (R,R;S_{al},S_{al};R,R)-**1a** and its counterpart (R,R;R_{al},R_{al};R,R)-**1a**, with the former being the matched combination for the selective preparation of (*R*)-*N*-acetylalanine methyl ester (**4′**), (*R*)-*N*-acetylphenylalanine methyl ester (**5′**), and (*S*)-2-methylsuccinic acid dimethyl ester (**6′**). Moreover, the absolute configurations of the different hydrogenation products depend on the configuration of the chiral centers of the terminal fragment (entries 1, 8, and 13 vs 2, 9, and 14). Similar conversion and ee values and the same configuration of the major enantiomer of the hydrogenated products were obtained by changing the bridging fragment derived from (*R*,*R*)-butanediol, in (R,R;R_{al},R_{al};R,R)-**1a**, for the conformationally more rigid group derived from (*R*,*R*)-cyclohexanediol, in (R,R;R_{al},R_{al};R,R)-**1b** (entries 2 vs 3, 9 vs 10, and 14 vs 15). These results indicate that with rhodium complexes containing ligands **1a,b**, which both have a short spacer, the enantioselectivity is not affected by changing the conformational rigidity of the bridge. Hydrogenation reactions with a precursor containing the (R,R;R_{al},R_{al};R,R)-**1c** ligand showed a very low enantiomeric excess (up to 26% for **4′** and racemic for **5′** and **6′**; entries 4, 11, and 16). The conformational flexible and rather long spacer derived from di-*O*-isopropylidenethreitol (**c**) diminishes the enantioselectivity of the process. A slightly lower enantioselectivity was observed with the precursor containing the (R,R;S_{al},S_{al};R,R)-**2a** ligand derived from the dimethylcyclohexyldiamine in comparison to that with (R,R;S_{al},S_{al};R,R)-**1a** derived from the dibenzylciclohexyldiamine (entries 1 vs 7, 8 vs 12, and 13 vs 18). Presumably the presence of the bulkier benzyl substituent on the nitrogen atom induces greater steric crowding around the phosphorus atom, resulting in increased enantiomeric control.

It is worth noting that the rhodium precursor based on the ligand (R,R;S_{al};R,R)-**1d** failed to hydrogenate the substrates **4** and **6**. The reaction was carried out with the catalyst generated in situ from [Rh(COD)$_2$]BF_4 and 1 equiv of (R,R,S_{al},R,R)-**1d**. This result is in agreement with the fact, explained in the previous section, that all attempts to prepare the cationic complex [Rh(COD)(R,R;S_{al};R,R)-**1d**]BF_4 were unsuccessful. In contrast, Gavrilov et al.[23] reported high activity and excellent enantioselectivity in the hydrogenation of **5** and **6** with bis(diamidophosphite) ligands with a terminal fragment derived from anilinomethylpyrrolidine (diazaphospholidine cycle) and the same binaphthol bridging fragment **d**.

Table 3 gives the results obtained with rhodium complexes containing the bidentate bis(diamidophosphite) ligands **3a,c,d** with the *N*,*N*′-dimethylbinaphthyldiamine terminal fragment. Good activities were obtained for the hydrogenation of substrates **4−6**, but low conversions were achieved for dimethyl itaconate when a precursor with the **3d** ligand was used (entries 19 and 20). Large match−mismatch effects were noted with the ligands **3a,d**; while (S;S_{al},S_{al};S)-**3a** showed high enantioselectivity (up to 98% ee, entries 2, 11, and 17), lower values were obtained with the counterpart diastereoismer (R;S_{al},S_{al};R)-**3a** (up to 29% ee, entries 1, 10, and 16). Similar results were obtained with the ligand **3d**; better ee values were obtained with (R;S_{al};R)-**3d** (entries 4, 13, and 19) than with (S;S_{al};S)-**3d** (entries 6, 14, and 20). On comparison of the results obtained with (S;R_{al};S)-**3d** and (R;S_{al};R)-**3d**, the expected change in the absolute configuration of the major enantiomer of the hydrogenation product **4′** can be observed (entries 5 vs 7). Excellent enantioselectvity was attained with the compound [Rh(COD)((R,R_{al},R_{al},R)-**3c**)]BF_4 in the hydrogenation of the three benchmark substrates (up to >99% ee, entries 3, 12, and 18). Remarkably, this result is in sharp contrast with the low levels of enantioselectivity when the ligand is (R,R;R_{al},R_{al};R,R)-**1c**, which contains the same bridging fragment derived from di-*O*-isopropylidene-threitol and the benzylcyclohexyldiamine

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terminal fragment. A long and flexible bridging fragment enhances enantioselectivity when the binaphthyl terminal fragment is present. Reetz[35] also observed good enantioselectivity with BINOL-derived diphosphite and diphosphoramidite ligands containing long bridging fragments.

We also tested the hydrogenation reaction with a Rh(I) precursor with the monodentate diamidophosphite (R,S_{al})-**3e** ligand described previously by our group.[20] This ligand, which contains a diazaphosphepine heterocyclic ring from (*R*)-dimethylbinaphthyldiamine and the (*S*)-bornyloxy group as the third substituent in the phosphorus atom (see footnote in Table 3), led to good conversion and enantioselectivity in the hydrovinylation reaction of styrene. Total conversion and moderate enantioselectivity in the hydrogenation of the substrates **4**−**6** were observed (53% *R* for **4′**, 79% *R* for **5′**, 78% *S* for **6′**; entries 9, 15, and 21). On comparison of these results with those described[25] with a similar monodentate diamidophosphite with the heterocyclic fragment (*S*)-dimethylbinaphthyldiamine and a methoxy group (ee 30% of **6′**) it can be concluded that the presence of the bulky chiral bornyloxy group substantially improves the enantiomeric excess, but the values are still far from those obtained with monodentate phosphoramidite BINOL-based ligands.[14]

It is worth noting that no linear correlation was found between the basicity of the new ligands (on the basis of their $^1J_{PSe}$ values) and the activity and selectivity of the hydrogenation process.

After exploring the catalytic potential of the Rh(I) precursors with the new ligands in the hydrogenation of **4**−**6**, we were interested in optimizing the reaction conditions when [Rh(COD)((*R*,R_{al},R_{al},*R*)-**3c**)]BF_4 is used in the hydrogenation of dehydro amino acid methyl ester **4** (Table 4).

Table 4. Asymmetric Hydrogenation[a] of Substrate 4 with [Rh(COD)((*R*;R_{al},R_{al};*R*)-3c)]BF_4

entry	*P* (bar)	**4**/[Rh]	time (h)	conversion (%)	ee (%)	TOF[b]
1	10	100/1	6	100	>99 (*R*)	
2	10	100/1	0.5	100	>99 (*R*)	**200**
3[c]	10	1000/1	6	98	>99 (*R*)	163
4	1.5	100/1	1	100	>99 (*R*)	
5	1.5	100/1	0.5	80	>99 (*R*)	160

[a]Reaction conditions: 25 mL of CH_2Cl_2, 0.01 mmol of [Rh]. [b]In units of (mol of substrate)(mol of cat.)$^{-1}$ (h)$^{-1}$. [c]5 × 10^{-3} mmol of [Rh].

The excellent enantioselectivity obtained (>99%) is not affected by changing the pressure, reaction time, substrate:[Rh] ratio, or catalyst concentration under the reaction conditions described in Table 4. The highest TOF value (TOF = 200, entry 2) is obtained at 10 bar of pressure, with a substrate:[Rh] ratio of 100:1 and a 0.5 h reaction. The catalyst is also efficient at 1.5 bar of pressure, reaching a TOF value of 160 (entry 3). These values are close to those reported in the literature for Rh-catalyzed asymmetric hydrogenation of similar substrates with monodentate and bidentate phosphoramidite ligands.[14,18]

After the promising results obtained with [Rh(COD)((*R*;R_{al},R_{al};*R*)-**3c**)]BF_4 precursor, we examined its efficiency in the asymmetric hydrogenation of a structurally diverse array of substrates shown in Figure 3. The results are summarized in Table 5.

To the best of our knowledge, only a few catalytic systems based on rhodium precursors have been efficient in the metal-catalyzed asymmetric hydrogenation of cyclic enamides (e.g.,

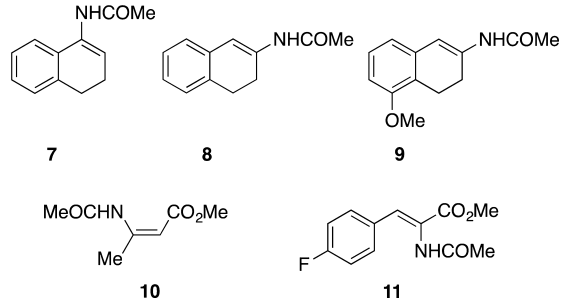

Figure 3. Prochiral olefins hydrogenated with [Rh(COD)((*R*;R_{al},R_{al};*R*)-**3c**)]BF_4 precursor.

Table 5. Asymmetric Hydrogenation[a] of Substrates 7−11 with [Rh(COD)((*R*;R_{al},R_{al};*R*)-3c)]BF_4

entry	substrate	substrate/[Rh]	time (h)	conversion (%)	ee[b] (%)
1	**7**	100/1[c]	6	100	55 (*S*)[d]
2	**8**	50/1	6	77	51 (*R*)[e]
3	**9**	50/1	6	100	44 (*R*)[e,f]
4	**10**	50/1	20	50	18 (*S*)[d]
5	**11**	50/1	6	100	92 (*S*)[d]

[a]Standard reaction conditions: 25 mL of CH_2Cl_2, 0.5 mmol of substrate, 0.01 mmol of [Rh(COD)(P,P)]BF_4, 10 bar of H_2, room temperature. [b]The absolute configuration was determined by comparison with the known sign of specific rotation. [c]1 mmol of substrate, 0.01 mmol of [Rh(COD)(P,P)]BF_4. [d]Conversion and ee were determined by GC. [e]Conversion and ee were determined by HPLC. [f]The absolute configuration was assigned assuming the same enantioselection as in **8′**.

the Rh-PennPhos, Rh-BIPHEP, and Rh-supraphos systems).[36−38] As shown in Table 5, cyclic enamides **7**−**9** have been hydrogenated with good yields and moderate enantioselectivities (44−55% ee, entries 1−3). The aliphatic ((*Z*)-*β*-methylacylamino)acrylate **10** was hydrogenated with low efficiency in terms of both activity and enantioselectivity (entry 4). The complete hydrogenation of substrate **11** that contains a *p*-fluoro electron-withdrawing group confirms the efficacy of (*R*;R_{al},R_{al};*R*)-**3c** in the hydrogenation of *α*-dehydro amino acids. Only a slight decrease in the enantioselectivity in comparison to the nonsubstituted substrate was observed (entry 5 in Table 5 vs entry 12 in Table 3).

CONCLUSIONS

Two different series of new enantiopure bidentate bis(diamidophosphite) ligands have been prepared by a simple two-step synthesis: one containing a heterocycle derived from disubstituted cyclohexyldiamine (**1** and **2**) and the other derived from dimethylbinaphthyldiamine (**3**). The corresponding cationic complexes [Rh(COD)(P,P)]BF_4 have been prepared and fully characterized in order to be used as catalytic precursors.

The new Rh(I) complexes have been tested in the asymmetric hydrogenation of prochiral benchmark substrates *α*-dehydro amino acid methyl esters and dimethyl itaconate. Good conversion and ee values were obtained with most of them. The precursors containing the ligand with a benzylcyclohexyl terminal fragment and the butanediol derived bridging group ((*R*,*R*;S_{al},S_{al};*R*,*R*)-**1a**) yielded up to 99% ee. This result is remarkable, as it is the only bidentate diamidophosphite ligand without the atropoisomeric binaphthyl group that achieves excellent enantioselectivity in asymmetric hydrogenation. It is

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noteworthy that excellent enantioselectivity (ee > 99%) was obtained for the hydrogenation of all the tested substrates with the complex containing the (*R*;R_{al},R_{al};*R*)-**3c** ligand. The activity with this ligand is similar to those reported for bidentate diamidophosphites and some monodentate phosphoramidites with the binaphthyl fragment. Large match−mismatch effects have been observed for the diastereoisomers of the ligands **1a** and **3a,d** tested in the process studied. The results obtained suggest that within bis(diaminophosphites) with a cyclohexyldiamine terminal fragment, those with a short and flexible bridge induce better enantioselectivities, while for those with the binaphthyldiamine terminal fragment, the best enantioselectivities are obtained when the bridging fragment is long and flexible. We applied the best catalytic precursor, [Rh(COD)-((*R*,R_{al},R_{al},*R*)-**3c**)]BF_4, in the asymmetric hydrogenation of cyclic enamides and *β*-amino esters, providing good conversion and moderate enantioselectivities.

EXPERIMENTAL SECTION

General Remarks. All reactions were carried out under a purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen; Et_3N and *i*-Pr_2EtN were distilled from CaH_2 and collected over 4 Å molecular sieves before use. The diols (*R*,*R*)- and (*S*,*S*)-2,3-butanediol, (*R*,*R*)-1,2-cyclohexanediol, (−)-2,3-*O*-isopropylidene-D-threitol, and (*R*)- and (*S*)-1,1′-bi-2-naphthol, (*R*,*R*)-1,2-cyclohexanediamine, (*R*,*R*)-*N*,*N*′-dimethyl-1,2-cyclohexanediamine, (*R*)- and (*S*)-*N*,*N*′-dimethyl-1,1′-binaphthyl-2,2′-diamine, and PCl_3 were used as supplied from Aldrich. (*R*,*R*)-*N*,*N*′-dibenzyl-1,2-cyclohexanediamine was prepared as previously described.[39] [$Rh(COD)_2$]-BF_4 used in the synthesis of the precatalysts was purchased from Alfa Aesar, and the starting substrates dimethyl itaconate and methyl 2-acetamidoacrylate were obtained from Aldrich. (*Z*)-*α*-acetamidocinnamate was synthesized by a previously described method.[40]

^1H, ^{13}C (^1H, ^{13}C, standard $SiMe_4$), and ^{31}P (^{31}P, standard H_3PO_4) NMR spectra were recorded on Bruker DRX 250 (^{31}P, 101 MHz), Varian Unity 300 MHz (^{13}C, 75 MHz; ^{31}P, 121.4 MHz), Varian Mercury 400 MHz (^{13}C, 100 MHz; ^{31}P, 161.9 MHz), and Varian Mercury 500 MHz (^{13}C, 125 MHz) spectrometers in $CDCl_3$ unless otherwise stated. Chemical shifts in ppm are reported downfield from standards. The two-dimensional experiments were carried out on a Varian Mercury 400 MHz or a Varian Mercury 500 MHz instrument. Mass spectra were recorded with a LC/MSD-TOF (Agilent Technologies) spectrometer (ESI). The GC analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph (30 m Chiraldex DM column for dimethyl itaconate **6**, 25 m Chirasil-L-Val for methyl *α*-acetamidoacrylate **4**, (*Z*)-*α*-acetamidocinnamate **5**, and (*Z*)-*α*-acetamido(*p*-fluorophenyl)acrylate **11**, 30 m Beta-DEX for cyclic enamide **7**, and (*Z*)-*β*-acetamidoacrylate **10**) with an FID detector. Enantiomeric excesses for hydrogenation products of cyclic enamides **8** and **9** were determined by HPLC on a Chiracel OD H and Chiracel OJ, respectively. Elemental analyses were carried out in an Eager 1108 microanalyzer. Optical rotations were measured on a Perkin-Elmer 241 MC spectropolarimeter at 25 °C.

General Procedure for the Synthesis of Bis(diamidophosphites) (*R*,*R*;S_{al},S_{al};*R*,*R*)-1a, (*R*,*R*;R_{al},R_{al};*R*,*R*)-1a, (*R*,*R*;R_{al},R_{al};*R*,*R*)-1b, (*R*,*R*;R_{al},R_{al};*R*,*R*)-1c, and (*R*,*R*;S_{al};*R*,*R*)-1d. (*R*,*R*)-*N*,*N*′-Dibenzyl-1,2-cyclohexanediamine (1.06 g, 3.6 mmol) and NEt_3 (1.50 mL, 10.8 mmol) were dissolved in 10 mL of toluene. PCl_3 (0.40 mL, 4.6 mmol) dissolved in 5 mL of toluene was added dropwise at 0 °C. The mixture was warmed to room temperature and was stirred for 2 h. The formation of the chlorodiazaphospholidine was monitored by ^{31}P NMR spectroscopy (*δ* 174.5 ppm), being complete after this period. The solvent and the excess of PCl_3 were thoroughly removed under reduced pressure to afford a viscous oil. This oil was dissolved in toluene (10 mL), and the corresponding diol (1.8 mmol) (*R*,*R*)-/(*S*,*S*)-2,3-butanediol in toluene (10 mL) or (*R*,*R*)-1,2-cyclohexanediol, (−)-2,3-*O*-isopropylidene-D-threitol, or (*R*)-/(*S*)-1,1′-bi-2-naphthol in THF (10 mL) was added dropwise at 0 °C. After 4 h of stirring, hexane (5 mL) was added and the white precipitate of triethylamine hydrochloride was filtered off. The solvent was removed under vacuum, and a yellowish oil was obtained and used without purification.

*(R,R;S_{al},S_{al};R,R)-**1a**:* yield 0.47 g (36%); HR-MS (ESI) *m*/*z* $C_{44}H_{56}N_4O_2P_2$ 735.3943 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = −40.90°; ^{31}P NMR ($CDCl_3$, 101.25 MHz), *δ* (ppm) 137.6 (s); ^1H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) (*J* (Hz)) 7.46 −7.12 (om, 20H, C*H*(Ar)), 4.40−4.17 (om, 6H, CH_2(Bn)), 3.99 (m, 2H, OC*H*), 3.80 (dd, $^2J_{HH}$= 15.2, $^3J_{HP}$ = 9.2, 2H, CH_2(Bn)), 2.98 (m, 2H, C*H*(Cy)), 2.52 (m, 2H, C*H*(Cy)), 1.79−0.81 (om, 16H, CH_2(Cy)), 1.11 (d, $^3J_{HH}$ = 6.0, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* (ppm) (*J* (Hz)) 141.4 (d, $^3J_{CP}$ = 9.0, 2C, *C*(Ar)), 140.8 (d, $^3J_{CP}$ = 3.0, 2C, *C*(Ar)), 129.3−126.5 (om, 20C, *C*H(Ar)), 72.1 (dd, $^2J_{CP}$ = 14.0, $^3J_{CP}$ = 3.0 2C, OCH), 67.3 (d, $^2J_{CP}$ = 7.0, 2C, *C*H(Cy)), 66.2 (d, $^2J_{CP}$ = 8.0, 2C, *C*H(Cy)), 50.2 (d, $^2J_{CP}$ = 33.0, 2C, CH_2(Bn)), 48.3 (d, $^2J_{CP}$ = 14.0, 2C, CH_2(Bn)), 30.4 (s, 2C, CH_2(Cy)), 30.2 (s, 2C, CH_2(Cy)), 24.5 (s, 2C, CH_2(Cy)), 24.2 (s, 2C, CH_2(Cy)), 16.4 (d, $^3J_{CP}$ = 2.0, 2C, CH_3).

*(R,R;R_{al},R_{al};R,R)-**1a**:* yield 0.60 g (45%); HR-MS/ESI *m*/*z* $C_{44}H_{56}N_4O_2P_2$ 735.3923 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = −36.12°; ^{31}P NMR ($CDCl_3$, 101.25 MHz) *δ* (ppm) 138.2 (s); ^1H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) (*J* (Hz)) 7.63−7.00 (om, 20H, C*H*(Ar)), 4.40−4.11 (om, 6H, CH_2(Bn)), 3.93 (m, 2H, OC*H*), 3.80 (dd, $^2J_{HH}$ = 15.0, $^3J_{HP}$ = 10.2, 2H, CH_2(Bn)), 2.98 (m, 2H, C*H*(Cy)), 2.48 (m, 2H, C*H*(Cy)), 2.10−0.76 (om, 16H, CH_2(Cy)), 1.14 (d, $^3J_{HH}$ = 6.4, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz), *δ*(ppm) (*J* (Hz)) 141.2 (d, $^3J_{CP}$ = 8.0, 2C, *C*(Ar)), 140.5 (d, $^3J_{CP}$ = 3.0, 2C, *C*(Ar)), 129.7−126.6 (om, 20C, *C*H(Ar)), 72.1 (dd, $^2J_{CP}$ = 14.0, $^3J_{CP}$ = 2.0, 2C, OCH), 67.1 (d, $^2J_{CP}$ = 7.0, 2C, *C*H(Cy)), 66.0 (d, $^2J_{CP}$ = 8.0, 2C, *C*H(Cy)), 50.0 (d, $^2J_{CP}$ = 34.0, 2C, CH_2(Bn)), 48.2 (d, $^2J_{CP}$ = 14.0, 2C, CH_2(Bn)), 30.3 (d, $^3J_{CP}$ = 3.0, 2C, CH_2(Cy)), 30.1 (s, 2C, CH_2(Cy)), 24.4 (s, 2C, CH_2(Cy)), 24.2 (s, 2C, CH_2(Cy)), 15.5 (d, $^3J_{CP}$ = 3.4, 2C, CH_3).

*(R,R;R_{al},R_{al};R,R)-**1b**:* yield 0.28 g (22%); HR-MS/ESI *m*/*z* $C_{46}H_{58}N_4O_2P_2$ 761.4079 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = −49.15°; ^{31}P NMR ($CDCl_3$, 101.25 MHz) *δ* (ppm) 136.5 (s); ^1H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) (*J* (Hz)) 7.64−7.12 (om, 20H, C*H*(Ar)), 4.50−4.06 (om, 6H, CH_2(Bn)), 3.82 (m, 4H, 2OC*H* + 2CH_2(Bn)), 3.00 (m, 2H, C*H*(Cy)), 2.47 (m, 2H, C*H*(Cy)), 2.05−0.81 (om, 24H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* (ppm) (*J* (Hz)) 141.6 (d, $^3J_{CP}$ = 8.0, 2C, *C*(Ar)), 140.4 (s, 2C, *C*(Ar)), 129.0−125.2 (om, 20C, *C*H(Ar)), 73.5 (d, $^2J_{CP}$ = 12.0 2C, OCH), 66.5 (d, $^2J_{CP}$ = 7.0, 2C, *C*H(Cy)), 66.3 (d, $^2J_{CP}$ = 8.0, 2C, *C*H(Cy)), 49.7 (d, $^2J_{CP}$ = 33.0, 2C, CH_2(Bn)), 48.3 (d, $^2J_{CP}$ = 14.0, 2C, CH_2(Bn)), 30.4 (s, 2C, CH_2(Cy)), 30.2 (s, 2C, CH_2(Cy)), 29.8 (s, 2C, CH_2(Cy)), 24.4 (s, 2C, CH_2(Cy)), 24.2 (s, 2C, CH_2(Cy)), 24.1 (s, 2C, CH_2(Cy)).

*(R,R;R_{al},R_{al};R,R)-**1c**:* yield 0.54 g (41%); HR-MS/ESI *m*/*z* $C_{47}H_{60}N_4O_4P_2$ 807.4163 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = −35.78°; ^{31}P NMR ($CDCl_3$, 101.25 MHz) *δ* (ppm) 136.3 (s); ^1H NMR ($CDCl_3$, 400 MHz) *δ* (ppm) (*J* (Hz)) 7.68−7.05 (om, 20H, C*H*(Ar)), 4.39−4.15 (om, 6H, CH_2(Bn)), 3.98−3.85 (om, 4H, 2CH_2(Bn) + 2OCH_2), 3.83 (m, 2H, OC*H*), 3.53 (m, 2H, OCH_2), 3.01 (m, 2H, C*H*(Cy)), 2.55 (m, 2H, C*H*(Cy)), 2.00−0.80 (om, 16H, CH_2(Cy)), 1.40 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz), *δ*(ppm) (*J* (Hz)) 140.9 (d, $^3J_{CP}$ = 7.0, 2C, *C*(Ar)), 140.5 (d, $^3J_{CP}$ = 3.0, 2C, *C*(Ar)), 129.1−126.4 (m, 20C, *C*H(Ar)), 109.4 (s, 1C, O_2CMe_2), 78.4 (d, $^3J_{CP}$ = 4,0, 2C, OCH), 67.4 (d, $^2J_{CP}$ = 6.0, 2C, *C*H(Cy)), 66.4 (d, $^2J_{CP}$ = 8.0, 2C, *C*H(Cy)), 64.6 (d, $^2J_{CP}$ = 9.0, 2C, OCH_2), 50.3 (d, $^2J_{CP}$ = 33.0, 2C, CH_2(Bn)), 48.1 (d, $^2J_{CP}$ = 14.0, 2C, CH_2(Bn)), 30.3 (s, 2C, CH_2(Cy)), 29.9 (s, 2C, CH_2(Cy)), 27.2 (s, 2C, CH_3), 24.5 (s, 2C, CH_2(Cy)), 24.2 (s, 2C, CH_2(Cy)).

*(R,R;S_{al};R,R)-**1d**:* yield 1.11 g (84%); HR-MS/ESI *m*/*z* $C_{60}H_{60}N_4O_2P_2Se_2$ 1091.2580 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = −9.59°; ^{31}P NMR (toluene, 101.25 MHz) *δ* (ppm) 139.3 (s); ^1H NMR (C_6D_6, 400 MHz) *δ* (ppm) (*J* (Hz)) 7.81−6.85 (om, 32H, C*H*(Ar)), 4.23−3.92 (om, 6H, CH_2(Bn)), 3.09 (dd, $^2J_{HH}$ = 16.0, $^3J_{HP}$ = 8.0, 2H, CH_2(Bn)), 2.61 (m, 2H, C*H*(Cy)), 2.41 (m, 2H, C*H*(Cy)), 1.66−0.47 (ms, 16H, CH_2(Cy)); ^{13}C NMR (C_6D_6, 100 MHz) *δ* (ppm) (*J* (Hz)) 151.6 (s, 2C, *C*(Ar)), 141.8 (m, 4C, *C*(Ar)), 140.4 (s,

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2C, *C*(Ar)), 135.4 (s, 2C, *C*(Ar)), 130.4 (s, 2C, *C*(Ar)), 129.3−121.6 (om, 32C, *C*H(Ar)), 67.2 (bs, 2C, *C*H(Cy)), 66.9 (bs, 2C, *C*H(Cy)), 49.9 (d, $^2J_{CP}$ = 34.0, 2C, CH_2(Bn)), 48.8 (d, $^2J_{CP}$ = 15.0, 2C, CH_2(Bn)), 30.7 (s, 2C, CH_2(Cy)), 30.1 (s, 2C, CH_2(Cy)), 24.5 (s, 2C, CH_2(Cy)), 24.3 (s, 2C, CH_2(Cy)).

Synthesis of Bis(diamidophosphite) Ligand (*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)-2a. (*R,R*)-*N,N*′-Dimethylcyclohexane-1,2-diamine (0.51 g, 3.6 mmol) and NEt_3 (1.50 mL, 10.8 mmol) were dissolved in 10 mL of toluene. PCl_3 (0.4 mL, 4.6 mmol) dissolved in 5 mL of toluene was added dropwise at 0 °C. The mixture was warmed to room temperature and was stirred for 2 h. The formation of the chlorodiazaphospholidine was monitored by phosphorus NMR spectroscopy (δ 174.5 ppm), being complete after this period. The solvent and the excess PCl_3 were thoroughly removed under reduced pressure to afford a viscous oil. This oil was dissolved in toluene (10 mL), and DMAP (2.6×10^{-3} g, 0.021 mmol) was added. A solution of a stoichiometric amount of the diol (*S,S*)-2,3-butanediol (0.16 g, 1.8 mmol) and 1.3 mL of NEt_3 (9,0 mmol) in toluene (10 mL) was added dropwise in three portions at 0 °C. After the mixture was stirred overnight at room temperature, hexane (5 mL) was added and the white precipitate of triethylamine hydrochloride was filtered off. The solvent was removed under vacuum, and a brownish oil was obtained and used without further purification: yield 0.41 g (53.7%); HR-MS/ESI (*m*/*z*) $C_{20}H_{40}N_4O_2P_2$ 431.2697 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = −125.48°; ^{31}P NMR ($CDCl_3$, 121.44 MHz) δ (ppm) 139.1 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (*J* (Hz)) 4.06 (m, 2H, OC*H*), 2.69 (d, $^3J_{HP}$ = 16.0, 6H, CH_3(NMe)), 2.66 (m, 2H, C*H*(Cy)), 2.56 (d, $^3J_{HP}$ = 16.0, 6H, CH_3(NMe)), 2.30 (m, 2H, C*H*(Cy)), 2.10−1.00 (om, 16H, CH_2(Cy)), 1.11 (d, $^3J_{HH}$ = 4.0, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ (ppm) (*J* (Hz)) 71.8 (dd, $^2J_{CP}$ = 10.0, $^3J_{CP}$ = 3.0, 2C, OCH), 69.4 (d, $^2J_{CP}$ = 7.0, 2C, *C*H(Cy)), 65.8 (d, $^2J_{CP}$ = 9.0, 2C, *C*H(Cy)), 32.7 (d, $^2J_{CP}$ = 37.0, 2C, CH_3(NMe)), 30.2 (d, $^2J_{CP}$ = 11.0, 2C, CH_3(NMe)), 29.4 (s, 2C, CH_2(Cy)), 29.1 (s, 2C, CH_2(Cy)), 24.3 (s, 2C, CH_2(Cy)), 24.2 (s, 2C, CH_2(Cy)), 16.2 (d, $^3J_{CP}$ = 1.0, 2C, CH_3)

General Procedure for the Synthesis of Bis-(diamidophosphites) (*R;S*$_{al}$,*S*$_{al}$;*R*)-3a, (*S;S*$_{al}$,*S*$_{al}$;*S*)-3a, (*R;R*$_{al}$,*R*$_{al}$;*R*)-3c, (*S;S*$_{al}$;*S*)-3d, and (*R;S*$_{al}$;*R*)-3d. (*R*)- and (*S*)-*N,N*′-dimethyl-1,1′-binaphthyldiamine (0.5 g, 1.6 mmol) and ethyldiisopropylamine (2.20 mL, 12.6 mmol) were dissolved in 10 mL of toluene at 0 °C. PCl_3 (0.30 mL, 3.5 mmol) dissolved in 5 mL of toluene was added dropwise at 0 °C. The mixture was warmed to room temperature and was stirred for 20 h. The formation of the chlorodiazaphosphepine was monitored by phosphorus NMR spectroscopy (δ 205.0 ppm), being complete after this period. The solvent and excess PCl_3 and ethyldiisopropylamine were thoroughly removed under reduced pressure to afford a viscous oil. This oil was dissolved in toluene (10 mL), and DMAP (2.6×10^{-3} g, 0.021 mmol) was added. The corresponding diol (0.8 mmol; ((*S,S*)-2,3-butanediol) in toluene (10 mL) or (−)-2,3-*O*-isopropylidene-D-threitol or (*R*)-/(*S*)-1,1′-bi-2-naphthol) in THF (10 mL)) and triethylamine (2.2 mL, 15.8 mmol) were added in three portions at 0 °C. After it was stirred overnight at room temperature, the mixture was cooled at 4 °C. The white precipitate of amine hydrochloride was filtered off. The solvent was removed under vacuum, and a yelow solid was obtained and used without further purification.

(R;S$_{al}$,*S*$_{al}$;*R)-**3a**:* yield 0.29 g (48%); HR-MS/ESI (*m*/*z*) $C_{48}H_{44}N_4O_2P_2$ 771.3021 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = −263.35°; ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ (ppm) 178.3 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (*J* (Hz)) 8.06−7.02 (om, 24H, C*H*(Ar)), 4.40 (m, 2H, OC*H*), 3.03 (*d*, $^3J_{HP}$ = 12.0, 6H, CH_3(NMe)), 2.99 (d, $^3J_{HP}$ = 12.0, 6H, CH_3(NMe)), 1.21 (d, $^3J_{HH}$ = 8,0, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) (*J* (Hz)) 144.9 (d, $^2J_{CP}$ = 5.0, 2C, *C*(Ar)), 141.9 (d, $^2J_{CP}$ = 6.0, 2C, *C*(Ar)), 133.1 (s, 2C, *C*(Ar)), 132.8 (s, 2C, *C*(Ar)), 131.8 (s, 2C, *C*(Ar)), 131.2 (s, 2C, *C*(Ar)), 130.8 (s, 2C, *C*(Ar)), 129.0−121.3 (om, 26C, 2*C*(Ar) + 24*C*H(Ar)), 73.7 (dd, $^2J_{CP}$ = 23.5, $^3J_{CP}$ = 2.5, 2C, OCH), 37.8 (d, $^2J_{CP}$ = 45.0, 2C, CH_3(NMe)), 35.4 (d, $^2J_{CP}$ = 26.0, 2C, CH_3(NMe)), 14.8 (d, $^3J_{CP}$ = 5.0, 2C, CH_3).

(S;S$_{al}$,*S*$_{al}$;*S)-**3a**:* yield 0.32 g (51%); HR-MS/ESI (*m*/*z*) $C_{48}H_{44}N_4O_2P_2$ 771.3004 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = +327.15°; ^{31}P NMR ($CDCl_3$, 121.44 MHz) δ (ppm) 176.6 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (*J* (Hz)) 7.97−7.00 (om, 24H, C*H*(Ar)), 4.26 (m, 2H, OC*H*), 2.96 (d, $^3J_{HP}$ = 12.0, 6H, CH_3(NMe)), 2.90 (d, $^3J_{HP}$ = 12,0, 6H, CH_3(NMe)), 1.25 (d, $^3J_{HH}$ = 4.0, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) (*J* (Hz)) 145.6 (s, 2C, *C*(Ar)), 145.0 (s, 2C, *C*(Ar)), 142.2 (d, $^2J_{CP}$ = 6.0, 2C, *C*(Ar)), 133.1 (s, 2C, *C*(Ar)), 132.7 (s, 2C, *C*(Ar)), 131.7 (s, 2C, *C*(Ar)), 131.3 (s, 2C, *C*(Ar)), 130.7 (s, 2C, *C*(Ar)), 129.7−121.4 (om, 24C, *C*H(Ar)), 72,6 (dd, $^2J_{CP}$ = 19.0, $^3J_{CP}$ = 6.0, 2C, OCH), 37.7 (d, $^2J_{CP}$ = 45.0, 2C, CH_3(NMe)), 35.5 (d, $^2J_{CP}$ = 25.4, 2C, CH_3(NMe)), 16.8 (d, $^3J_{CP}$ = 3.5, 2C, CH_3).

(R;R$_{al}$,*R*$_{al}$;*R)-**3c**:* yield 0.40 g (59%); HR-MS/ESI (*m*/*z*) $C_{51}H_{48}N_4O_4P_2$ 843.3210 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = −325.13°; ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ (ppm) 168.9 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (*J* (Hz)) 7.99−7.00 (om, 24H, C*H*(Ar)), 3.86 (m, 2H, OC*H*), 3.78 (m, 2H, OCH_2), 3.68 (m, 2H, OCH_2), 3.05 (d, $^3J_{HP}$ = 12.0, 6H, CH_3(NMe)), 2.85 (d, $^3J_{HP}$ = 10.0, 6H, CH_3(NMe)), 1.42 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) (*J* (Hz)) 144.9 (d, $^2J_{CP}$ = 5.0, 2C, *C*(Ar)), 142.7 (d, $^2J_{CP}$ = 7.0, 2C, *C*(Ar)), 133.0−121.1 (om, 36C, 12*C*(Ar) + 24CH(Ar)), 109.7 (s, 1C, O_2CMe_2), 77.9 (s, 2C, OCH), 64.3 (d, $^2J_{CP}$ = 7.0, 2C, OCH_2), 38.0 (d, $^2J_{CP}$ = 44.2, 2C, CH_3(NMe)), 35.1 (d, $^2J_{CP}$ = 26.2, 2C, CH_3(NMe)), 27.2 (s, 2C, CH_3).

(S;S$_{al}$;*S)-**3d**:* yield 0.39 g (51.0%); HR-MS/ESI (*m*/*z*) $C_{64}H_{48}N_4O_2P_2$ 967.3317 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = +202.93°; ^{31}P NMR ($CDCl_3$, 121.44 MHz) δ (ppm) 173.6 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (*J* (Hz)) 8.07−6.86 (om, 34H, C*H*(Ar)), 5.98 (d, $^4J_{HP}$ = 2.0, 2H, C*H*(Ar)), 2.20 (d, $^3J_{HP}$ = 16.0, 6H, CH_3(NMe)), 1.98 (d, $^3J_{HP}$ = 8,0, 6H, CH_3(NMe)); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) (*J* (Hz)) 151.3 (d, $^2J_{CP}$ = 8.0, 2C, *C*(Ar)), 144.7 (d, $^2J_{CP}$ = 5.0, 2C, *C*(Ar)), 141.8 (d, J_{CP} = 6.0, 2C, *C*(Ar)), 134.2−120.1 (54C, 18*C*(Ar) + 36*C*H(Ar)), 36.5 (d, $^2J_{CP}$ = 43.0, 2C, CH_3(NMe)), 34.0 (d, $^2J_{CP}$ = 25.0, 2C, CH_3(NMe)).

(R,S$_{al}$,*R)-**3d**:* yield 0.34 g (44%); HR-MS/ESI (*m*/*z*) $C_{64}H_{48}N_4O_2P_2$ 967.3322 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = −28.09°; ^{31}P NMR ($CDCl_3$, 101.25 MHz) δ (ppm) 174.6 (s); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (*J* (Hz)) 8.08−6.96 (om, 36H, C*H*(Ar)), 2.68 (d, $^3J_{HP}$ = 13.6, 6H, CH_3(NMe)), 2.21 (d,$^3J_{HP}$ = 9.2, 6H, CH_3(NMe)); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) (*J* (Hz)) 150.6 (d, $^2J_{CP}$ = 8.0, 2C, *C*(Ar)), 144.8 (d, $^2J_{CP}$ = 5.0, 2C, *C*(Ar)), 141.7 (d, $^2J_{CP}$ = 6.0, 2C, *C*(Ar)), 134.7−121.7 (54C, 18*C*(Ar) + 36*C*H(Ar)), 38.0 (d, $^2J_{CP}$ = 50.0, 2C, CH_3(NMe)), 34.7 (d, $^2J_{CP}$ = 24.0, 2C, CH_3(NMe)).

(S,R$_{al}$,*S)-**3d**:* yield 0.39 g (51%); HR-MS/ESI (*m*/*z*) $C_{64}H_{48}N_4O_2P_2$ 967.3322 $[MH]^+$; $[\alpha]^{298}$(*c* 1.0, CH_2Cl_2) = +23.30°.

General Procedure for the Synthesis of Selenide Derivatives. 0.15 mmol of ligand dissolved in 2 mL of toluene in the presence of 2.4 mmol of selenium powder was stirred under N_2 for 24 h at room temperature. The reaction mixture was filtered through Celite. The compounds were characterized by ^{31}P NMR (101 MHz) in toluene.

General Procedure for the Synthesis of Rhodium Complexes. A solution of the corresponding bis(diamidophosphite) ligand (0.1 mmol) in toluene (5 mL) was added dropwise to a vigorously stirred CH_2Cl_2 solution (20 mL) of $[Rh(COD)_2]BF_4$ (0.041 g, 0.10 mmol), in the presence of free COD when not freshly prepared (0.032 g, 0.3 mmol). The mixture was stirred for an additional 15 min and concentrated to dryness at reduced pressure. The solid was washed with ether (3 × 8 mL) and dried under vacuum.

[Rh(COD)((R,R;S$_{al}$,*S*$_{al}$;*R,R)-**1a**)]BF*$_4$*:* yellow solid; yield 0.062 g (60%); mp 222−226 °C dec; ^{31}P NMR ($CDCl_3$, 121.44 MHz) δ (ppm) (*J* (Hz)) 139.8 (d, $^1J_{PRh}$ = 228.3 Hz); ^{1}H NMR (CD_2Cl_2, 500 MHz) δ (ppm) (*J* (Hz)) 7.84−6.96 (m, 20H, C*H*(Ar)), 5.70 (pt, $^2J_{HH}$ = $^3J_{HP}$ = 12.5, 2H, CH_2(Bn)), 5.42 (bs, 2H, C*H*(COD)), 5.29 (bs, 2H, C*H*(COD)), 4.56 (bs, 4H, 2OC*H* + 2CH_2(Bn)), 4.19 (dd, $^2J_{HH}$ = 17.5, $^3J_{HP}$ = 7.5, 2H, CH_2(Bn)), 3.63 (d, $^2J_{HH}$ = 15.0, 2H, CH_2(Bn)), 2.91 (m, 2H, C*H*(Cy)), 2.65 (m, 2H, C*H*(Cy)), 2.44 (*m*, 4H, CH_2(COD)), 2.28 (m, 4H, CH_2(COD)), 2.15−0.75 (om, 16H, CH_2(Cy)), 1.11 (d, $^3J_{HH}$ = 5.0, 6H, CH_3); HR-MS (ESI) *m*/*z* 945.3874 $[M]^+$. Anal. Calcd for $C_{52}H_{68}BF_4N_4O_2P_2Rh$: C, 60.47; H, 6.64; N, 5.42. Found: C, 59.55; H, 6.65; N, 5.82.

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*[Rh(COD)((R,R;R_{ax},R_{ax};R,R)-**1a**)]BF_4:* yellow solid; yield 0.064 g (62%); mp 222−228 °C dec; ^{31}P NMR ($CDCl_3$, 121.44 MHz) δ (ppm) (J (Hz)) 136.8 (d, $^1J_{PRh}$ = 216.2); ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm) (J (Hz)) 7.76−6.73 (m, 20H, C*H*(Ar)), 5.84 (pt, $^2J_{HH}$ = $^3J_{HP}$ = 15.0, 2H, CH_2(Bn)), 5.74 (bs, 2H, C*H*(COD)), 5.08 (bs, 2H, C*H*(COD)), 4.22 (bs, 4H, 2OC*H* + 2CH_2(Bn)), 3.48 (m, 2H, CH_2(Bn)), 3.23 (m, 2H, CH_2(Bn)), 2.91 (m, 4H, C*H*(Cy)), 2.49 (bs, 4H, CH_2 (COD)), 2.38 (bs, 4H, CH_2(COD)), 1.94− 0.87 (om, 16H, CH_2(Cy)), 1.14 (d, $^3J_{HH}$ = 3.0, 6H, CH_3); HR-MS (ESI) m/z 945.3878 [M]$^+$. Anal. Calcd for $C_{52}H_{68}BF_4N_4O_2P_2Rh$: C, 60.47; H, 6.64; N, 5.42. Found: C, 59.81; H, 6.59; N, 5.60.

*[Rh(COD)((R,R;R_{ax},R_{ax};R,R)-**1b**)]BF_4:* yellow solid; yield 0.065 g (61%). mp 202−216 °C dec; ^{31}P NMR (CH_2Cl_2/toluene, 121.44 MHz) δ (ppm) (J (Hz)) 134.8 (d, $^1J_{PRh}$ = 216.2); ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm) (J (Hz)) 7.82−6.82 (m, 20H, C*H*(Ar)), 5.91 (bs, 2H, CH_2(Bn)), 5.79 (bs, 2H, C*H*(COD)), 5.04 (bs, 2H, C*H*(COD)), 4.22 (bs, 4H, 2OC*H* + 2CH_2(Bn)), 3.49 (d, $^2J_{HH}$ = 20.0, 2H, CH_2(Bn)), 2.92 (dd, $^2J_{HH}$ = 20.0, $^3J_{HP}$ = 8.0, 2H, CH_2(Bn)), 2.47−2.32 (m, 8H, 4C*H*(Cy) + 4CH_2(COD)), 2.08- 0.65 (om, 28H, 24CH_2(Cy) + 4CH_2(COD)); HR-MS (ESI) m/z $C_{54}H_{70}BF_4N_4O_2P_2Rh$ 971.4023 [M]$^+$. Anal. Calcd for $C_{54}H_{70}BF_4N_4O_2P_2Rh$: C, 61.25; H, 6.66; N, 5.29. Found: C, 60.32; H, 6,66; N, 4.99.

*[Rh(COD)((R,R;R_{ax},R_{ax};R,R)-**1c**)]BF_4:* yellow solid; yield 0.068 g (62%). mp 220−223 °C dec; ^{31}P NMR ($CDCl_3$, 121.44 MHz) δ (ppm) (J (Hz)) 125.0 (d, $^1J_{PRh}$ = 227.1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (J (Hz)) 7.86−6.66 (m, 20H, C*H*(Ar)), 5.47 (pt, $^2J_{HH}$ = $^3J_{HP}$ = 14.0, 2H, CH_2(Bn)), 5.26 (bs, 2H, C*H*(COD)), 5.07 (bs, 2H, C*H*(COD)), 4.42−4.34 (m, 4H, CH_2(Bn)), 4.10−4.05 (m, 4H, 2CH_2(Bn) + 2OCH_2), 3.80 (bs, 2H, OC*H*), 3.05 (m, 2H, C*H*(Cy), 2.86 (m, 2H, C*H*(Cy)), 2.74 (m, 2H, CH_2(COD)), 2.65 (m, 2H, CH_2(COD)), 2.40 - 0.56 (om, 22H, 16CH_2(Cy) + 4CH_2(COD) + 2OCH_2), 1.15 (s, 6H, CH_3); HR-MS (ESI) m/z 1017.4091 [M]$^+$. Anal. Calcd for $C_{55}H_{72}BF_4N_4O_4P_2Rh$: C, 59.79; H, 6.57; N, 5.07. Found: C, 59.37; H, 6.21; N, 5.17.

*[Rh(COD)((R,R;S_{ax},S_{ax};R,R)-**2a**)]BF_4:* yellow solid; yield 0.046 g (63%). mp 212−215 °C dec; ^{31}P NMR (CH_2Cl_2/toluene, 121.44 MHz) δ (ppm) (J (Hz)) 134.0 (d, $^1J_{PRh}$ = 228.3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (J (Hz)) 5.17 (bs, 2H, C*H*(COD)), 5.04 (bs, 2H, C*H*(COD)), 4.18 (bs, 2H, OC*H*), 2.99 (d, $^3J_{HP}$ = 16.0, 6H, CH_3(NMe)), 2.59 (d, $^3J_{HP}$ = 16.0, 6H, CH_3(NMe)), 2.17 (m, 2H, C*H*(Cy)), 2.06 (m, 2H, C*H*(Cy)), 1.86 (bs, 8H, CH_2(COD)), 1.10 (d, $^3J_{HH}$ = 4.0, 6H, CH_3) 1.56−0.98 (om, 16H, CH_2(Cy)); HR-MS (ESI) m/z 533.1687 [M − (COD)]$^+$. Anal. Calcd for $C_{28}H_{52}BF_4N_4O_2P_2Rh$: C, 46.17; H, 7.20; N, 7.69. Found: C, 45.94; H, 7.05; N, 6.52.

*[Rh(COD)((R;S_{ax},S_{ax};R)-**3a**)]BF_4:* yellow solid; yield 0.047 g (44%). mp 204−210 °C dec; ^{31}P NMR (CH_2Cl_2/toluene, 121.44 MHz) δ (ppm) (J (Hz)) 130.7 (d, $^1J_{PRh}$ = 219.8); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (J (Hz)) 8.00−6.98 (m, 24H, C*H*(Ar)), 5.09 (bs, 2H, C*H*(COD)), 4.87 (bs, 2H, OC*H*), 4.75 (bs, 2H, C*H*(COD)), 3.68 (m, 6H, CH_3(NMe)), 3.05 (bs, 6H, CH_3(NMe)), 2.33 (m, 2H, CH_2 (COD)), 2.21 (m, 4H, CH_2 (COD)), 2.08 (m, 2H, CH_2 (COD)), 1.43 (bs, 6H, CH_3); MALDI/TOF m/z 981.29 [M]$^+$. Anal. Calcd for $C_{56}H_{56}BF_4N_4O_2P_2Rh$: C, 62.93; H, 5.28; N, 5.24. Found: C, 62.24; H, 5.34; N, 4.92.

*[Rh(COD)((R;R_{ax},R_{ax};R)-**3c**)]BF_4:* yellow solid; yield 0.081 g (71%). mp 216−220 °C dec; ^{31}P NMR ($CDCl_3$, 121.44 MHz) δ (ppm) (J (Hz)) 130.6 (d, $^1J_{PRh}$ = 227.1); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (J (Hz)) 8.05−6.81 (m, 24H, C*H*(Ar)), 5.56 (bs, 2H, C*H*(COD)), 4.59 (bs, 2H, C*H*(COD)), 4.27 (bs, 2H, OC*H*), 3.93 (d, $^3J_{PH}$ = 12.0, 6H, CH_3(NMe)), 3.62 (m, 4H, CH_2), 3.28 (d, $^3J_{PH}$ = 8.0, 6H, CH_3(NMe)), 2.37 (m, 2H, CH_2 (COD)), 2.24 (bs, 4H, CH_2(COD)), 2.00 (bs, 2H, CH_2(COD)), 1.38 (s, 6H, OCCH_3); HR-MS (ESI) m/z 945.2197 [M − COD]$^+$. Anal. Calcd for $C_{59}H_{60}BF_4N_4O_4P_2Rh$: C, 62.12; H, 5.30; N, 4.91. Found: C, 61.43; H, 5.49; N, 4.75.

*[Rh(COD)((R;S_{ax};R)-**3d**)]BF_4:* yellow solid; yield 0.066 g (51.6%). mp 270−273 °C dec; ^{31}P NMR (CH_2Cl_2/toluene, 121.44 MHz) δ (ppm) (J (Hz)) 132.0 (d, $^1J_{PRh}$= 222.2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) (J (Hz)) 8.24−6.86 (m, 34H, C*H*(Ar)), 6.22 (d, $^3J_{HH}$ = 12.0, 2H, C*H*(Ar)), 5.18 (bs, 2H, C*H*(COD)), 5.08 (bs, 2H, C*H*(COD)), 3.31 (d, $^3J_{PH}$ = 8.0, 6H, CH_3(NMe)), 2.50 (d, $^3J_{PH}$ = 12.0, 6H, CH_3(NMe)), 2.45−2.30 (m, 4H, CH_2(COD)), 2.08 (m, 4H, CH_2(COD)); HR-MS (ESI) m/z $C_{72}H_{60}BF_4N_4O_2P_2Rh$ 1177.3241 [M]$^+$. Anal. Calcd for $C_{72}H_{60}BF_4N_4O_2P_2Rh$: C, 68.37; H, 4.78; N, 4.43. Found: C, 67.69; H, 5.00; N, 4.57.

General Procedure for the Hydrogenation Reactions. Hydrogenation reactions at 10 bar of hydrogen pressure were carried out in a 50 mL stainless steel autoclave, while experiments at 1.5 bar of hydrogen pressure were carried out in a Fischer−Porter glass tube reactor. In both cases the reactor was carefully dried and purged with H_2.

When the reaction was carried out with the preformed precursor, a mixture of 0.01 mmol of [Rh(COD)(P,P)]BF_4 and 1.0 mmol of substrates **4**−**7** or 0.5 mmol of substrates **8**−**11** was dissolved in 25 mL of CH_2Cl_2 in a Schlenk tube under nitrogen. The yellow solution was stirred at room temperature for 15 min and then was transferred into the autoclave. For the in situ experiments a solution of the bis(diamidophosphite) (0.011 mmol) with [Rh(COD)$_2$]BF_4 (0.01 mmol) in CH_2Cl_2 (5 mL) under nitrogen was used. After 15 min of stirring at room temperature CH_2Cl_2 (20 mL) solutions of the substrates **4**−**6** (1.0 mmol) were added and transferred into the reactor. For both cases the reactor was pressurized with 10 or 1.5 bar of H_2 and stirred at 800 rpm. After 6 h (or the desired time) the hydrogen pressure was carefully released. The reaction mixture was filtered through a short pad of silica, eluted with CH_2Cl_2, and subjected to conversion and ee determination by chiral GC analysis or HPLC.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text giving experimental details for the determination procedures of conversion and ee of the hydrogenation reaction and figures giving ^{1}H and ^{13}C NMR spectra for the new bis(diamidophosphite) ligands. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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