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# $C_2$-Symmetric Diphosphinite Ligands Derived from Carbohydrates. The Strong Influence of Remote Stereocenters on Asymmetric Rhodium-Catalyzed Hydrogenation

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Modular ligands of $C_2$ symmetry (**13a**−**e**, **14a**,**b**,**d**, and **ent-9**), systematically modified at positions 2 and 5, were easily prepared from D-glucosamine, D-glucitol, and tartaric acid, respectively. The application of these ligands in the rhodium-catalyzed hydrogenation of methyl acetamidoacrylate, methyl acetamidocinnamate, and dimethyl itaconate shows that both the configuration and the substituents at positions 2 and 5 of the tetrahydrofuran backbone have a strong influence on the enantioselectivty of the processes.

## Introduction

In recent decades, carbohydrates have been widely used as chiral synthons for the synthesis of enantiomerically pure compounds.[1] A variety of structures can be obtained from carbohydrates, mainly pyranoses and furanoses, through well-established procedures. Because hydroxyl groups are present, phosphinite, phosphonite, and phosphite functional groups are easily introduced so that they can be used as ligands in metal-catalyzed reactions.[2] The first reports on the use of carbohydrates as chiral frameworks for preparing chiral ligands date back to the 1970s when Cullen[3] and Thompson[4] reported the synthesis of diphosphinites **1** and **2** with pyranose and furanose structures, respectively (Figure 1).

Selke[5] systematically studied different modifications of diphosphinite **2** and found that diphosphinite **3** provided the best enantioselectivity in the hydrogenation of enamido acids. He also proved that the corresponding ligand with unprotected hydroxyl groups at positions 4 and 6 also provided excellent enantiomeric excesses when water was used as the solvent.[6] Other ligands have recently been prepared with this purpose and have proven to be highly efficient.[7,8]

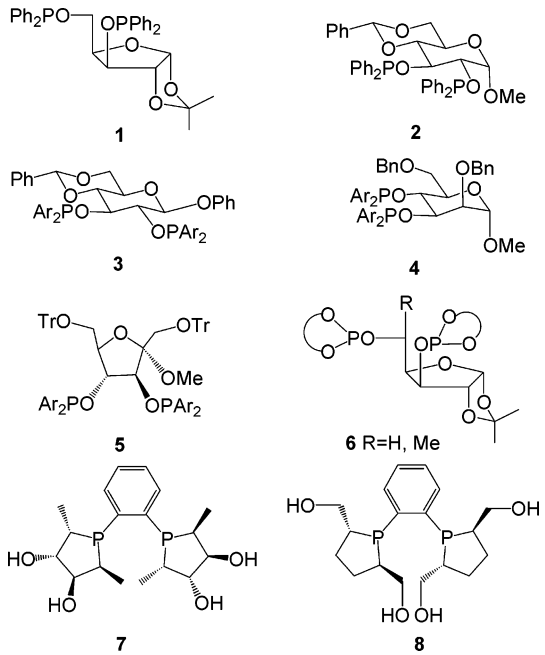


**FIGURE 1.** Relevant phosphorus ligands with $C_1$ and $C_2$ symmetries derived from carbohydrates.

RajanBabu subsequently improved the efficiency of these ligands by modifying the electronic properties of the aryl groups bonded to the phosphorus atoms.[9] These ligands were successfully used in the rhodium-catalyzed hydrogenation of enamido acids[10] and in the nickel-catalyzed hydrocyanation of alkenes.[11]

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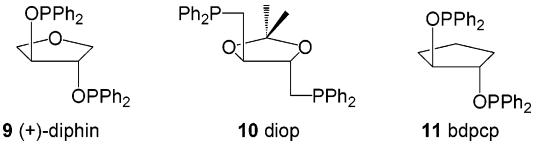


**FIGURE 2.** (+)-Diphin, diop, and bdpcp ligands with a five-membered ring in their structures.

One of the limitations of the ligands prepared from the chiral pool is that only one enantiomer is accessible. Ligand **4**, however, proved to function as a pseudoenantiomer of **3**, and in fact, it provides the opposite enantiomer in the asymmetric hydrogenation of prochiral olefins.[12]

Although ligand **1** is one of the first reported ligands derived from carbohydrates, there are only a few examples of ligands with a furanose structure. Ligand **5** provided high enantioselectivity in the nickel-catalyzed hydrocyanation of alkenes.[13]

Our group has prepared ligands with a furanose structure, such as **6** and other similar structures, and they have proven to be efficient in rhodium-catalyzed hydrogenation[14,15] and hydroformylation[16,17] and palladium allylic alkylation.[18]

Ligands with $C_2$ symmetry have also been prepared from carbohydrates, mainly from mannitol. Notable examples are the duphos analogues **7**[19] and **8**[20] where the phospholane ring was prepared from D-mannitol. These ligands are water soluble and behave like duphos. Recently, a diop analogue, which provides excellent enantioselectivity in asymmetric hydrogenation,[21] has also been prepared from mannitol.

As far as ligands with a tetrahydrofuran structure are concerned, Jackson[22] reported that diphosphinite **9** (Figure 2), which was obtained from diethyl tartrate, provided an enantiomeric excess of 20% in the rhodium-catalyzed hydrogenation of enamido acids. However, the closely related ligand diop (**10**)[22] and the cyclopentane derivative (**11**)[22,23] provided enantiomeric excesses of 55 and 43%, respectively. This indicates that small structural changes in the ligand can induce significant changes in the enantioselectivity.

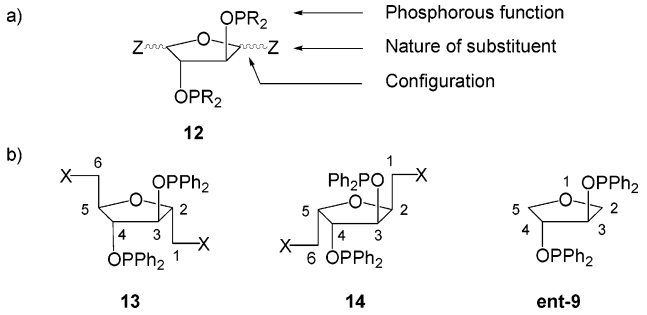


**FIGURE 3.** (a) Structural modifications in the modular ligands of **12**. (b) Tetrahydrofuran-derived diphosphinite ligands without (**ent-9**) and with substituents of different configurations (**13** and **14**) at positions 2 and 5.

In this context, we decided to prepare a series of new modular ligands with a tetrahydrofuran backbone, such as **12** (Figure 3), which can be modified by changing the phosphorus function, the nature of substituents, and the configuration at positions 2 and 5. In this paper, we report the synthesis of diphosphinites **13**, **14**, and **ent-9**, which are related to **9**, in which the substituents and configuration at positions 2 and 5 have been systematically varied. We also report their rhodium complexes. We show that the presence of these additional stereocenters has a dramatic influence on the enantioselectivity of the rhodium-catalyzed hydrogenation of enamidoesters.

## Results and Discussion

**Synthesis of Ligands and Complexes.** Ligands **13** and **14** can be easily prepared from the corresponding 2,5-bis-hydroxymethyl tetrahydrofuran-3,4-diol derivatives, which in turn can be prepared from D-glucosamine and D-glucitol, respectively, in a straightforward manner (Schemes 1 and 2).

Thus, the treatment of D-glucosamine with sodium nitrite followed by reduction with sodium borohydride provided tetrol **15** in 82% yield[24] (Scheme 1). To study the effect of the groups at positions 2 and 5, we protected the primary alcohol in **15** by reaction with TrCl, TBDPSCl, and TIPSCl to afford diols **16a**,[25] **16b**, and **16e**, respectively. We were also interested in determining the effect of a methyl group at positions 2 and 5. To this end, tetrol **15** was selectively ditosylated to give **16c**,[25] which was treated with $LiAlH_4$ to afford compound **16d**.[25]

Compounds **16a**−**e** were treated with chlorodiphenylphosphine to obtain the diphosphinites **13a**−**e** in 60−80% yield.

Tetrol **17** was obtained from D-glucitol following a reported procedure (Scheme 2).[26] The yield was only 5%,

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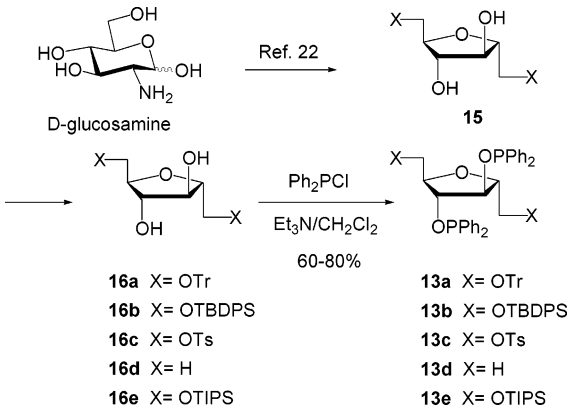
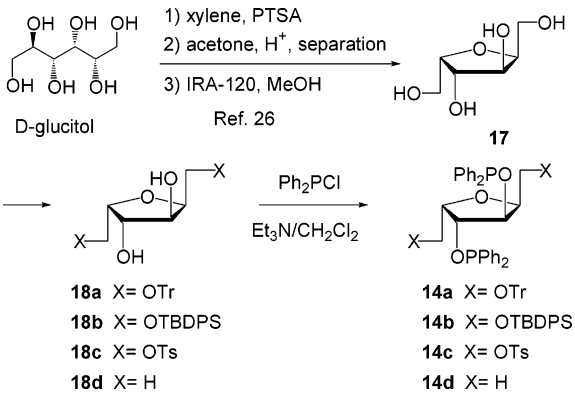
**SCHEME 1**




**SCHEME 2**

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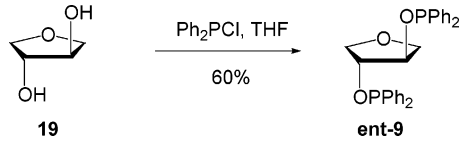


similar to previously reported yields, but this procedure allows **17** to be easily obtained from a very accessible nonexpensive starting material in a multigram scale. Primary alcohols were also protected by reaction with TrCl and TBDPSCl to give compounds **18a** and **18b**. The 2,5-dimethyl derivative **18d** was obtained by selective ditosylation of **17** to give **18c** and further reduction with $LiAlH_4$.

Treatment of **18a**, **18b**, and **18d** with $Ph_2PCl$ in basic medium afforded the ligands **14a**, **14b**, and **14d**, respectively, with yields higher than 80%. Ligand **14c** was not prepared.

Since the configuration of stereocenters bonded to the phosphinite moiety in ligand **9** is opposite to those of ligands **13** and **14**, we prepared enantiomer **ent-9** for the purpose of comparison. Thus, diol **19**[27] reacted with $Ph_2PCl$ to give **ent-9** in 60% yield (Scheme 3).

Rhodium complexes [Rh(cod)(**13a**−**e**)]$BF_4$, [Rh(cod)(**14a**,**b**,**d**)]$BF_4$, and [Rh(cod)(**ent-9**)]$BF_4$ (eqs 1−3) were prepared by reacting $[Rh(cod)_2]BF_4$ with ligands **13a**−**e**, **14a**,**b**,**d**, and **ent-9**, respectively. All of the complexes were isolated as colored solids and were stable in air.

$$[Rh(cod)_2]BF_4 + \mathbf{13a-e} \rightarrow [Rh(cod)(\mathbf{13a-e})]BF_4 \quad (1)$$

$$[Rh(cod)_2]BF_4 + \mathbf{14a,b,d} \rightarrow [Rh(cod)(\mathbf{14a,b,d})]BF_4 \quad (2)$$

$$[Rh(cod)_2]BF_4 + \mathbf{ent\text{-}9} \rightarrow [Rh(cod)(\mathbf{ent\text{-}9})]BF_4 \quad (3)$$

Ligands **13a**−**e**, **14a**,**b**,**d**, and **ent-9**, as well as their alcohol precursors, showed very simple $^1H$ and $^{13}C$ NMR spectra, characteristic of compounds with a $C_2$ symmetry. The $^{31}P$ NMR spectrum of **13a**−**e**, **14a**,**b**,**d**, and **ent-9** showed only one signal between 112 and 119 ppm, characteristic of a phosphinite function.

NMR spectra of complexes [Rh(cod)(**13a**−**e**)]$BF_4$, [Rh(cod)(**14a**,**b**,**d**)]$BF_4$, and [Rh(cod)(**ent-9**)]$BF_4$ at 25 °C show they have $C_2$ symmetry in solution. In the $^{31}P$ NMR spectrum, only one signal appeared between 120 and 129.7 ppm ($J_{P-Rh}$ = 164.8−170.8 Hz). The chemical shift and coupling constant values are in agreement with those observed for structurally related cationic diphosphinite rhodium complexes.[11a] The mononuclearity of complexes was confirmed by FAB and L-SIMS spectra, which in all of the cases showed molecular ions corresponding to the cation $[Rh(cod)L]^+$.

The crystal structure of complex [Rh(cod)(**14d**)]$BF_4$ was obtained by slow diffusion of hexane into a $CH_2Cl_2$ solution of the complex. Two cationic units only differing slightly in the relative disposition of the phenyl rings were detected, but only one of them is discussed here. The cationic rhodium complex consists of discrete mononuclear units, [Rh(cod)(**14d**)]$^+$, in the solid state, where the diphosphinite ligand acts as a chelate, and there is no interaction between the counterion and Rh. As expected, the complex is square planar and the P1−Rh−P2 angle is around 90°. Cyclooctadiene (cod) is disordered in two different conformations. Selected bonds and angles are listed in Figure 4.

The determination of the conformation of the metalocycle in the solid state is of interest since it has been shown that there is a good correlation between this conformation and the sense of the enantioinduction of the catalyst in the hydrogenation of enamidoesters, the conformation $\lambda$ leading preferentially to the *S* enantiomer, and the $\delta$ conformer leading to the *R* (Figure 5).[29] As it is shown in Figure 4, the complex is not $C_2$ symmetric in the solid state, and the aryl substituents are in a nonalternating pseudoaxial−pseudoequatorial array providing an achiral environment around Rh.

Comparing the structures of complexes [Rh(**14d**)(cod)]$BF_4$ and **20**,[12b] which has (1*S*,2*S*)-bis-diphenylphosphinoxycyclohexane as a chiral ligand (Figure 5), we observed several differences. (a) The cyclohexane ring in **20** has a chair conformation, while the tetrahydrofuran ring in [Rh(**14d**)(cod)]$BF_4$ has an envelope conformation. (b) The seven-membered chelate has a twist-chair conformation in **20** and a distorted boat conformation in [Rh(**14d**)(cod)]$BF_4$, as deduced from the parameters $\alpha$, $\beta$, $\alpha'$,

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**TABLE 1. Angles (α−δ and α′−δ′) and Dihedral Angles (ω and ω′) for Rh Complexes [Rh(cod)(14d)]$BF_4$ and 20[a,b]**

| entry | complex | α | β | α′ | β′ | γ | δ | γ′ | δ′ | ω | ω′ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | [Rh(cod)(**14d**)]$BF_4$ cation 1 | 9.9(f) | 72.5(r) | 70.4(r) | 11.2(f) | 21.7 | 86.0 | 84.1 | 22.8 | 52.7 | −53.2 |
| 2 | **20** (L = NBD, boat)[c] | 8.3(f) | 72(r) | 64(−) | 54(−) | 15 | 58 | 37 | 31 | 7 | −57 |
| 3 | **20** (L = cod, chair λ)[c] | 75(r) | 47(f) | 90(r) | 31(f) | 41 | 29 | 48 | 21 | −19 | −36 |

[a] In degrees. For definitions of parameters see Figure 1 in the Supporting Information. [b] Position: f = front, r = rear, − = position uncertain. [c] From ref 12b.

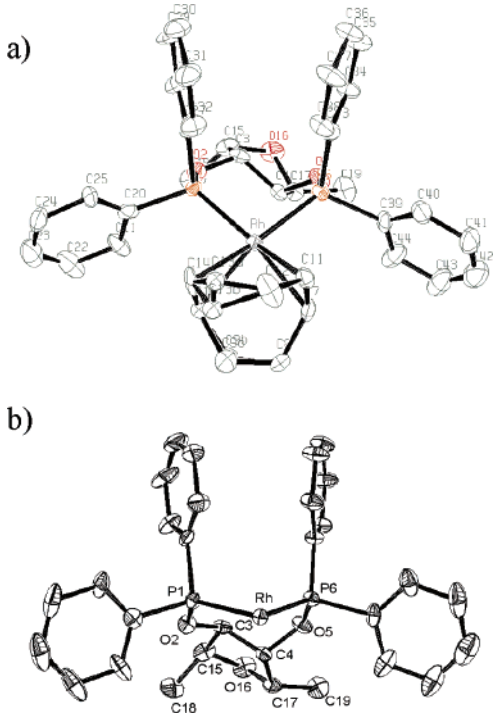



**FIGURE 4.** ORTEP[28] representation of the crystal structure of complex [Rh(cod)(**14d**)]$BF_4$. Counterions, solvates, and H atoms are omitted (a; front view) for clarity, and (b; front, bottom view) cyclooctadiene is also omitted in order to see the conformations of tetrahydrofuran and chelate rings. Selected distances and angles: Rh−P(6) = 2.288(2) Å, Rh−P(1) = 2.309(2) Å, P(6)−Rh−P(1) = 93.83(9)°, C(11)−Rh−P(6) = 91.1(2)°, C(7)−Rh−P(6) = 92.4(3)°, C(7)−Rh−C(10) = 77.9(4)°, and C(14)−Rh−P(1) = 89.2(3)°.

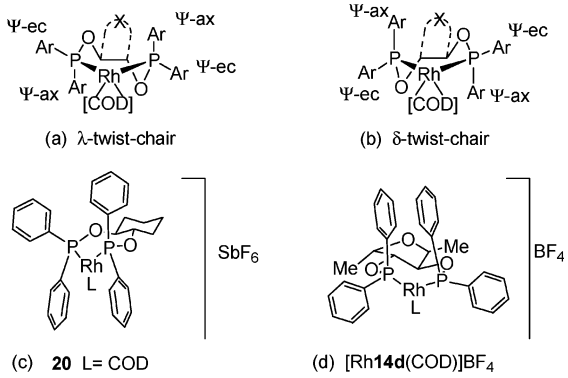
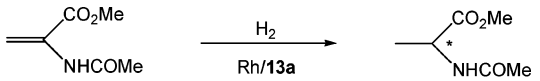



**FIGURE 5.** Conformations, λ (a) and δ (b), of seven-membered cationic chelates. Conformation of complexes **20** (c) and [Rh(**14d**)(cod)]$BF_4$ (d) in the solid state.

β′, γ, δ, γ′, δ′, ω, and ω′ (entry 1, Table 1), determined after Paulov[30] and Seebach.[31] In the chair conformation, values for angles α and α′, β and β′, and γ and γ′, as well as δ and δ′, are similar (entry 3, Table 1); furthermore, ω and ω′ values have an identical sign. By contrast, in complex [Rh(**14d**)(cod)]$BF_4$, correlations exist between angles α and β′, α′ and β, δ and γ′, and δ′ and γ. Moreover, angles ω = 52.69° and ω′ = −53.25° are of opposite sign (Table 1). These data correlate better with values of entry 2 and consequently with a boat conformation.

**TABLE 2. Hydrogenation of 21 with the Catalytic System [Rh]/13a[a]**




**21** **22**

| entry | solvent | substrate/Rh ratio | time (min) | conv (%) | % ee |
|---|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | 100 | 5 | 100 | 67(*R*) |
| 2 | $CH_2Cl_2$ | 500 | 35 | 93 | 67(*R*) |
| 3 | THF | 500 | 15 | 36 | 63(*R*) |
| 4 | toluene | 500 | 15 | 14 | 41(*R*) |
| 5 | MeOH | 500 | 15 | 63 | 73(*R*) |
| 6 | MeOH | 100 | 5 | 100 | 73(*R*) |
| 7 | acetone | 500 | 15 | 99 | 75(*R*) |

[a] Conditions: solvent = 15 mL, [Rh] = 15 × $10^{-6}$ mol, L/Rh = 1.05, room temperature, $P(H_2)$ = 1 bar.

**Catalysis.** Complexes [Rh(cod)**13a**−**e**]$BF_4$, [Rh(cod)-**14a**,**b**,**d**]$BF_4$, and [Rh(cod)**ent-9**]$BF_4$, as well as in situ catalysts formed by adding ligands **13a**−**e**, **14a**,**b**,**d**, and **ent-9** to [Rh$(cod)_2$]$BF_4$, were used as catalyst precursors in asymmetric hydrogenation. We initially studied the effect of the solvent on the hydrogenation of methyl acetamidoacrylate (**21**) with the catalytic system Rh/**13a** in an attempt to find the best conditions for a comparative study of ligands.

Table 2 shows that this catalytic system is active in the hydrogenation of enamidoester **21** in very mild conditions. It mainly affords enantiomer *R*. When the reaction was carried out in dichloromethane with a substrate/Rh ratio = 100, the conversion was complete in 5 min, and reached 93% in 35 min when this ratio was 500. In both cases, the enantiomeric excess was 67% (entries 1 and 2, Table 2). When the experiment was carried out using THF or toluene, both the conversion and the enantiomeric excessess were lower (entries 3 and 4). Although these types of ligands can hydrolyze in alcohol, we performed the experiment with MeOH at different substrate/Rh ratios and found that at substrate/Rh = 500, the enantiomeric excess attained 73%, but conversion stopped at 63% (entry 5). However, at substrate/Rh = 100, the conversion was complete in 5 min, which suggests that in the former case the catalyst

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**TABLE 3. Hydrogenation of 21 with the Catalytic Systems [Rh]/13a−e, 14a,b,d, and ent-9 and Complexes [Rh(cod)(13a−e)]$BF_4$, [Rh(cod)(14a,b,d)]$BF_4$, and [Rh(cod)(ent-9)]$BF_4$ [a]**

| entry | L | $[Rh(cod)_2]BF_4$/L (% ee) | $[Rh(cod)L]BF_4$ (% ee) |
|---|---|---|---|
| 1 | **13a**[b] | 75(*R*) | 76(*R*) |
| 2 | **13b**[c] | 85(*R*) | 85(*R*) |
| 3 | **13c** | 82(*R*) | 80(*R*) |
| 4 | **13d**[c] | 79(*R*) | 78(*R*) |
| 5 | **13e** | 87(*R*) | 87(*R*) |
| 6 | **14a** | 5(*R*) | 5(*R*) |
| 7 | **14b** | 59(*R*) | 59(*R*) |
| 8 | **14d** | 26(*R*) | 26(*R*) |
| 9 | **ent-9** | 16(*R*) | 18(*R*) |

[a] Conditions: solvent = acetone, 15 mL, [Rh] = $15 \times 10^{-6}$ mol, L/Rh = 1.05, substrate/Rh = 100, room temperature, $P(H_2)$ = 1 bar, 100% conversion. [b] Substrate/Rh = 500, 15 min. [c] Solvent = acetone/$CH_2Cl_2$, 13:2.

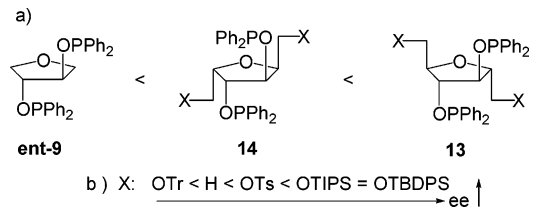



**FIGURE 6.** Influence of substituent configuration at C2 and C5 (a) and of the nature of substituents (b) on the enantioselectivity of the hydrogenation of **21**.

decomposes, probably by ligand solvolysis (entry 6). Ligands were stable in other solvents, and the best result was obtained in acetone, with the enantiomeric excess being 75% (entry 7).

Rhodium catalytic systems formed in situ from $[Rh(cod)_2]BF_4$ and ligands **13a**−**e**, **14a**−**c**, and **ent-9** were then used in the hydrogenation of **21** in acetone. Ligands **13b**,**d** were not soluble in acetone, and the experiment was carried out with an acetone/dichloromethane mixture. The results are listed in Table 3.

In the presence of rhodium, all of the ligands gave catalytic systems that were active in the hydrogenation of **20**. Experiments carried out by catalytic systems formed in situ provided essentially the same enantioselectivity values as those obtained from preformed complexes (Table 3). On the other hand, preformed complexes made it possible to carry out catalytic experiments in methanol without apparent solvolysis.

A comparison of the results provided by ligand **ent-9** (entry 9) and ligands **13a**−**e** (entries 1−5) and **14a**,**b**,**d** (entries 6−8) shows that the enantioselectivity is strongly influenced by (a) the presence of additional stereogenic centers at positions 2 and 5 of the tetrahydrofuran ring and (b) the steric effect of groups X (see Schemes 1 and 2). It can also be concluded that there is a synergy (match effect) among stereocenters 3,4 and 2,5 in ligands **13a**−**e** and an antagonism (mismatch effect) in ligands **14a,b,d**, which is modulated by groups X.

The main enantiomer obtained in the hydrogenation was always *R*. This suggests that chirality is determined by the stereocenters at C3 and C4, which are bonded to the coordinating atoms. Figure 6 summarizes the effect of the stereogenic centers at C2 and C5 on the enantioselectivity.

**TABLE 4. Influence of Temperature and Pressure on the Hydrogenation of 21 with the Catalytic Systems [Rh]/13b and 13e[a]**

| entry | ligand | *P* (bar) | *T* (°C) | time (min) | conv (%) | ee (%) |
|---|---|---|---|---|---|---|
| 1 | **13b**[b] | 1 | rt | 5 | 100 | 85(*R*) |
| 2 | **13b**[b] | 1 | 0 | 5 | 100 | 88(*R*) |
| 3 | **13b**[b] | 1 | −25 | 20 | 100 | 91(*R*) |
| 4 | **13b**[b] | 1 | −40 | 150 | 95 | 91(*R*) |
| 5[c] | **13b**[b] | 10 | rt | 30 | 98 | 83(*R*) |
| 6[c] | **13b**[b] | 10 | 50 | 50 | 100 | 78(*R*) |
| 7 | **13e**[c] | 1 | rt | 5 | 100 | 87(*R*) |
| 8 | **13e**[c] | 1 | −25 | 30 | 100 | 93(*R*) |

[a] Conditions: solvent = 15 mL, [Rh] = $15 \times 10^{-6}$ mol, L/Rh = 1.05, substrate/Rh = 100, room temperature, $P(H_2)$ = 1 bar. [b] Acetone/$CH_2Cl_2$, 13:2. [c] Acetone.

As far as the substituents at C2 and C5 are concerned, results were best with *tert*-butyldiphenylsilyloxymethyl and triisopropylsilyloxymethyl chains (entries 2, 5, and 7), while trityloxymethyl chains led to the lowest enantiomeric excesses (entries 1 and 6). On the other hand, the less-bulky methyl derivatives (entries 4 and 8) provided intermediate enantiomeric excess values. Figure 6 shows the relative influence of these factors on the enantioselectivity.

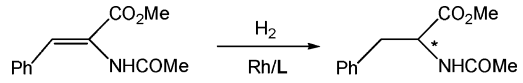
The effects of pressure and temperature on the enantioselectivity of the reduction of **21** were studied next. Ligands **13b**,**e**, which had provided the best results, were selected. Initially, we tried the catalytic system Rh/**13b** at 0 °C and maintained all of the other reaction conditions. The conversion was also complete in 5 min, and the enantiomeric excess increased slightly to 88% (entries 1 and 2, Table 4). Because the activity was maintained, we decreased the temperature to −25 °C and achieved a 91% ee in 20 min (entry 3). When the temperature was decreased to −40 °C, the enantiomeric excess did not improve and the activity decreased (entry 4). Performing the experiment at 10 bar at room temperature decreased the enantiomeric excess and the conversion (entry 5). When the temperature was increased to 50 °C and the pressure was increased to 10 bar, there was an additional decrease in the enantiomeric excess (entry 6). When the catalytic system Rh/**13e** was used at −25 °C and 1 bar, the enantiomeric excess reached 93%.

We next studied the reduction of methyl α-acetamidocinnamate **23** with the catalytic systems Rh/L (L = **13a**−**e**, **14a**,**b**,**d**, and **ent-9**). The results are listed in Table 5. The influence of the different parameters on the enantioselectivity was similar to that observed for the reduction of substrate **21**. Thus, the synergy among additional stereocenters at C2, C5, and X groups in ligands **13a**−**e** was also observed in this substrate (entries 1−5).

These ligands form more efficient catalytic systems than ligands **14a**,**b**,**d** (entries 6−8), although in general both are more enantioselective than **ent-9** (entry 9). The effect of substituents in the lateral chains also showed a similar trend, and the silyloxymethyl chains provided the best results in ligands **13** (entries 2 and 5) and ligands **14** (entry 7). In this case, ligand **14a** also provided a very low enantiomeric excess, which confirms that the structural elements are particularly mismatched in this ligand (entry 6).

A comparison of Tables 2 and 4 shows that the behavior of these catalytic systems toward the reduction of substrates **21** and **23** is similar. In general terms,

**TABLE 5. Hydrogenation of 23 with the Catalytic Systems [Rh]/13a−e, 14a,b,d, and ent-9[a]**

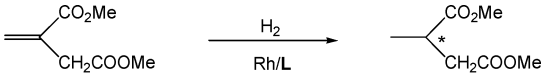



**23** **24**

| entry | L | conv (%) | ee (%) |
|---|---|---|---|
| 1 | **13a** | 95 | 73(*R*) |
| 2 | **13b**[b] | 96 | 81(*R*) |
| 3 | **13c** | 100 | 77(*R*) |
| 4 | **13d**[b] | 100 | 75(*R*) |
| 5 | **13e** | 100 | 86(*R*) |
| 6 | **14a** | 100 | 18(*R*) |
| 7 | **14b** | 100 | 59(*R*) |
| 8 | **14d** | 100 | 32(*R*) |
| 9 | **ent-9** | 100 | 27(*R*) |

[a] Conditions: solvent = acetone, 15 mL, [Rh] = 15 × $10^{-6}$ mol, L/Rh = 1.05, substrate/Rh = 100, room temperature, $P(H_2)$ = 1 bar, $t$ = 5 min. [b] Acetone/$CH_2Cl_2$, 13:2.

**TABLE 6. Hydrogenation of 25 with the Catalytic Systems [Rh]/13a−e, 14a,b,d, and ent-9[a]**




**25** **26**

| entry | L | solvent | time (min) | ee (%) |
|---|---|---|---|---|
| 1 | **13a** | $CH_2Cl_2$ | 5 | 48(*S*) |
| 2 | **13b** | $CH_2Cl_2$ | 5 | 48(*S*) |
| 3 | **13b** | acetone/$CH_2Cl_2$ [b] | 75 | 29(*S*) |
| 4 | **13c** | $CH_2Cl_2$ | 5 | 54(*S*) |
| 5 | **13d** | $CH_2Cl_2$ | 5 | 53(*S*) |
| 6 | **13d** | acetone/$CH_2Cl_2$ [b] | 60 | 63(*S*) |
| 7 | **13e** | $CH_2Cl_2$ | 5 | 51(*S*) |
| 8 | **14a** | $CH_2Cl_2$ | 5 | 53(*R*) |
| 9 | **14b** | $CH_2Cl_2$ | 5 | 9(*R*) |
| 10 | **14d** | $CH_2Cl_2$ | 5 | 19(*R*) |
| 11 | **ent-9** | $CH_2Cl_2$ | 5 | 4(*R*) |

[a] Conditions: solvent = 15 mL, [Rh] = 15 × $10^{-6}$ mol, L/Rh = 1.05, substrate/Rh = 100, room temperature, $P(H_2)$ = 1 bar, 100% conversion. [b] Acetone/$CH_2Cl_2$, 13:2.

ligands **13** are superior to **14**, and ligand **ent-9** results in the poorest enantiomeric excess.

The catalytic systems Rh/L (L = **13a**−**e**, **14a**,**b**,**d**, and **ent-9**) were also very active in the hydrogenation of dimethyl itaconate **25** (Table 6). However, the hydrogenation of this substrate was very different than those of substrates **21** and **23**. With regard to the solvent, the reaction rate in acetone was slower. Furthermore, the enantioselectivity in acetone was also much lower, with the exception of ligands **13d** and **14d**. In general, the catalytic systems Rh/**13a**−**e** (entries 1−7) provided better enantioselectivities than Rh/**14a**,**b**,**d** and Rh/**ent-9** (entries 8−11). Curiously, ligand **14a**, which provided very low enantioselectivities with substrates **21** and **23**, gives better enantioselectivity than **14b**,**d** in the hydrogenation of **25**, and values similar to those of ligands **13a**−**e**. Furthermore, a noteworthy difference is that the configuration of the main isomer of hydrogenated compound **26** depends on the configuration of stereogenic centers at C2 and C5. Ligands **13a**−**e** preferably give the isomer *S*; ligands **14a**,**b**,**d** give isomer *R*, and **ent-9** gives no enantiomeric excess. Interestingly, in some cases, for instance **13a** and **14a**, the enantiomeric excess values obtained are similar but of opposite sign, while ligand **ent-9** provides a value that is the average. It is not easy to rationalize these results, although the fact that substrate **25** behaves differently from substrates **20** and **22** may be related to the different coordination of these substrates to the metal.

When the phenyl groups in the $PPh_2$ were modified by introducing groups such as *p*-OMe of *p*-$CF_3$, ligand **13b** did not improve the enantioselectivity of reduction of **20** and **22**.

Concerning the origin of the enantioselectivity, it has been seen before that complex [Rh**14d**(cod)]$BF_4$ has practically an achiral structure in the solid state, which may account for the modest enantioselectivity obtained with this complex in the hydrogenation of substrates **21**, **23**, and **25**, but does not allow one to find a relation between the conformation and the sense of the enantioselectivity. However, comparing the configuration of the main enantiomer obtained in hydrogenation of enamidoesters and dimethylitaconate using complex **20**[12b] and related complexes,[5−12] which give the *S* enantiomer, and [Rh**14d**(cod)]$BF_4$, which gives the *R* enantiomer (see Tables 3, 5, and 6), one can conclude that the sense of the enantioinduction is determined by the configuration of carbons of the tetrahydrofuran frame attached to the phosphinoxy groups. In parts c and d of Figure 5, it can be seen that the carbons bonded to the phosphinoxy groups have opposite configuration in complexes **20** and [Rh**14d**(cod)]$BF_4$. This conclusion can be extended to the complexes with ligands **13** and **14** (see Tables 2−6), which show a similar trend.

Despite our efforts, we were unable to obtain crystals of a complex with ligands **13** and **ent-9** that would allow us to gain information about the influence of the lateral chain in the conformation of complexes in the solid state.

It is well-known that five-membered rings are very flexible, and that the presence of substituents in the ring increases the energy for the conformational changes. On the other hand, the limitation of flexibility usually increases the enantioselectivity.[32] In this context, the influence of substituents at positions 2 and 5 of ligands **13** and **14** in the level of asymmetric induction may be related to restrictions of the conformational mobility in the tetrahydrofuran ring and, consequently, in the seven-membered quelate ring.[33] The different sense of optical induction for catalysts having close structures (see entries 1 and 8, Table 6) has also been observed by other authors and attributed to changes of the metal−ligand chelate conformation.[32] Mechanistic studies in order to prove these facts are in progress.

## Conclusion

New families of ligands **13a**−**e**, **14a**,**b**,**d**, and **ent-9**, which have a tetrahydrofuran backbone, were easily prepared from D-glucosamine, D-glucitol, and (2*S*,3*S*)-diethyl tartrate, respectively. These ligands were used to prepare catalyst precursors of the general formula [Rh(cod)L]$BF_4$ (L = **13a**−**e**, **14a**,**b**,**d**, and **ent-9**). The catalytic systems obtained from [Rh(cod)L]$BF_4$ or [Rh(cod)$_2$]$BF_4$/L were active in the hydrogenation of enamidoesters

(32) Li, W.; Waldkirch, J. P.; Zhang, X. *J. Org. Chem.* **2002**, *67*, 7618−7623.

(33) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: NewYork, 1982; Vol. 8, p 463.

**21** and **23** and of diester **25**. The results showed that in the hydrogenation of **21** and **23**, the configuration of the main enantiomer obtained is determined by the configuration of C3 and C4, which support the coordinative heteroatoms. However, the enantiomeric excess values are strongly influenced by the configuration of the remote stereogenic centers at C2 and C5 and the steric effect of substituents. These effects are synergic for ligands **13**, which provide the best results. In contrast, in the hydrogenation of **25**, the sense of asymmetric induction is determined by the configuration at positions 2 and 5. Ligands **13** lead to enantiomer *S*, while ligands **14** lead to enantiomer *R*.

## Experimental Section

**1,6-Di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (16b).** *tert*-Butyldiphenylsilyl chloride (3 mL, 11.66 mmol) was added dropwise to a solution of **15** (0.87 g, 5.3 mmol) and imidazole (1.5 g, 22.28 mmol) in 12 mL of dry DMF at 0 °C. The reaction mixture was left to warm to room temperature and stirred for 25 h. The solvent was then removed in vacuo, and the residue was dissolved in $CH_2Cl_2$ and washed with water. The organic layer was dried with $Na_2SO_4$, concentrated, and purified by column chromatography (hexane/ethyl acetate, 4:1) to afford 1.36 g (40%) of **16b** as a white syrup: mp = 90−91 °C; $[\alpha]^{25}_D$ +19.66° ($CHCl_3$, *c* 1.15); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.06 (s, 18 H), 3.75 (dd, $J$ = 2.4, 11.1 Hz, 2 H), 3.86 (dd, $J$ = 3.6, 11.1 Hz, 2 H), 4.03 (d, $J$ = 9 Hz, 2 H), 4.17 (m, 2 H), 4.25 (m, 2 H), 7.25−7.80 (m, 20 H); $^{13}$C NMR ($CDCl_3$, 75.4 MHz) $\delta$ 19.0, 26.7, 65.5, 79.7, 87.1, 127.8−135.7. Anal. Calcd for $C_{38}H_{48}O_5Si_2$: C, 71.21; H, 7.55. Found: C, 70.92; H, 7.54.

**1,6-Di-*O*-(triisopropylsilyl)-2,5-anhydro-D-mannitol (16e).** Silylation was carried out from 0.687 g (4.18 mmol) of **15**, 1.19 g (17.48 mmol) of imidazole, and 1.94 mL (9.16 mmol) of triisopropylchlorosilane in 9.5 mL of dry DMF for 48 h. The crude oil of the reaction was purified by column chromatography with hexane/ethyl acetate (5:1) to give **16e** (1.4 g, 70%) as a colorless syrup: $[\alpha]^{25}_D$ +14.78° ($CHCl_3$, *c* 1.11); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.05−1.20 (m, 42 H), 3.83 (dd, $J$ = 10.8, 2.4 Hz, 2 H), 3.91 (dd, $J$ = 10.8, 2.8 Hz, 2 H), 4.10 (d, $J$ = 10.4 Hz, 2 H), 4.14 (m, 2 H), 4.60 (d, $J$ = 10.4 Hz, 2 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 11.7, 17.7, 17.7, 65.3, 79.6, 88.2. Anal. Calcd for $C_{24}H_{52}O_5Si_2$: C, 60.45; H, 10.99. Found: C, 60.42; H, 11.00.

**1,6-Di-*O*-(triphenylmethyl)-2,5-anhydro-L-iditol (18a).** A solution of **17** (0.51 g, 3.1 mmol) and trityl chloride (1.92 g, 6.88 mmol) in 8 mL of dry pyridine was heated at 100 °C for 72 h. The mixture was then diluted with $CH_2Cl_2$ and washed successively with 0.03 M aqueous HCl (3 × 50 mL), with a saturated aqueous solution of $NaHCO_3$, and with $H_2O$. The organic phase was dried over $Na_2SO_4$ and concentrated to dryness. The purification of the resulting residue by column chromatography with hexane/ethyl acetate (3:1) gave 1.17 g (58%) of **18a** as a white foam: mp = 92−93 °C; $[\alpha]^{25}_D$ −8.75° ($CHCl_3$, *c* 0.93); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.23 (s, 2 H), 3.40 (dd, $J$ = 3.8, 9.8 Hz, 2 H), 3.48 (dd, $J$ = 5.4, 9.8 Hz, 2 H), 4.25 (d, $J$ = 2.8 Hz, 2 H), 4.41 (m, 2 H), 7.0−7.0 (m, 30 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 62.8, 78.6, 78.8, 87.2, 127.0−143.2. Anal. Calcd for $C_{44}H_{40}O_5$: C, 81.46; H, 6.21. Found: C, 81.19; H, 6.19.

**1,6-Di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-L-iditol (18b).** *tert*-Butyldiphenylsilyl chloride (1.6 mL, 6.15 mmol) was added dropwise to a cold suspension (0 °C) of **17** (0.45 g, 2.74 mmol) and imidazole (0.8 g, 11.75 mmol) in 6.5 mL of dry DMF under an argon atmosphere. The mixture was left to warm to room temperature and stirred for 48 h. The solvent was then removed in vacuo. The crude oil obtained was diluted in $CH_2Cl_2$ and washed with water, and the aqueous phase extracted with $CH_2Cl_2$. The combined organic layer was dried over $Na_2SO_4$, and the evaporation of the solvent provided a residue that was purified by column chromatography with hexane/ethyl acetate (4:1) to render 1.28 g (72%) of **18b** as white crystals: mp = 122−123 °C; $[\alpha]^{25}_D$ −12.61° ($CHCl_3$, *c* 1.19); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.06 (s, 18 H), 3.98 (d, $J$ = 3.2 Hz, 2 H), 4.04 (dd, $J_{1',2}$ = 3.6, 11.2 Hz, 2 H), 4.07 (dd, $J$ = 4.4, 11.2 Hz, 2 H), 4.26 (m, 2 H), 4.38 (t, $J$ = 3.2 Hz, 2 H), 7.25−7.80 (m, 20 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 19.2, 26.8, 63.7, 78.9, 79.7, 127.7−135.5. Anal. Calcd for $C_{38}H_{48}O_5Si_2$: C, 71.21; H, 7.55. Found: C, 70.92; H, 7.55.

**1,6-Di-*O*-(*p*-toluensulfonyl)-2,5-anhydro-L-iditol (18c).** To a cold solution (0 °C) of **17** (0.98 g, 5.97 mmol) in 40 mL of dry pyridine was added 2.62 g (13.74 mmol) of *p*-toluensulfonyl chloride under an inert atmosphere. The resulting mixture was stirred for 48 h at room temperature, diluted with $CH_2Cl_2$, and washed with an aqueous solution of 1 N HCl (100 mL × 3). The combined aqueous layer was extracted with $CH_2Cl_2$. The combined organic layer was washed with an aqueous solution of $NaHCO_3$ and $H_2O$, dried over $Na_2SO_4$, and concentrated. Chromatography on silica gel with hexane/ethyl acetate (1:1) yielded 31.7 g (60%) of **18c** as a white solid: mp = 147−148 °C; $[\alpha]^{25}_D$ +7.95° (THF, *c* 1.065); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.44 (s, 6 H), 2.59 (s, 2 H), 4.03 (dd, $J$ = 4.6, 8.6 Hz, 2 H), 4.28−4.21 (m, 6 H), 7.75 (d, $J$ = 8.4 Hz, 4 H), 7.33 (d, $J$ = 8.4 Hz, 4 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 21.8, 67.2, 76.5, 77.8, 127.9−145.1. Anal. Calcd for $C_{20}H_{24}O_9S_2$: C, 50.84; H, 5.12; S, 13.57. Found: C, 51.02; H, 5.13; S, 13.57.

**1,6-Dideoxy-2,5-anhydro-L-iditol (18d).** To a solution of 1.69 g (3.57 mmol) of **18c** in 10 mL of dry THF was added 0.407 g (10.7 mmol) of $LiAlH_4$. The resulting suspension was heated to reflux for 2 h. After the mixture was cooled to room temperature, Arberlite IR-120($H^+$) was carefully added, and the mixture was stirred continuously until the evolution of $H_2$ could no longer be observed. The mixture was filtered through a Celite pad and washed with THF. The solvent was then removed and the crude product chromatographed over silica gel in $CH_2Cl_2$/MeOH (12:1) to render 0.36 g (77%) of **18d** as a white solid: mp = 75−76 °C; $[\alpha]^{25}_D$ +24.94° (THF, *c* 1.15); $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.17 (d, $J$ = 6.6 Hz, 6 H), 3.90 (d, $J$ = 3.0 Hz, 2 H), 4.22 (qd, $J_{2,3}$ = 3.0, 6.6 Hz, 2 H), 4.87 (s, 2 H); $^{13}$C NMR ($CDCl_3$, 75.4 MHz) $\delta$ 14.7, 77.3, 79.7. Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.70; H, 9.14.

**General Procedure for Synthesizing Diphosphinites from the Corresponding Diols.** To a solution of the diol (1 mmol) in dry and degassed $CH_2Cl_2$ or THF (5 mL) was added dry $Et_3N$ (4.4 mmol). After the mixture was cooled to −15 °C, a solution of chlorophosphine (2.2 mmol) in 3 mL of dry and degassed $CH_2Cl_2$ was slowly added. The mixture was then stirred, and the temperature gradually increased. Completion of the reaction was monitored by TLC. The mixture was then diluted with ether in order to precipitate $Et_3N{\cdot}HCl$. The solids were filtered off through a Celite pad, and the filtrate was concentrated to dryness. The crude product was purified by chromatographic techniques.

**3,4-Bis-*O*-(diphenylphosphino)-1,6-di-*O*-(triphenylmethyl)-2,5-anhydro-D-mannitol (13a).** The synthesis of **13a** was carried out in accordance with the general procedure from 0.40 g (0.61 mmol) of **16a**, 3 mL of dry and degassed $CH_2Cl_2$, 378 mL (2.71 mmol) of dry $Et_3N$, and 243 mL (1.35 mmol) of $Ph_2PC$, dissolved in 1.5 mL of $CH_2Cl_2$. After 15 min, the reaction was complete, and the residue obtained was purified by column chromatography in hexane/ethyl acetate (4:1) to afford 0.5 g (80%) of **13a** as a white foam: mp = 64−65 °C; $[\alpha]^{25}_D$ +0.36° ($CHCl_3$, *c* 1.04); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.17 (dd, $J$ = 5.6, 10.8 Hz, 2 H), 3.19 (dd, $J$ = 5.6, 10.8 Hz, 2 H), 4.28 (m, 2 H), 4.62 (md, $J$ = 8.8 Hz, 2 H), 7.10−7.50 (m, aromatic, 50 H); $^{13}$C NMR ($CDCl_3$, 100.6 MH) $\delta$ 64.2, 83.5 (m), 86.1 (m), 86.6, 126.8−144.0; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 115.63 (s). Anal. Calcd for $C_{68}H_{58}O_5P_2$: C, 80.30; H, 5.75. Found: C, 79.99; H, 5.73.

**3,4-Bis-*O*-(diphenylphosphino)-1,6-di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-D-mannitol (13b).** The title

compound was prepared in accordance with the general method from 0.58 g (0.9 mmol) of **16b**. The reaction was complete after 15 min, and the residue obtained was purified by column chromatography with hexane/ethyl acetate (4:1) to afford 0.75 g (81%) of the diphosphinite **13b** as a white syrup: $[\alpha]^{25}_D$ +9.9° ($CHCl_3$, *c* 1.8); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.01 (s, 18 H), 3.62 (dd, $J$ = 4.6, 11.0 Hz, 2 H), 3.75 (dd, $J$ = 5.2, 11.0 Hz, 2 H), 4.18 (m, 2 H), 4.88 (md, $J$ = 8.4 Hz, 2 H), 7.19−7.63 (m, aromatic, 40 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 19.2, 26.8, 63.8, 84.2 (m), 85.5 (m), 127.6−142.1; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 115.51 (s). Anal. Calcd for $C_{62}H_{66}O_5P_2Si_2$: C, 73.78; H, 6.59. Found: C, 73.65; H, 6.57.

**3,4-Bis-*O*-(diphenylphosphino)-1,6-di-*O*-(*p*-toluensulfonyl)-2,5-anhydro-D-mannitol (13c).** This compound was sythesized from 0.51 g (1.09 mmol) of diol **16c** in 3 mL of THF, 669 mL (4.8 mmol) of $Et_3N$, and a solution of 431 mL (2.4 mmol) of $Ph_2PCl$ in 2 mL of THF. The reaction, which was monitored by TLC with the system hexane/ethyl acetate (1:2), was complete in 30 min. Chromatography on silica using the system hexane/ethyl acetate yielded 0.64 g (71%) of **13c** as a white syrup: $[\alpha]^{25}_D$ +15.48° ($CHCl_3$, *c* 1.13); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.39 (s, 6 H), 3.87 (dd, $J$ = 5.6, 10.4 Hz, 2 H), 3.92 (dd, $J$ = 4.4, 10.4 Hz, 2 H), 4.01 (m, 2 H), 4.38 (md, $J$ = 8.8 Hz, 2 H), 7.23 (d, $J$ = 8.0 Hz, 4 H), 7.66 (d, $J$ = 8.0 Hz, 4 H), 7.27−7.34 (m, aromatic, 20 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 21.6, 68.4, 81.2 (m), 84.1 (m), 128.0−144.8; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 119.17 (s). Anal. Calcd for $C_{44}H_{42}O_9P_2S_2$: C, 62.85; H, 5.03; S, 7.63. Found: C, 62.94; H, 5.01; S, 7.60.

**3,4-Bis-*O*-(diphenylphosphino)-1,6-dideoxy-2,5-anhydro-D-mannitol (13d).** This ligand was prepared in accordance with the general method from 0.84 g (6.35 mmol) of diol **16d** in 13 mL of THF, 3.92 mL (28.09 mmol) of $Et_3N$, and a solution of 2.52 mL (14.04 mmol) of $Ph_2PCl$ in 6.5 mL of THF. The reaction, which was controlled by TLC using $CH_2Cl_2$/MeOH (3:1), was complete in l.7 h. The reaction crude product was purified by column chromatography using hexane/ethyl acetate (4:1) as eluent to render 2.6 g (80%) of **13d** as a colorless syrup: $[\alpha]^{25}_D$ −20.4° ($CHCl_3$, *c* 1.04); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.21 (d, $J$ = 6.4 Hz, 6 H), 4.12 (m, 2 H), 4.26 (md, $J$ = 8.8 Hz, 2 H), 7.2−7.5 (m, aromatic, 20 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 19.1, 78.3 (m), 90.7 (m), 128.0−141.9; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 114.38 (s). Anal. Calcd for $C_{30}H_{30}O_3P_2$: C, 71.99; H, 6.04. Found: C, 72.22; H, 6.06.

**3,4-Bis-*O*-(diphenylphosphino)-1,6-di-*O*-(triisopropylsilyl)-2,5-anhydro-D-mannitol (13e).** The title compound was synthesized from 0.457 g (0.95 mmol) of diol **16e**. The reaction, which was monitored by TLC using hexane/ethyl acetate (3:2), was complete in 2 h. The residue obtained was purified by column chromatography using the system hexane/ethyl acetate (4:1) to give 0.48 g (60%) of **13e** as a colorless syrup: $[\alpha]^{25}_D$ +8.34° ($CHCl_3$, *c* 1.11); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.10−0.98 (m, 42 H), 3.67 (dd, $J$ = 5.2, 10.4 Hz, 2 H), 3.74 (dd, $J$ = 5.6, 10.4 Hz, 2 H), 4.15 (m, 2 H), 4.71 (md, $J$ = 8.8 Hz, 2 H), 7.20−7.47 (m, aromatic, 20 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 11.8, 17.9, 17.9, 63.7, 84.8 (m), 85.6 (m), 130.6−142.2; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 115.13 (s). Anal. Calcd for $C_{48}H_{70}O_5P_2Si_2$: C, 68.21; H, 8.35. Found: C, 67.96; H, 8.35.

**3,4-Bis-*O*-(diphenylphosphino)-1,6-di-*O*-(triphenylmethyl)-2,5-anhydro-L-iditol (14a).** This compound was prepared following the general method from 0.61 g (0.94 mmol) of **18a**, 5 mL of dry $CH_2Cl_2$, 578 mL (4.14 mmol) of dry $Et_3N$, and 372 mL (2.07 mmol) of $Ph_2PCl$, dissolved in 1.5 mL of $CH_2Cl_2$. The reaction was monitored by TLC in hexane/ethyl acetate (3:2). After 1.5 h, the reaction was complete, and the residue obtained was purified by column chromatography using the hexane/ethyl acetate (3:2) system to give 0.8 g (83%) of **14a** as a white solid: mp = 119−120 °C; $[\alpha]^{25}_D$ +9.53° ($CHCl_3$, *c* 1.025); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.18 (dd, $J$ = 5.8, 9.4 Hz, 2 H), 3.47 (dd, $J$ = 6.6, 9.4 Hz, 2 H), 4.37 (dd, $J$ = 3.0, 8.0 Hz, 2 H), 4.30 (m, 2 H), 7.25−7.10 (m, 50 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 62.8, 79.6 (m), 82.6 (m), 86.8, 126.6−141.8; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 114.12 (s). Anal. Calcd for $C_{68}H_{58}O_5P_2$: C, 80.30; H, 5.75. Found: C, 79.97; H, 5.76.

**3,4-Bis-*O*-(diphenylphosphino)-1,6-di-*O*-(*tert*-butyldiphenylsilyl)-2,5-anhydro-L-iditol (14b).** This compound was prepared in accordance with the general method from 0.40 g (0.62 mmol) of diol **18b**. The reaction was controlled by TLC in hexane/ethyl acetate (3:2) as eluent. The reaction was complete after 1.5 h. Chromatography on silica gel with hexane/ethyl acetate (3:2) yielded 0.56 g (91%) of **14b** as a white syrup: $[\alpha]^{25}_D$ −17.8° ($CHCl_3$, *c* 0.88); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 0.94 (s, 18 H), 3.72 (dd, $J$ = 5.8, 10.0 Hz, 2 H), 3.85 (dd, $J$ = 7.4, 10.0 Hz, 2 H), 4.20 (m, 2 H), 4.51 (dd, $J$ = 2.8, 8.0 Hz, 2 H), 7.15−7.65 (m, 30 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 19.2, 26.9, 61.7, 80.7 (m), 83.1 (m), 127.4−135.5; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 115.73 (s). Anal. Calcd for $C_{62}H_{66}O_5P_2Si_2$: C, 73.78; H, 6.59. Found: C, 73.99; H, 6.57.

**3,4-Bis-*O*-(diphenylphosphino)-1,6-dideoxy-2,5-anhydro-L-iditol (14d).** This ligand was prepared in accordance with the general procedure described above from 0.33 g (2.49 mmol) of diol **18d** in 5 mL of THF, 1.53 mL (10.97 mmol) of $Et_3N$, and a solution of 0.98 mL (5.45 mmol) of $Ph_2PCl$ in 2.5 mL of THF. The reaction, which was controlled by TLC in $CH_2Cl_2$/MeOH (3:1), was complete in l.75 h. The crude oil was purified by column chromatography using the hexane/ethyl acetate (3:1) system to render 0.98 g (79%) of **14d** as a white syrup: $[\alpha]^{25}_D$ −34.37° ($CHCl_3$, *c* 0.98); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 1.20 (d, $J$ = 6.4 Hz, 6 H), 4.23 (dd, $J$ = 3.2, 9.2 Hz, 2 H), 4.35 (qd, $J$ = 3.2, 6.4 Hz, 2 H), 7.45−7.20 (m, 20 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 15.2, 76.0, 85.0, 128.1−141.9; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 114.04 (s). Anal. Calcd for $C_{30}H_{30}O_3P_2$: C, 71.99; H, 6.04. Found: C, 72.27; H, 6.02.

**(3*R*,4*R*)-(−)-3,4-Bis(diphenylphosphinoxy)tetrahydrofuran (ent-9).** The title compound was prepared in accordance with the general procedure beginning with 0.28 g (2.68 mmol) of **19**, 1.69 mL (12.12 mmol) of dry $Et_3N$, and a solution of 1.10 mL (6.12 mmol) of $Ph_2PCl$, dissolved in 3.5 mL of THF. The reaction, which was controlled by TLC in $CH_2Cl_2$/MeOH (4:1), was complete in 30 min. The crude oil was purified by column chromatography using the hexane/ethyl acetate (3:1) system to give 0.82 g (63%) of **ent-9** as a white solid: mp = 60−61 °C; $[\alpha]^{25}_D$ −71.68° ($CHCl_3$, *c* 1.055); $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 3.92 (d, $J$ = 9.8 Hz, 2 H), 4.05 (dd, $J$ = 3.4, 9.8 Hz, 2 H), 4.05 (dd, $J$ = 3.4, 9.8 Hz, 2 H), 4.51 (dd, $J$ = 3.4, 8.8 Hz, 2 H), 7.20−7.45 (m, 20 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 72.9, 83.7, 128.2−141.3; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 112.43 (s). Anal. Calcd for $C_{28}H_{26}O_3P_2$: C, 71.18; H, 5.55. Found: C, 71.18; H, 5.52.

**Preparation of Rh Complexes [Rh(cod)(L)]$BF_4$, L = Diphosphinite: General Procedure.** The complexes were prepared by adding a solution of 0.088 mmol of diphosphinite in 3 mL of $CH_2Cl_2$ to a solution of 0.030 g (0.073 mmol) of [Rh(cod)$_2$]$BF_4$ in 10 mL of $CH_2Cl_2$. The mixture was then stirred for 30 min, and the solvent was removed in vacuo. The residue was washed with dry hexane first and then with dry ether in order to remove the excess diphosphinite and free cyclooctadiene.

**[Rh(cod)(13a)]$BF_4$.** Beginning with 0.030 g (0.073 mmol) of [Rh(cod)$_2$]$BF_4$ in 10 mL of $CH_2Cl_2$ and 0.090 g (0.088 mmol) of diphosphinite **13a** and following the general procedure, we obtained 0.042 g (43%) of complex [Rh(cod)(**13a**)]$BF_4$ as a yellow solid: MS (FAB positive) *m*/*z* 1227.4 $[M]^+$, 1119.3 $[M - (cod)]^+$; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 2.15−2.32 (m, C*H*$_2$, cod, 8 H), 3.16 (dd, $J$ = 3.2, 10.8 Hz, 2 H), 3.58 (dd, $J$ = 2.6, 10.8 Hz, 2 H), 4.46 (m, 2 H), 4.70 (s, 4 H), 5.36 (s, 2 H), 7.00−7.50 (m, 50 H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz) $\delta$ 30.2, 30.3, 63.3, 82.4 (m), 82.7, 87.0, 104.1 (m), 106.0 (m), 127.3−143.6; $^{31}$P NMR ($CDCl_3$, 161.97 MHz) $\delta$ 122.60 (d, $J_{Rh,P}$ = 166.1 Hz).

**[Rh(cod)(13b)]$BF_4$.** Beginning with 0.050 g (0.12 mmol) of [Rh(cod)$_2$]$BF_4$ in the minimum quantity of $CH_2Cl_2$ and 138 mg (0.136 mmol) of diphosphinite **13b** and following the general procedure, we obtained 0.132 g (68%) of complex [Rh(cod)(**13b**)]$BF_4$ as an orange solid: MS (FAB positive) *m*/*z*

1219.4 $[M]^+$, 1111.3 $[M - (cod)]^+$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.09 (s, 18 H), 2.60−2.20 (m, 8 H), 3.69 (dd, $J$ = 3.2, 11.6 Hz, 2 H), 3.85 (dd, $J$ = 2.2, 11.6 Hz, 2 H), 4.18 (s, 2 H), 4.66 (s, 2 H), 4.76 (bs, 2 H), 5.24 (s, 2 H), 7.20−7.80 (m, 40 H); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 19.4, 26.9, 29.9, 30.8, 63.1, 81.2, 82.5 (m), 104.4, 106.2, 127.6−135.5; $^{31}P$ NMR ($CDCl_3$, 161.97 MHz) $\delta$ 125.13 (d, $J_{Rh,P}$ = 167.9 Hz).

**[Rh(cod)(13c)]$BF_4$.** Complex [Rh(cod)(**13c**)]$BF_4$ (130 mg, 92%) was prepared as a yellow solid from 0.050 g (0.123 mmol) of [Rh(cod)$_2$]$BF_4$, dissolved in the minimum quantity of $CH_2Cl_2$, and 0.108 g (0.128 mmol) of diphosphinite **13c** in 3 mL of $CH_2Cl_2$: HRMS (L-SIMS) calcd for $[C_{52}H_{54}O_9P_2S_2Rh]^+$ 1051.173957; found 1051.173930; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 2.44 (s, 6 H), 2.25−2.60 (m, 8 H), 3.90 (dd, $J$ = 2.4, 11.2 Hz, 2 H), 4.01 (m, 2 H), 4.07 (dd, $J$ = 4, 11.2 Hz, 2 H), 4.72 (m, 2 H), 4.88 (m, 2 H), 5.06 (m, 2 H), 7.34 (d, $J$ = 8 Hz, 4 H), 7.71 (d, $J$ = 8 Hz, 4 H), 7.47−7.66 (m, 20 H); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 21.7, 29.8, 30.7, 68.1, 78.3 (m), 79.2, 104.7 (m), 104.9 (m), 127.9−145.7; $^{31}P$ NMR ($CDCl_3$, 161.97 MHz) $\delta$ 127.81 (d, $J_{Rh,P}$ = 169.4 Hz).

**[Rh(cod)(13d)]$BF_4$.** The general procedure was followed as 50 mg (0.12 mmol) of [Rh(cod)$_2$]$BF_4$, dissolved in the minimum quantity of $CH_2Cl_2$, was treated with 74 mg (0.147 mmol) of diphosphinite **13d** in 3 mL of $CH_2Cl_2$ to afford 54 mg (55%) of complex [Rh(cod)(**13d**)]$BF_4$ as an orange solid: MS (FAB positive) *m/z* 711.1 $[M]^+$, 603 $[M - (cod)]^+$; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.13 (d, $J$ = 6 Hz, 6 H), 2.20−2.60 (m, C*H*$_2$, cod, 8 H), 3.91 (m, 2 H), 4.39 (m, 2 H), 4.63 (m, 2 H), 4.73 (m, 2 H), 7.40−7.80 (m, 20 H); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 18.6, 30.0, 30.5, 75.7 (m), 85.7, 104.1 (m), 105.6 (m), 128.8−132.6; $^{31}P$ NMR ($CDCl_3$, 161.97 MHz) $\delta$ 127.39 (d, $J_{Rh,P}$ = 169.4 Hz).

**[Rh(cod)(13e)]$BF_4$.** According to the standard procedure, 50 mg (0.12 mmol) of [Rh(cod)$_2$]$BF_4$, dissolved in the minimum quantity of $CH_2Cl_2$, was treated with 109 mg (0.128 mmol) of diphosphinite **13e** in 3 mL of $CH_2Cl_2$ to render 138 mg (98%) of complex [Rh(cod)(**13e**)]$BF_4$ as a yellow solid: HRMS (L-SIMS) calcd for $[C_{56}H_{82}O_5P_2Si_2Rh]^+$ 1055.423113, found 1055.423167; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.01−1.13 (m, 42 H), 2.35−2.51 (m, 8 H), 3.77 (dd, $J$ = 3.0, 11.4 Hz, 2 H), 3.90 (dd, $J$ = 2.6, 11.4 Hz, 2 H), 4.12 (m, 2 H), 4.69 (m, 2 H), 4.81 (m, 2 H), 5.25 (m, 2 H), 7.25−7.60 (m, 20 H); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 11.9, 17.9, 18.0, 29.9, 30.7, 62.7, 81.2, 82.6 (m), 104.9 (m), 105.4 (m), 128.0−132.2; $^{31}P$ NMR ($CDCl_3$, 161.97 MHz) $\delta$ 124.97 (d, $J_{Rh,P}$ = 167.8 Hz).

**[Rh(cod)(14a)]$BF_4$.** The general procedure was followed as 37.7 mg (0.092 mmol) of [Rh(cod)$_2$]$BF_4$, dissolved in 2 mL of $CH_2Cl_2$, was treated with 99 mg (0.097 mmol) of diphosphinite **14a** to give 110 mg (90%) of complex [Rh(cod)(**14a**)]$BF_4$ as a yellow solid: HRMS (L-SIMS) calcd for $[C_{76}H_{70}O_5P_2Rh]^+$ 1227.375 356, found 1227.375 310; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 2.20−2.50 (m, 8 H), 3.14 (dd, $J$ = 3.6, 10.4 Hz, 2 H), 3.47 (dd, $J$ = 4.4, 10.4 Hz, 2 H), 4.72 (s, 4 H), 4.99 (m, 2 H), 5.44 (m, 2 H), 7.00−7.50 (m, 50 H); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 30.2, 30.7, 63.7, 78.4, 83.2, 87.7, 103.9, 104.6, 126.9−143.4; $^{31}P$ NMR ($CDCl_3$, 161.97 MHz) $\delta$ 122.03 (d, $J_{Rh,P}$ = 164.8 Hz).

**[Rh(cod)(14b)]$BF_4$.** This complex (184 mg, 95%) was prepared as an orange solid from 0.060 g (0.148 mmol) of [Rh(cod)$_2$]$BF_4$, dissolved in the minimum quantity of $CH_2Cl_2$, and 0.159 g (0.157 mmol) of the diphosphinite [Rh(cod)(**14b**)]$BF_4$ in 3 mL of $CH_2Cl_2$: HRMS (L-SIMS) calcd for $[C_{70}H_{78}O_5P_2Si_2Rh]^+$ 1219.391 813, found 1219.391 784; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 0.90 (s, 18 H), 2.20−2.60 (m, 8 H), 3.61 (dd, $J$ = 2, 11.2 Hz, 2 H), 3.75 (dd, $J$ = 3.6, 11.2 Hz, 2 H), 4.61 (s, 4 H), 4.70 (m, 2 H), 5.26 (m, 2 H), 7.20−7.85 (m, 40 H); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 19.0, 26.8, 30.3, 30.4, 63.2, 78.0, 81.0, 102.3 (m), 107.81 (m), 127.61−135.48; $^{31}P$ NMR ($CDCl_3$, 161.97 MHz) $\delta$ 129.74 (d, $J_{Rh,P}$ = 170.8 Hz).

**[Rh(cod)(14d)]$BF_4$.** The general procedure was followed as 58 mg (0.144 mmol) of [Rh(cod)$_2$]$BF_4$, dissolved in the minimum quantity of $CH_2Cl_2$, was treated with 76 mg (0.150 mmol) of diphosphinite **14d** in 3 mL of $CH_2Cl_2$ to give 97 mg (84%) of complex [Rh(cod)(**14d**)]$BF_4$ as an orange solid: HRMS (L-SIMS) calcd for $[C_{38}H_{42}O_3P_2Rh]^+$ 712.169 780, found 712.170 007; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 1.28 (d, $J$ = 6.4 Hz, 6 H), 2.20−2.60 (m, 8 H), 4.55 (q, $J$ = 6.4 Hz, 2 H), 4.77 (s, 4 H), 5.08 (m, 2 H), 7.25−7.60 (m, 20 H); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 15.1, 30.5, 30.5, 73.8 (m), 84.1, 103.7 (m), 104.7 (m), 128.7−131.8; $^{31}P$ NMR ($CDCl_3$, 161.97 MHz) $\delta$ 121.97 (d, $J_{Rh,P}$ = 166.0 Hz).

**[Rh(cod)(14d)]$BF_4$. X-ray Crystallography.** Crystals of [Rh(cod)(**14d**)]$BF_4$ were obtained by slow diffusion of hexane into a solution of [Rh(cod)(**14d**)]$BF_4$ in dichloromethane. Crystal data: $C_{38}H_{42}O_3P_2RhBF_4 \cdot 2(CH_2Cl_2)$, orange blocks. Empirical formula: $C_{80}H_{92}B_2Cl_8F_8O_6P_4Rh_2$. FW = 968.23. $T$ = 125.0(1) K. $\lambda$ = 0.710 73 Å. Crystal system: monoclinic. Space group: $P21$. Unit cell dimensions: $a$ = 11.0767(19) Å, $b$ = 20.018(4) Å, $c$ = 19.139(3) Å, $\alpha$ = 90°, $\beta$ = 94.683(3)°, $\gamma$ = 90°. Volume = 4229.6(13) Å$^3$; $Z$ = 2. Density (calculated) = 1.521 mg/m$^3$. Absorption coefficient = 0.787 mm$^{-1}$. $F(000)$ = 1976. Crystal size = 0.6 × 0.17 × 0.14 mm$^3$. $\theta$ range for data collection = 1.07−28.27°. Index ranges = $-14 \leftarrow h \leftarrow 14$, $0 \leftarrow k \leftarrow 26$, $0 \leftarrow l \leftarrow 25$. Reflections collected: 30 560. Independent reflections: 10 448 [$R$(int) = 0.0385]. Completeness to $\theta$ = 28.27°, 96.7%. Absorption correction: semiempirical from equivalents. Maximum and minimum transmission = 1.000 and 0.811. Refinement method: full-matrix least-squares on $F^2$. Data/restraints/parameters: 10448/1/992. Goodness of fit on $F^2$ = 1.090. Final R indices [$I > 2\sigma(I)$]: R1 = 0.0447, wR2 = 0.1026. R indices (all data): R1 = 0.0635, wR2 = 0.1120. Absolute structure parameter = 0.09(4). Largest differential peak and hole = 0.965 and −0.851 e Å$^{-3}$.

The asymmetric unit consists of two independent cations, with two $BF_4^-$ counterions and four dichloromethane solvate molecules. Cyclooctadiene is disordered in two different conformations.

**[Rh(cod)(ent-9)]$BF_4$.** This complex was prepared in accordance with the general procedure using 350 mg (0.123 mmol) of [Rh(cod)$_2$]$BF_4$, dissolved in $CH_2Cl_2$, and 61 mg (0.129 mmol) of diphosphinite **ent-9** to afford 77 mg (82%) of complex [Rh(cod)(**ent-9**)]$BF_4$ as a yellow solid: HRMS (L-SIMS) calcd for $[C_{36}H_{38}O_3P_2Rh]^+$ 683.135 125, found 683.135 336; $^1H$ NMR ($CDCl_3$, 400 MHz) $\delta$ 2.25−2.45 (m, 4 H), 2.45−2.65 (m, 4 H), 3.86 (dd, $J$ = 6.0, 10.0 Hz, 2 H), 4.31 (dd, $J$ = 6.6, 10.0 Hz, 2 H), 4.78 (s, 4 H), 5.13 (m, 2 H), 7.20−7.80 (m, 20 H); $^{13}C$ NMR ($CDCl_3$, 100.6 MHz) $\delta$ 30.4, 30.6, 72.2 (m), 82.8, 103.5 (m), 104.3 (m), 128.5−131.8; $^{31}P$ NMR ($CDCl_3$, 161.97 MHz) $\delta$ 122.75 (d, $J_{Rh,P}$ = 164.8 Hz).

**General Procedure for the Rh-Catalyzed Hydrogenation of C=C.** In a typical experiment, a dichloromethane solution (15 mL) of [Rh(cod)$_2$]$BF_4$ (6.1 mg, 0.015 mmol), the corresponding ligand (0.016 mmol), and the substrate (1 mmol) under nitrogen were transferred into a Schlenk flask and purged three times with vacuum and hydrogen. The reaction mixture was then shaken under $H_2$ (1 atm) at room temperature, unless otherwise stated. Conversion and enantiomeric excesses were determined by gas chromatography.

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**Supporting Information Available:** General methods, atomic coordinates, thermal parameters, and a complete list of bond lengths and angles of compound [Rh(cod)(**14d**)]$BF_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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