A New Diphosphane Derived from Carbohydrates as an Effective Ligand for Asymmetric Hydrogenation

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Keywords: Asymmetric hydrogenation / Phosphanes / Chiral ligands / Carbohydrates / Rhodium

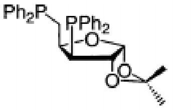
A novel chiral diphosphane derived from D-(+)-xylose, 3,5-dideoxy-1,2-*O*-isopropylidene-3,5-bis(diphenylphosphanyl)-α-D-xylofuranose (Xylophos), and its cationic cyclooctadiene rhodium(I) complex have been synthesised and characterised. Excellent results were obtained with Xylophos in the asymmetric Rh-catalysed hydrogenation of acrylic acid derivatives (*ee*'s up to 98%). Hydrogenation results are explained in terms of the structure of the precatalyst $[Rh(cod)(Xylophos)]^+BF_4^-$.

Introduction

The use of chiral metal complexes as homogeneous molecular catalysts is one of the most powerful strategies in asymmetric synthesis.[1] A careful molecular design of the chiral ligands is particularly important for efficient asymmetric catalysis. Although much progress has been made in this area, and despite the large amount of relevant literature,[2] there is no straightforward way of predicting, a priori, the type of ligand required to achieve high levels of enantioselectivity.[3] The design of new ligands is still often the result of empirical methodology.

Since the work of Kagan with Diop[4] and Knowles with Dipamp,[5] many optically active chelating diphosphanes have been successfully used in transition-metal-based asymmetric catalysis.[1,2,6] In a chiral diphosphane, chirality can occur within the tethering carbon chain between the two phosphanes or at the phosphorus atoms. In spite of the early success achieved with Dipamp,[5] bisphosphanes containing stereogenic phosphorus atoms have been outnumbered by ligands based on PPh_2 groups attached to C-chiral backbones.[2] One advantage of these C-chiral diphosphanes is that their design makes use of the great abundance of naturally occurring chiral compounds. Surprisingly, although carbohydrates are easily available and results with bisphosphinites derived from glucose are excellent,[3,7] the number of diphosphanes derived from these kinds of natural compounds is rather low.[8]

Following our previous work on ligands derived from furanoses,[9] we report here the synthesis of a new diphosphane derived from xylofuranose, Xylophos (Figure 1), the solution structure of the precatalyst $[Rh(cod)(Xylophos)]^+BF_4^-$ and its use in the asymmetric Rh-catalysed hydrogenation of alkenes. An important feature of this new ligand is its lack of C_2 symmetry. It is commonly held that C_2-symmetric diphosphane ligands are endowed with superior properties in catalysis, principally because of the fewer competing diastereomeric intermediates.1,10 Nevertheless, ligands without C_2 symmetry can eventually match the intermediates better and lead to very good enantioselective discriminations.[3,6i–6l,7,11]



Xylophos

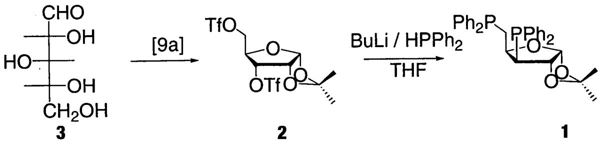
Figure 1. 3,5-Dideoxy-1,2-*O*-isopropylidene-3,5-bis(diphenylphosphanyl)-α-D-xylofuranose, Xylophos (**1**)

The related bisdiphenylphophinite,[12,13] 5-diphenylphosphane-3-diphenylphosphinite,[13] diphosphite,[9d,14] 5-diphenylphosphane[13] and 5-phosphane-3-methoxy[8a,15] molecules with the same protected xylofuranose backbone have already been described and applied to asymmetric catalysis with varying degrees of success.

Results and Discussion

Synthesis and Characterisation of Xylophos

The new diphosphane Xylophos (**1**) was obtained by adding a slight excess of lithium diphenylphosphide, in THF solvent at room temperature, to 1,2-*O*-isopropylidene-3,5-di-*O*-trifluoromethansulfonyl-D-ribofuranose (**2**), which had been prepared from commercially available D-(+)-xylose **3**[9a] (Scheme 1). It was isolated in high yield (75%) by flash chromatography under argon as a white crystalline solid, stable in the air in the solid state and slightly stable in solution.



Scheme 1. Synthesis of Xylophos **1**

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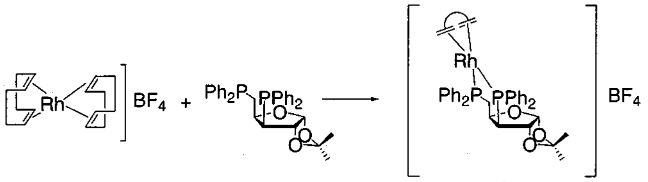
Xylophos (**1**) was characterised by elemental analysis, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and mass spectrometry. The signals of each of the phosphorus nuclei in the ^{31}P NMR spectrum are doublets, at $\delta = -27.4$ and -21.1, respectively, with $^{4}J(P,P) = 8.0$ Hz. Mass spectrometry shows the highest ion at $m/z = 526$, which corresponds to the molecular weight of Xylophos.

Synthesis and Characterisation of the Rh^{I} Complex

The reaction of Xylophos with $[Rh(cod)_2]^+BF_4^-$ in dichloromethane solution proceeded with the displacement of one cycloocta-1,5-diene ligand to afford the cationic complex $[Rh(cod)(Xylophos)]^+BF_4^-$ (**4**) (Scheme 2).



4

Scheme 2. Synthesis of the complex $[Rh(cod)(xylophos)]^+BF_4^-$ (**4**)

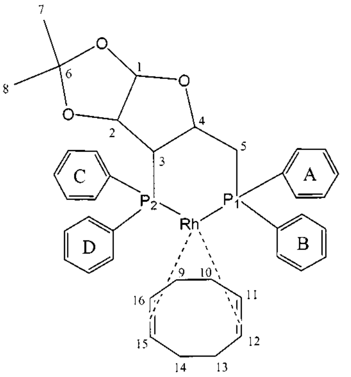
$[Rh(cod)(Xylophos)]^+BF_4^-$ was isolated as a yellow, moderately air-stable powder by adding diethyl ether. The elemental analysis of C and H matches the stoichiometry $[Rh(cod)(Xylophos)]_n^+(BF_4)_n^-$. The FAB mass spectrum shows the highest ion at $m/z = 737$, corresponding to the cationic mononuclear species. The IR spectrum shows a strong band between 1090 and 1050 cm^{-1} and a medium intensity band at 450 cm^{-1}, which are characteristic of the non-coordinated BF_4^- anion.[16]

Further details of the structure of the cation $[Rh(cod)(Xylophos)]^+$ were obtained by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The spectral assignments (Table 1 and 2 and Experimental Section) were based on the information obtained by $^{1}H/^{1}H$ COSY, $^{13}C/^{1}H$ and $^{31}P/^{1}H$ correlation measurements in combination with the $^{1}H/^{1}H$ NOESY results. Special attention has been paid to conformational analysis of the six-membered chelate ring. This is directly related to the spatial orientation of the phenyl groups, which have been linked with the enantioselective efficiency of the catalysts.

Vicinal $^{1}H,^{1}H$ couplings in the sugar ring are in the typical range (0−7 Hz) of furanoside ring systems (Table 1)[17] and are similar to those found in other ligands derived from the same protected xylofuranose ring.[9] The coupling constant ^{3}J(1-H, 2-H) is larger than 3.5 Hz, which is consistent with the *cis* disposition of these protons in the 1,2-protected xylofuranose.[17]

In the ^{31}P NMR spectrum eight lines were obtained due to the ^{31}P, ^{31}P and ^{31}P, ^{103}Rh couplings (ABX system) (see Experimental Section). The signals of the phosphorus atoms P-1 and P-2 were assigned from the $^{31}P/^{1}H$ correlation spectrum, using the vicinal couplings between P-1/5-H and P-2/3-H, and the long range couplings between P-1/1-H and P-2/2-H (See supporting information).

Table 1. ^{1}H NMR assignments (500 MHz) of compound **4** in $CDCl_3$ solution (except aromatic protons)



Atom	δ (ppm)	Atom	δ (ppm)	Coupling constants (Hz)
1-H	5.27 (dd)	9-H	2.05 (m, 2 H)	^{3}J(1-H,2-H) = 4.0
2-H	4.71 (dd)	10-H	2.13 (m, 2 H)	^{x}J(1-H,P-1) = 1.8[a]
3-H	2.71 (dd)	11-H	4.12 (m)	^{3}J(2-H,P-2) = 6.0
4-H	4.22 (m)	12-H	4.83 (m)	^{3}J(3-H,4-H) = 6.5
5-H	2.54 (m)	13-H	2.58 (m, 2 H)	^{2}J(3-H,P-2) = 2.5
5′-H	2.81 (dddd)	14-H	2.69 (m, 2 H)	^{3}J(5′-H,5-H) = 13.5
7-H	1.14 (s, 3 H)	15-H	4.98 (m)	^{3}J(5′-H,4-H) = 7.5
8-H	1.18 (s, 3 H)	16-H	4.18 (m)	^{x}J(5′-H,P-2) = 14[a]
				^{x}J(5′-H,Rh) = 3.0[a]

[a] Probably through space.

Table 2. Selected ^{1}H NMR spectroscopic data (500 MHz) of the aromatic part of compound **4** in $CDCl_3$ solution

	δ (ppm)			*J* (Hz)		
Phenyl	*o*	*m*	*p*	*J*(P, H-*o*)	*J*(H-*o*,H-*m*)	*J*(H-*o*,H-*p*)
A (P_1)	8.05	7.73	7.73	6.2	4.5	2.7
B (P_1)	7.73	7.51	7.51	5.8	4.5	1.2
C (P_2)	8.11	7.75	7.75	6.2	4.5	2.7
D (P_2)	7.35	7.56	7.56	6.1	4.3	2.4

The ^{1}H NMR signals of the four phenyl groups were assigned in pairs to the phosphorus atoms, P-1 and P-2, according to the $^{31}P/^{1}H$ correlation spectrum (See supporting information).

The signals at $\delta = 8.05$ (2 H) and 7.24 (2 H) were therefore assigned to the *ortho* protons of the phenyl groups (A and B) attached to the phosphorus atom P-1, whereas the *ortho* protons of the phenyl groups attached to P-2 (C and D) were found at $\delta = 8.11$ (2 H) and 7.36 (2 H). By means of a $^{1}H/^{1}H$ COSY experiment (See supporting information), it was also possible to assign the *meta*- and *para* protons of the corresponding phenyl groups (Table 2). It is interesting to note that, in the ^{1}H NMR spectra, the proton signals of the phenyl groups A and C appear as a symmetric group at room temperature. This could indicate that all of these protons, plus the two phosphorus atoms and the rhodium atom, are in the same spin system, giving a second order spectrum.

A 2D-NOESY experiment was performed to obtain a spatial orientation of phenyl groups A−D. In the 2D-

NOESY spectrum of **4**, strong cross-peaks of the furanose protons with the *ortho*-protons were found for only two of the four phenyl groups, which are attached to different phosphorus atoms (P-1 and P-2). The other two phenyl groups have strong cross peaks with the olefinic protons of the cod. This means that only two phenyl moieties are spatially close to the furanoside ring: the phenyl with the *ortho* protons at $\delta = 8.05$ (A), which correlate well with sugar proton 1-H, and the phenyl at $\delta = 8.11$ (C), which correlates with sugar proton 2-H. The *ortho* protons at $\delta = 7.24$ (B) correlate with proton 12-H and the *ortho* protons at $\delta = 7.36$ (D) correlate with proton 15-H and even with 3-H.

The ^{13}C NMR data are given in the Experimental Section. The absolute assignment of these signals was made possible by the ^{13}C/^{1}H correlation spectrum. For the furanoside ligand, the signals of the carbons C-2 and C-4 appear as doublets due to coupling with one of the phosphorus atoms, while the carbon atoms C-3 and C-5 appear as doublets of doublets due to coupling with both phosphorus atoms. In the aromatic part of the ^{13}C NMR spectra, the phenyl carbon atoms give well-separated signals, except for the quaternary carbon atoms, which could not be assigned absolutely. The olefinic carbons appear as a doublet due to the ^{13}C, ^{31}P coupling with the respective phosphorus atoms. The geminal couplings ^{2}J(P,C-*o*) of the phenyl moieties A and C are greater than those of moieties B and D, which indicates an axial spatial arrangement of the phenyls A and C.[18]

Examination of models of the different theoretically possible conformations of the six-membered chelate ring showed that only in the chair (Figure 2) and the twist-chair conformations are two axial phenyl groups close to the furanoside protons H-1 and H-2, whereas in the boat conformation (Figure 2) the axial phenyl groups (A and C) are located *trans* to the furanoside ring. The twist conformations δ and λ (Figure 2) can definitely be excluded because only one phenyl group is spatially close to the furanoside ring. Moreover, the λ twist conformation is inaccessible because of the strong steric hindrance between the axial phenyl group (attached to P-1) and the furanoside ring. For the different conformations, molecular mechanics calculations (CERIUS 2) showed that the λ-twist-chair conformation is the most stable (Figure 3). This conformation, which is compatible with the NMR spectroscopic data, follows from the distortion in the chair conformation due to the steric hindrance between both axial phenyl groups.

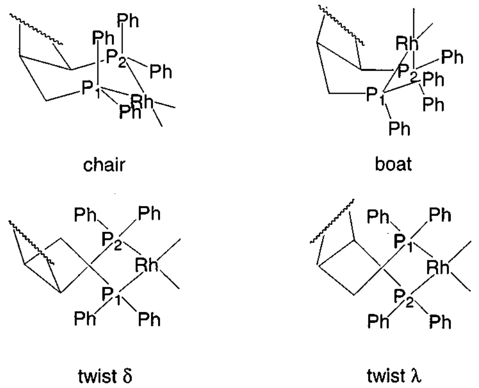


Figure 2. Schematic illustration of the usual possible conformations adopted by the six- membered chelate ring in **4**

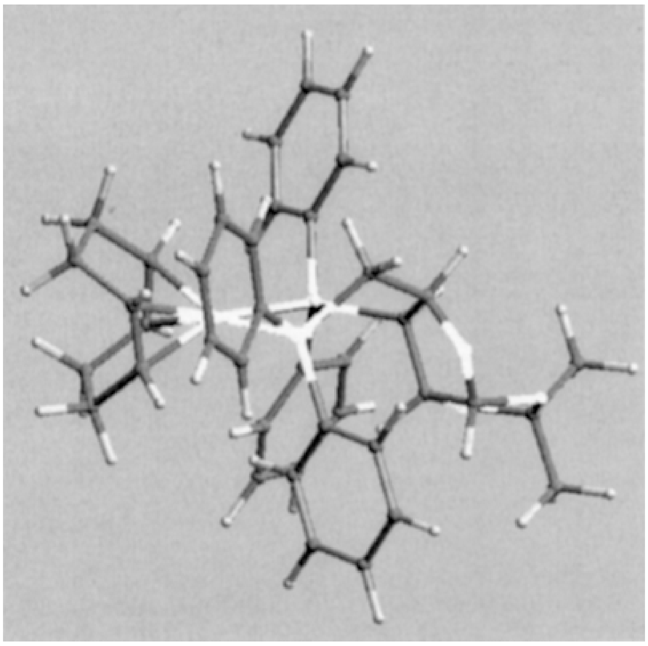
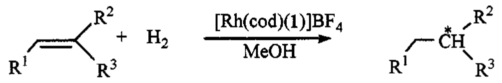


Figure 3. Minimised structure of [Rh(cod)(xylophos)]$^{+}$BF$_4^{-}$ (**4**) (CERIUS2)

The olefinic protons 11-H, 12-H, 15-H and 16-H of the cyclo-1,5-octadiene appear in the ^{1}H NMR spectrum as separate, broad signals, while the signals of the methylenic protons 9-H, 10-H, 13-H and 14-H are only partially resolved (Table 1). Only the signals of the two olefinic protons which are shifted downfield are well resolved, i.e. 12-H and 15-H. The relative assignment of the proton signals of the cod ring was made according to the ^{1}H/^{1}H COSY spectrum. The absolute assignment of these signals was possible from the NOESY spectrum. All carbon atoms of cyclo-1,5-octadiene are well resolved. The olefinic carbon atoms therefore appear as doublets of doublets due to the ^{13}C, ^{31}P and ^{13}C, ^{103}Rh couplings. The signals of only two methylenic carbons (C-13 and C-14) appear as doublets due to the ^{13}C, ^{31}P couplings, while the other two, which are significantly shifted downfield, appear as singlets.

Hydrogenation of Prochiral Olefins

The mononuclear cationic rhodium complex **4** with Xylophos was used in the asymmetric hydrogenation of prochiral olefins at 1 bar H$_2$ (Scheme 3). Conversion and enantioselectivities are shown in Table 3.



12 R^1 = Ph, R^2 = COOH, R^3 = NHCOCH$_3$

13 R^1 = H, R^2 = COOCH$_3$, R^3 = NHCOCH$_3$

14 R^1 = H, R^2 = COOH, R^3 = CH$_2$COOH

Scheme 3. Asymmetric hydrogenation of prochiral olefins

Table 3. Hydrogenation results using $[Rh(cod)(xylophos)]^{+}BF_4^{-}$ (**4**)[a]

Entry	Substrate	*t* (h)	% Conv.	% *ee*
1	**12**[b]	6	100	89 (*S*)
2	**13**[c]	6	100	91 (*S*)
3	**13**[c]	4	98	91 (*S*)
4	**13**[c]	1	50	92 (*S*)
5	**13**[c][d]	1	11	98 (*S*)
6	**14**[b]	6	100	62 (*R*)

[a] [Rh]/substrate = 1:100; substrate = 1 mmol; solvent = methanol (6 mL); *T* = 20 °C; *P* = 1 atm. – [b] Conversion measured by ^{1}H NMR and enantiomeric excesses determined by polarimetry. – [c] Conversions and enantiomeric excesses measured by GC. – [d] *T* = 0 °C.

Reaction of the prochiral olefin *Z*-α-acetamidocinnamic acid (**12**) afforded a quantitative yield of hydrogenation product with 89% *ee* at room temperature (entry 1). As with (*R*)-Prophos,[19] (*S*,*S*)-Diop[20] and (*R*,*R*)-Dipamp,[5b,21] the (*S*)-isomer of *N*-acetylphenylalanine was obtained. The sense of the asymmetric induction in this reaction has been widely studied and is correlated to the skewing of the ligand with respect to the P–Rh–P plane.[1e,3d,3e,11d] According to these studies, the formation of (*S*)-*N*-acetylphenylalanine indicates a λ-type array of the Rh-diphosphane chelate ring, which agrees with the structure determined by NMR spectroscopy (see NMR characterisation, above).

The related ester methyl 2-acetoamidoacrylate (**13**) gave similar results at room temperature (91% *ee*) (entries 2–4). Decreasing the temperature to 0 °C (entry 5) substantially improved the enantioselectivity (98% *ee*). These results are similar to those reported for such successful diphosphanes as Chiraphos, Dipamp, Diop, Binap, Bppfa, Duphos, Josiphos, Phanephos and Ferriphos.[22–25]

When itaconic acid (**14**) was used as the substrate, the enantioselectivity was significantly lower (62%) (entry 6). This agrees with the fact that diphosphanes which form five- or six-membered ring complexes are somewhat less tolerant in terms of substrate acceptability than the less-rigid seven-membered chelate rings e.g. 63% *ee* and 60% *ee* were obtained using the five-membered chelating ring Norphos[26] and the six-chelate ring Dioxop,[8a] respectively, while *ee*'s of up to 94% were obtained in the hydrogenation of **12**.[22]

Experimental Section

General Techniques: All syntheses were performed by standard Schlenk techniques under a nitrogen or argon atmosphere. The complex $[Rh(cod)_2]BF_4$ [16a] and 1,2-*O*-isopropylidene-3,5-di-*O*-trifluoromethan-sulfonyl-α-D-ribofuranose[9a] were prepared by previously described methods. Solvents were purified by standard procedures. All other reagents were used as purchased. Elemental analyses were performed on a Perkin–Elmer 240 B instrument. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Variant Gemini 300 MHz or 500 MHz Spectrometer. Chemical shifts are relative to $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. All assignments of NMR spectra were determined by means of COSY, ^{31}P-^{1}H and ^{13}C-^{1}H correlation experiments. Standard pulse sequences were employed for the ^{1}H-2D-NOESY.[27] The phase-sensitive NOESY experiments used mixing times of 0.4 s. EI mass spectra were obtained on a HP 5989 A spectrometer. A VG-Autospec mass spectrometer was used for FAB mass spectral analyses. The matrix was *m*-nitrobenzyl alcohol. Gas chromatography analyses to obtain the enantiomeric excesses in the hydrogenation of methyl 2-acetoamidoacrylate were performed on a Hewlett–Packard 5890A instrument (fused silica capillary column 25 m × 0.25 mm Permabond L-Chirasil-Val) equipped with a Hewlett–Packard HP 3396 series II integrator. Optical rotations were measured at 25 °C on a Perkin–Elmer 241 MC polarimeter. Hydrogenation reactions were performed in a previously described hydrogen-vacuum line.[28] The molecular mechanics calculations were carried out with the program CERIUS[29] developed by Molecular Simulations (MSI) and the force field UFF developed by Rappe.[30] The electrostatic interactions were taken into account from the atomic changes generated by the Qeq method.[31]

Synthesis of 3,5-Dideoxy-1,2-*O*-isopropylidene-3,5-bis(diphenylphosphanyl)-α-D-xylofuranose (Xylophos, 1): *n*-Butyllithium (3.36 mL, 5.0 mmol) was slowly added to a solution of diphenylphosphane (0.7 g, 5.0 mmol) in THF (5 mL) at 0 °C. After 10 min at room temperature, a solution of 1,2-*O*-isopropylidene-3,5-di-*O*-trifluoromethanesulfonyl-α-D-ribofuranose (1.2 g, 2.64 mmol) in THF (3 mL) was added dropwise and the mixture was allowed to react for 1 hour after which the solvent was evaporated. The residue was purified by column chromatography (toluene) under argon to give the diphosphane as a white solid. Yield: 1.4 g (75%) (m.p. 171–172 °C). – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.16 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 2.43 [ddd, ^{2}J(5′-H,5-H) = 13.2 Hz, ^{3}J(5′-H,4-H) = 6.6 Hz, ^{2}J(5′-H,P) = 1.9 Hz, 1 H, 5′-H′], 2.64 [ddd, ^{2}J(5-H,5′-H) = 13.2 Hz, ^{3}J(5-H,4-H) = 8.2 Hz, ^{2}J(5-H,P) = 2.2 Hz, 1 H, 5-H], 3.08 [d, ^{3}J(3-H,2-H) = 4.3 Hz, 1 H, 3-H], 4.41 (m, 1 H, 4-H), 4.49 [dd, ^{3}J(2-H,3-H)= 4.3 Hz, ^{3}J(2-H,1-H) = 4.0 Hz, 1 H, 2-H], 5.06 [d, ^{3}J(1-H,2-H) = 4.0 Hz, 1 H, H-1], 7.40–8.20 (m, 20 H, Ph). – ^{13}C NMR (75.432 MHz, $CDCl_3$, TMS): δ = 26.1 (CH_3), 26.3 (CH_3), 31.1 [dd, *J*(C-5,P) = 17.5 Hz, *J*(C-5,P) = 14.8 Hz, C-5], 46.2 [dd, *J*(C-3,P) = 20.9 Hz, *J*(C-3,P) = 5.5 Hz, C-3], 76.6 [dd, ^{2}J(C-4,P) = 16.9 Hz, ^{2}J(C-4,P) = 13.0 Hz, C-4], 83.9 [d, *J*(C-2,P) = 5.9 Hz, C-2], 104.2 (C-1), 110.7 (CMe_2), 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 129.0, 129.2, 132.6, 132.8, 133.0, 133.1, 133.2, 133.3, 133.9, 134.2 (CH=, Ph). – ^{31}P NMR (121.442 MHz, $CDCl_3$, H$_3$PO4): δ = −27.4 [d, ^{4}J(P,P) = 8 Hz, 1 P], −21.1 [d, ^{4}J(P,P) = 8 Hz, 1 P]. – MS (70 eV, EI): *m*/*z* = 526 [$M^{+\cdot}$]. – $C_{32}H_{32}O_3P_2$ (526.55): calcd. C 72.99, H 6.13; found C 72.61, H 6.25. – $[\alpha]_D^{20}$ = +16.1 (*c* = 1 in CH_2Cl_2)

Synthesis of $[Rh(cod)(Xylophos)]^{+}BF_4^{-}$ (4): Xylophos (**1**) (40.5 mg, 0.077 mmol) was added to a solution of $[Rh(cod)_2]^{+}BF_4^{-}$ (30 mg, 0.075 mmol) in dichloromethane (1 mL). After 10 minutes, the yellow product was obtained by precipitation with diethyl ether. Yield: 55 mg (88%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): see Table 1 and 2. – ^{13}C NMR (75.432 MHz, $CDCl_3$, TMS): δ = 26.2 (C-7 and C-8), 26.6 [dd, *J*(C-5,P) = 16.5 Hz, *J*(C-5,P) = 28.7 Hz, C-5], 27.6 (C-9), 27.7 (C-10), 32.6 [d, *J*(C-13,P) = 3.4 Hz, C-13], 32.9 [d, *J*(C-14,P) = 3.8 Hz, C-14], 43.4 [dd, *J*(C-3,P) = 12.9 Hz, *J*(C-3,P) = 25.8 Hz, C-3], 73.8 [d, *J*(C-4,P) = 7.6 Hz, C-4], 82.6 [d, *J*(C-2,P) = 4.78 Hz, C-2], 97.6 [dd, *J* = 8.1 Hz, *J* = 9.0 Hz, C-15], 100.15 [dd, *J* = 8.6 Hz, *J* = 10.0 Hz, C-16], 103.4 (C-1), 104.69 [dd, *J* = 9.8 Hz, *J* = 10.5 Hz, C-10], 105.8 [dd, *J* = 9.1 Hz, *J* = 10.8 Hz, C-9], 111.5 (C-6), 127.6 [dd, *J*(C,P) = 42.0 Hz, *J* = 1.9 Hz, C], 128.4 [d, *J*(C,P) = 43.8 Hz, C], 128.5 [d, *J*(C,P) = 40.5 Hz, C], 129.6 [d, *J*(C,P) = 10.3 Hz, C-*m* B], 129.8 [d, *J*(C,P) = 10.3 Hz, C-*m* D], 130.1 [d, *J*(C,P) = 12.2 Hz, C-*m* A], 130.2 [d, *J*(C,P) = 10.1 Hz, C-*o* B], 130.4 [d, *J*(C,P) = 13.7 Hz, C-*m* C], 130.6 [dd, *J*(C,P) = 43.9 Hz, *J* = 1.9 Hz, C], 130.9 [d, *J*(C,P) = 8.4 Hz, C-*o* D], 131.2 [d, *J*(C,P) = 2.3 Hz, C-*p* B], 131.4 [d, *J*(C,P) = 2.3 Hz, C-*p* D], 133.3 [d, *J*(C,P) = 2.3 Hz, C-*p* A], 133.6 [d, *J*(C,P) = 2.3 Hz, C-*p* C], 135.1 [d, *J*(C,P) = 12.2 Hz, C-*o* A], 135.5 [d, *J*(C,P) = 13.7 Hz, C-*o* C]. − ^{31}P NMR (121.442 MHz, CDCl$_3$, H$_3$PO$_4$): δ = 17 [dd, ^{2}J(P-1,P-2) = 43.7 Hz, ^{1}J(P-1,Rh) = 146.1 Hz, 1P, P-1], 17.4 [dd, ^{2}J(P-2,P-1) = 43.7 Hz, ^{1}J(P-2,Rh) = 145.4 Hz, 1P, P-2]. − MS (FAB): *m*/*z* = 737 [M$^{+\cdot}$]. − C$_{40}$H$_{44}$BF$_4$O$_3$P$_2$Rh (824.44): calcd. C 58.27, H 5.38; found C 58.11, H 5.64.

Hydrogenation of Prochiral Olefins: In a typical run, a Schlenk flask was filled with a methanol solution (6 mL) of substrate (1 mmol) and catalyst precursor (8.24 mg, 0.01 mmol). It was then evacuated and purged three times with H$_2$. The reaction mixture was the shaken under H$_2$ (1 atm.) at 293 K. After the desired reaction time, the solvent was removed.

Work-Up of the Hydrogenation Products: The following procedures were used to isolate the hydrogenation products. For 2-methylsuccinic acid and *N*-acetylphenylalanine, the residue was dissolved in 0.5 M NaOH and separated from the insoluble catalyst by filtration. The filtrate was acidified with diluted HCl, extracted with ether and washed with water. The ether phase was dried over sodium sulfate and evaporated to dryness. The extent of the conversion was measured by ^{1}H NMR spectroscopy. The enantiomeric excesses were determined by polarimetry.[8a]

For *N*-acetylalanine methyl ester the residue was dissolved in CH$_2$Cl$_2$ and filtered through a plug of silica to remove the catalyst. Conversion and enantiomeric excesses were determined by gas chromatography.

Acknowledgments

We would like to thank the Spanish Ministerio de Educación y Cultura and the Generalitat de Catalunya (CIRIT) for their financial support (PB97−0407-CO5−01) and the Generalitat de Catalunya (CIRIT) for awarding a research grant (to O. P.). We thank Dr. P. Sandor (Varian, Darmstad) for recording the 500 MHz NMR experiments.

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Received March 1, 2000
[I00079]