Chiral Diphosphites as Ligands for the Rhodium- and Iridium-Catalysed Asymmetric Hydrogenation: Precatalyst Complexes, Intermediates and Kinetics of the Reaction

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Rh^I and Ir^I complexes $[M(cod)PP]BF_4$ were synthesised from diphosphite ligands PP with a backbone derived from xylofuranose. They were used in the rhodium- and iridium-catalysed asymmetric hydrogenation of itaconic acid, α-acetamidocinnamic acid and methyl α-acetamidoacrylate. The kinetics of the reaction was investigated. The solution structures of the intermediates were studied by ^{31}P- and ^{1}H-HPNMR spectroscopy and a catalytic cycle is proposed.

Introduction

Most of the phosphorus ligands that have been developed for catalytic applications, particularly in asymmetric catalysis, are derivatives of aryl- or alkylphosphanes.[1] Recently, a group of less electron-rich phosphorous compounds, chelating diphosphite ligands, has received considerable attention. New reports on the use of these ligands in regio- and stereoselective hydroformylation[2] and asymmetric hydrocyanation,[3] have appeared, in which their potential utility have been demonstrated.

Very little attention has been paid to phosphites as ligands in hydrogenation, probably because of their high π-acidity, which makes the metal centre less suitable for bringing about the H_2-oxidative addition reactions. However, some catalysts based only on organyl phosphites have been applied to hydrogenation.[4] To our knowledge, only Selke et al.,[4g] Reetz et al.[4i] and Brunner et al.[4j] have reported the use of chiral diphosphites in asymmetric hydrogenation. In spite of the supposed disadvantage mentioned above and the ability to undergo hydrolysis or Arbuzov-type side reactions (starkly reduced in the case of bulky phosphites or coordinated phosphites[3b,5]), phosphites are a very attractive group of compounds for catalysis. They have many advantages, the most important of which are that they are easy to prepare from readily available starting materials and that they are less sensitive to air than phosphanes are.[3,6]

The large number of chiral diols available from asymmetric catalysis and from the chiral pool, the excellent results obtained in asymmetric hydrogenation with diphosphinites derived from D-glucose (intermediate basicity between diphosphanes and diphosphites)[7] and, more recently, with diphosphites[4i] encourage further study of the application of diphosphites in this reaction.

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Here we report the synthesis of rhodium and iridium complexes with diphosphites derived from D-(+)-xylose and their use in the asymmetric hydrogenation of acrylic acid derivatives. We also investigated the kinetics of the catalysis and the catalytic cycle. These ligands were developed by van Leeuwen and co-workers and were applied to the asymmetric hydroformylation of styrene with enantioselectivities up to 62%.[2o] These bulky diphosphites are not only derived from a readily available carbohydrate, they are also fairly robust towards hydrolysis.

Results and Discussion

1. Synthesis of Olefinic Complexes

The reaction of the corresponding chiral diphosphites **1−3** with $[M(cod)_2]^+BF_4^-$ (M = Rh, Ir) in dichloromethane solution proceeded rapidly, with the displacement of one molecule of 1,5-cyclooctadiene ligand, even in a large excess of diphosphite ligand, to afford the cationic mononuclear complexes $[M(PP)(cod)]^+$ **4−9** (Scheme 1). These complexes were characterised by elemental analysis, ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy and FAB mass spectrometry.

The presence of two sets of signals in the ^{31}P-NMR spectra of all these complexes revealed the existence of two isomers in very different proportions. The relative abundance of these isomers did not change with temperature in the NMR, thereby indicating that there is no interconversion between them. The presence of isomers may be attributed to different atropisomers of the bis(phenol) moiety in the bis(phosphite) ligands, but the rapid ring inversion of the seven-membered dioxaphosphepin rings detected on the ^{31}P-NMR time scale in the free ligands and its $[HRh(PP)(CO)_2]$[2o] complexes suggest another origin for these isomers. A second, more plausible possibility is that there are different conformers for the eight-membered metal chelate ring.

Molecular mechanics calculations for complexes **4−9** were carried out. Two different conformers, **a** (boat−chair) and **b** (twist−boat−chair), which differ in the orientation

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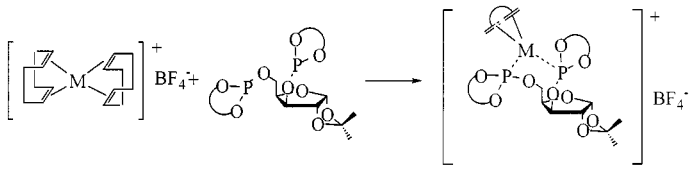
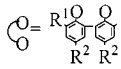




1 $R^1 = R^2 = H$
2 $R^1 = t$Bu, R^2 = OMe
3 $R^1 = R^2 = t$Bu

	M	diphosphite
4	Rh	1
5	Rh	2
6	Rh	3
7	Ir	1
8	Ir	2
9	Ir	3

Scheme 1. Synthesis of complexes $[M(cod)(PP)]^+BF_4^-$ **4–9**

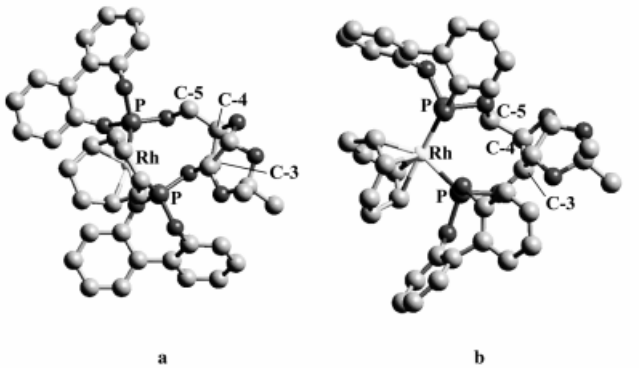


Figure 1. Conformers **a** and **b** for complex **4**

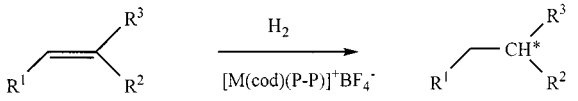
of the oxygen atom attached to C-5 in the sugar moiety, could be minimised for each complex. Figure 1 shows the minimised structures of the two conformers for complex **4**. The relative strain energies of these conformers for all complexes **4–9** are listed in Table 1. The results show that the most stable conformer is **a** for all the complexes. Their non-interconversion in VT-^{31}P NMR and the large difference in strain energy between the two conformers indicates that their transition state is extremely inaccessible.

The chemical shifts of the two different phosphorus atoms in **4–9** are in the range expected for tricoordinate P^{III} esters coordinated to Rh or Ir.[9] The rhodium–phosphorus coupling constants are very similar to those found for other $[Rh(diolefin)(PP)]^+$ complexes where PP is also a diphosphite.[4g] Coupling constants between 27 and 50 Hz can be observed between the two non-equivalent phosphorus atoms. The absence of P–P coupling in the free ligand[2o] suggests that these constants should be considered as ^2J(P–P), which means that the through-metal coupling predominates over through-backbone coupling.[9]

The characterisation by ^{13}C and ^{1}H NMR could not always be carried out because of the low intensity of some signals, partial overlapping of the spectra of mixtures of the two isomers or because the signals were too broad (especially important for product **7**). For **6**, a lowering of the temperature allowed the assignment of the ^{1}H-NMR peaks for both isomers.

2. Hydrogenation of Acrylic Acid Derivatives

The complexes $[M(cod)(PP)]^+$ (M = Rh, Ir; PP = **1**, **2**, **3**) **4–9** catalyse the asymmetric hydrogenation of itaconic acid **10** under mild conditions (5 bar, 40 °C) (Scheme 2, Table 2). In all cases, the (*R*) absolute configuration formed predominantly.



10 R^1 = H; $R^2 = CH_2COOH$; R^3 = COOH

11 R^1 = Ph; $R^2 = NHCOCH_3$; R^3 = COOH

12 R^1 = H; $R^2 = NHCOCH_3$; $R^3 = COOCH_3$

Scheme 2. Hydrogenation of acrylic acid derivatives with **4–9**

Table 1. Strain energies [kcal mol^{-1}] for conformers **a** and **b** of complexes **4–9**; experimental relative abundance (^{31}P-NMR data) in parentheses

Conformer[a]	4	5	6	7	8	9
a	484.4 (95)	380.7 (80)	237.8 (75)	404.8 (75)	297.0 (90)	153.1 (75)
b	530.1 (5)	401.0 (20)	268.9 (25)	456.6 (25)	318.9 (10)	184.5 (25)

[a] Recent investigations by our group have shown that relative strain energies between two conformers calculated by MM are very similar to those calculated with methods based on density functional theory (DFT) (see ref.[8]).

Table 2. Hydrogenation of itaconic acid **10** with $[M(cod)(PP)]BF_4$ **4−9**; M = Rh, Ir {conditions: [cat]/[itaconic acid] = 1:100; itaconic acid (2 mmol); solvent (12 mL)}

Entry	Precursor	*p* [bar]	*T* [°C]	*t* [h]	Conv. (%)	*ee* (%)
1[a]	**4**	5	40	20	20	20 (*R*)
2[a]	**5**	5	40	6	99	49 (*R*)
3[a]	**6**	5	40	6	70	45 (*R*)
4[b]	**6**	5	40	6	13	n.d.[c]
5[b]	**7**	5	40	20	100	13 (*R*)
6[b]	**8**	5	40	4	100	29 (*R*)
7[b]	**9**	5	40	4	100	35 (*R*)
8[b]	**7**	5	25	12	44	11 (*R*)
9[b]	**8**	5	25	12	68	32 (*R*)
10[b]	**9**	5	25	12	70	34 (*R*)
11[b]	**8**	1	40	4	87	47 (*R*)
12[b]	**9**	1	40	4	100	54 (*R*)
13[b]	**8**	1	25	8	70	26 (*R*)
14[b]	**9**	1	25	8	50	40 (*R*)

[a] Toluene/methanol (2:1). − [b] CH_2Cl_2/methanol (2:1). − [c] Not determined.

In contrast to the results reported by Reetz and Neugebauer,[4i] the precursors with the most hindered ligands (**2** and **3**) brought about the best conversions. The most hindered ligands, however, are also ligands with electron-donating groups, which probably enhance the rate of conversion because they favour the oxidative addition reactions in the catalytic cycle. The increase in activity with electron-donating groups in the phenyl groups is lower in the case of the iridium complexes.

The $[Rh(cod)(PP)]^+$ complexes **4−6** gave better conversions in toluene/methanol than in CH_2Cl_2/methanol (e.g., Entries 3 and 4) while the $[Ir(cod)(PP)]^+$ complexes **7−9** were more efficient in CH_2Cl_2/methanol. Within the accuracy of this experiment, there was no change in the enantioselectivities over time. This agrees with the presence of a unique catalytic species during the hydrogenation (though there is no proof for it).

The iridium complexes **7−9** were more active than their rhodium analogues, but the asymmetric inductions were lower (between 11 and 35% for the iridium compounds, between 20 and 50% for the rhodium compounds). The asymmetric inductions with precursors containing ligand **1** (Entries 1 and 5) are much lower than those with ligands **2** and **3** (Entries 2, 3, 6, and 7), as would be expected by its smaller bulkiness. The lower asymmetric induction of precursors containing ligand **1**, compared to **2** and **3**, was also observed in the hydroformylation of styrene.[2o] The change of the substituent at the *para* position of the bis(phenol) moiety showed very little effect on rate and asymmetric induction (Entries 2, 3, 6, and 7).

The high activity of the iridium complexes allowed a decrease of pressure and temperature of the reaction. Lowering the reaction temperature from 40 to 25 °C at 5 bar resulted in lower conversions but the asymmetric inductions did not change (Entries 5 vs. 8, 6 vs. 9, 7 vs. 10). Lowering the hydrogen pressure from 5 to 1 bar at 40 °C increased the asymmetric inductions (Entries 11 vs. 6, 12 vs. 7). In contrast to the observations at 5 bar, the asymmetric inductions at 1 bar are temperature-dependent. For both complexes with ligands **2** and **3**, the enantioselectivity of the reaction is decreased by a lowering of the temperature from 40 °C to 25 °C at 1 bar (Entries 11 vs. 13, 12 vs. 14). This is probably because there are different mixtures of hydride species at 1 bar and 5 bar.

Diphosphites **2** and **3** were also tested for the hydrogenation of other acrylic acid derivatives, α-acetamidocinnamic acid (**11**) and methyl α-acetamidoacrylate (**12**) (Scheme 2). The results obtained are given in Table 3.

Table 3. Hydrogenation of α-acetoamidocinnamic acid (**11**) and methyl α-acetamidoacrylate (**12**) with $[M(cod)(PP)]BF_4$ **5**, **6**, **8**, **9**; M = Rh, Ir {conditions: *T* = 40 °C, *t* = 20 h [cat]/[substrate] = 1:100; substrate (2 mmol); solvent (12 mL)}

Entry	Precursor	Substrate	*P* [bar]	Conv. (%)	*ee* (%)
1[a]	**5**	**11**	5	100	30 (*S*)
2[a]	**6**	**11**	5	100	31 (*S*)
3[b]	**8**	**11**	5	18	15 (*S*)
4[b]	**9**	**12**	5	20	19 (*S*)
5[a]	**5**	**12**	5	99	35 (*S*)
6[a]	**5**	**12**	2	100	21 (*S*)
7[c]	**5**	**12**	5	100	10 (*S*)
8[a]	**6**	**12**	5	94	33 (*S*)
9[b]	**8**	**12**	5	10	6 (*S*)
10[b]	**9**	**12**	5	9	7 (*S*)
11[b]	**8**	**12**	1	22	24 (*S*)
12[b]	**9**	**12**	1	31	35 (*S*)

[a] Toluene/methanol (2:1). − [b] CH_2Cl_2/methanol (2:1). − [c] CH_2Cl_2.

At 5 bar, the hydrogenation of **11** and **12** with the rhodium complexes **5** and **6** proceeded at a similar rate to the hydrogenation of itaconic acid (**10**), but enantiomeric excesses were lower (Entries 1, 2, 5, and 8). Lowering the pressure in the hydrogenation of **12** resulted in lower enantioselectivity (Entry 5 vs. 6). The effect was the same when the solvent was changed from toluene/methanol to CH_2Cl_2 (Entry 7 vs. 5). At 5 bar, the iridium complexes **8** and **9** were less active and enantioselective than their rhodium counterparts in the hydrogenation of **11** and **12** (Entry 1 vs. 3, 2 vs. 4; 5 vs. 9, 8 vs. 10). At 5 bar, the iridium complexes were more active and enantioselective in the hydrogenation of **11** than in that of **12** (Entries 3, 4 vs. 9, 10). The iridium compounds were unable to hydrogenate **11** at 1 bar, while they could hydrogenate **12** (Entries 11, 12) with better enantioselectivity than at 5 bar (Entries 11, 12 vs. 9, 10). However, the asymmetric induction was lower than for substrate **10** (Table 3, Entries 11, 12 vs. Table 2 Entries 11, 12).

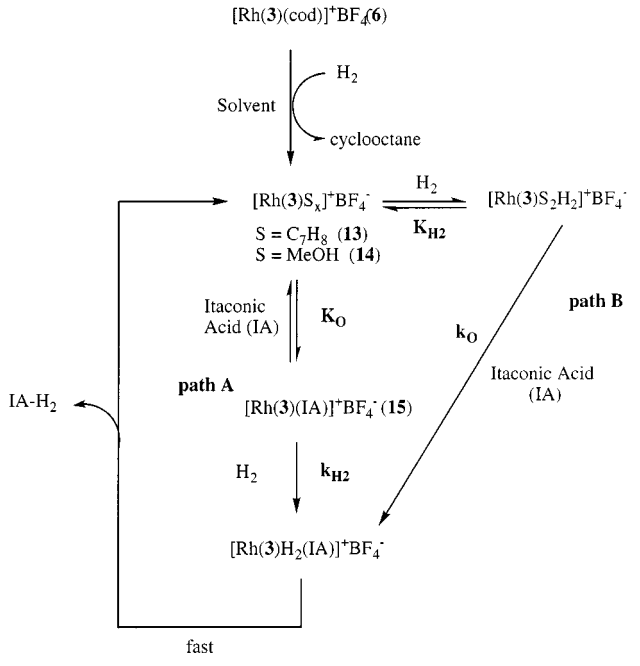
3. Catalytic Cycle Elucidation

Enantioselective hydrogenation catalysed by cationic (diolefin)(diphosphane)rhodium complexes has been thoroughly studied mechanistically. The widely accepted catalytic cycle, a result of the work of the groups of Brown, Halpern, Landis and Bosnich[10] involves the so-called alkene path, the first step of which is the hydrogenation of the diolefin coordinated to the rhodium centre, followed by the coordination of the alkene to the free site generated on the metal centre, the oxidative addition of molecular hydrogen, insertion and reductive elimination. Complexes with diphosphites do not necessarily have to follow the same se-

quence of steps, because their electronic properties are different from those of phosphanes. To identify the intermediates of the Rh-catalytic cycle of the hydrogenation of itaconic acid with phosphites and therefore to determine the sequence in the catalytic cycle, ^{1}H- and ^{31}P-HPNMR studies were carried out with the complexes of the most hindered ligand, **3**.

3.1. Characterisation Experiments of Rhodium-Cycle Intermediates

When complex [Rh(**3**)(cod)]$^+$BF$_4^-$ was dissolved in [D$_8$]toluene and kept for four hours at room temperature under 5 bar of H$_2$ pressure, an ABX pattern was obtained in ^{31}P HPNMR, which did not change after the system was cooled to −40 °C and then warmed up to 60 °C. The new compound was identified as [Rh(**3**)(C$_7$D$_8$)$_x$]$^+$ (Scheme 3). The stable yellow compound [Rh(**3**)(C$_7$H$_8$)$_x$]$^+$ (**13**) was isolated in a larger-scale preparative experiment in toluene. Elemental analysis and ^{1}H NMR in CCl$_4$ suggested that two toluene molecules was present in the compound. In general, arenes show a high tendency to form [M(η^6-arene)L$_2$]$^+$ species when L is a phosphane.[11] The (benzene)(dppe) compound was isolated as [Rh(dppe)(η^6-C$_6$H$_6$)]$^+$BF$_4^-$ · C$_6$H$_6$.[12] Compound **13** could then be formulated as [Rh(**3**)(η^6-C$_7$H$_8$)]BF$_4^-$ · C$_7$H$_8$. However, only one kind of methyl signal for toluene was detected in the ^{1}H-NMR spectrum of this complex. It appeared at δ = 2.71, in contrast to 2.37 for free toluene. There is probably a rapid exchange between them on the NMR time scale.



Scheme 3. Intermediates of the Rh catalytic cycle of the hydrogenation of itaconic acid

The two different phosphorous atoms in [Rh(**3**)(η^6-C$_7$H$_8$)]$^+$ show large P−Rh coupling constants (344.5 and 333.6 Hz), more than 100 Hz larger than in [Rh(**3**)(cod)]$^+$BF$_4^-$. These large constants may be explained by the smaller *trans* influence of the toluene rather than an olefin as ligand.

When [Rh(**3**)(η^6-C$_7$H$_8$)]$^+$BF$_4^-$ · C$_7$H$_8$ was treated with 5 bar of H$_2$, no formation of hydride species was detected by HPNMR as has been reported for different arene [M(η^6-arene)L$_2$]$^+$ complexes.[13]

Moreover, when the complex [Rh(**3**)(cod)]$^+$BF$_4^-$ was dissolved in [D$_8$]toluene/[D$_4$]methanol (2:1) and pressurised to 5 bar of H$_2$ at room temperature for four hours, the ABX pattern in the ^{31}P-HPNMR spectrum was similar. The compound could be assigned to [Rh(**3**)(CD$_3$OD)$_x$]$^+$ (Scheme 3). Cooling it to −40 °C did not change the spectrum. [Rh(**3**)(CH$_3$OH)$_2$]$^+$BF$_4^-$ (**14**) was isolated in a larger scale experiment in methanol as a stable yellow solid. The P−Rh coupling constants are also very large and similar to those obtained with the toluene complex (341.9 and 332.1 Hz). As has been reported for methanol [Rh(diphosphane)(CH$_3$OH)$_2$]$^+$ complexes,[14] the formation of hydride species was not detected by HPNMR when complex [Rh(**3**)(CH$_3$OH)$_2$]$^+$ was treated with 5 bar of H$_2$.

To study the coordination of itaconic acid in the cationic complex, the complex [Rh(**3**)(cod)]$^+$BF$_4^-$ was dissolved in [D$_8$]toluene and was pressurised to 5 bar at room temperature for four hours. After [Rh(**3**)(η^6-C$_7$D$_8$)]$^+$BF$_4^-$ · C$_7$D$_8$ was formed, the system was depressurised and an excess of itaconic acid in [D$_4$]methanol (2:1 with respect to [D$_8$]toluene) was added. After 17 minutes, two products, [Rh(**3**)(IA)]$^+$ (**15**) (IA denotes itaconic acid) and [Rh(**3**)(CD$_3$OD)$_2$]$^+$ were observed by ^{31}P-NMR spectroscopy. After 50 minutes, only [Rh(**3**)(IA)]$^+$ was observed in solution. Itaconic acid makes competitive or cooperative binding by α- and β-carboxylates possible. This usually results in three distinct types of complexes (for a 1:1 stoichiometry), which may coexist, where coordination takes place through the olefin and the α-carboxylate, the β-carboxylate, or both (Figure 2).[15] Despite the moderate enantiomeric excesses obtained in the asymmetric hydrogenation of itaconic acid with [Rh(**3**)(cod)]$^+$BF$_4^-$, complex [Rh(**3**)(IA)]$^+$ exists as a single isomer. Unfortunately, all attempts to isolate this compound were unsuccessful. The P−Rh coupling constants are very large (329.5 and 334.5 Hz). The P−P coupling constant is much larger than those for **13** and **14**, which could suggest that the complex has another geometry. This means that the itaconic acid is probably terdentate-coordinated through the olefin and both α- and β-carboxylates. Five-coordination is a usual geometry for itaconic acid diphosphane Rh$^{\mathrm{I}}$ complexes.[15] An IR spectrum of the solution revealed a broad carboxylic band at higher energy than in the free acid (1667 cm^{-1} vs. 1635 cm^{-1}), which supports the hypothesis about the coordination of both carboxylates. The 2D-NOESY spectrum showed cross-peaks between the olefinic protons of the itaconic acid and the *tert*-butyl groups of the ligand. This supports the hypothesis that the structure is five-coordinated.

No hydride species were observed in the ^{1}H-HPNMR spectra when a solution of complex **15** was pressurised at 5 bar of H$_2$.

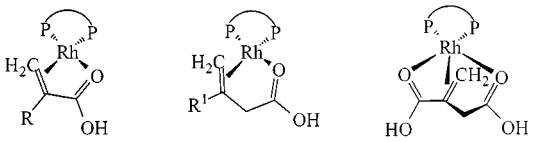


Figure 2. Possible types of coordination for itaconic acid

We can assume from the HPNMR results that the first step is the formation of $[Rh(\mathbf{3})S_2]^+$ by hydrogenation of the olefin coordinated to the rhodium centre. From this species, there are two ways in which itaconic acid can be hydrogenated (Scheme 3). The first (path A) involves the oxidative addition of the H_2 after the coordination of the alkene, while in the second (path B) the oxidative addition of H_2 takes place first.

3.2. Kinetic Study

To find out more about the mechanism of the Rh-catalyzed hydrogenation of itaconic acid at 5 bar of H_2 and 40 °C, we studied the dependence of the rate on the reaction parameters (itaconic acid concentration, H_2 pressure and Rh concentration). The formation of the hydrogenated product over time at [Rh] = 1.66 mM is depicted in Figure 3. The rate of hydrogenation increases after an initial induction period (which is independent on the H_2 pressure used), due to the hydrogenation of the coordinated cyclooctadiene. The formation of methylsuccinic acid is zero-order in substrate concentration, first-order in rhodium concentration (Table 4) and almost first-order in hydrogen pressure (Figure 4) between 5 and 11 bar. Above 11 bar, the pressure dependence of the rate is no longer linear and declines, which suggests a change in the mechanism.

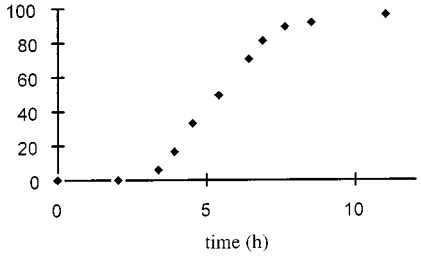


Figure 3. Variation of the conversion of itaconic acid vs. time

Table 4. Influence of the total rhodium concentration on the reaction rate at 5 bar and 40 °C

$[Rh]_T$ 10^{-3} M	k [h^{-1}]
0.83	8.1
1.66	18.9
3.33	35.6

Consequently, and due to the complexity of such a system (Scheme 3), the individual steps of the catalytic cycle had to be studied separately. K_O[IA] (Scheme 4) can be estimated from the HPNMR populations. In this way, and from the solubility of H_2 at 40 °C in toluene/methanol (2:1) ($s = 2.2 \cdot 10^{-2}$ M), which was calculated by HPNMR with CH_3CN as a standard, we can estimate K_{H2} (Scheme 4). A

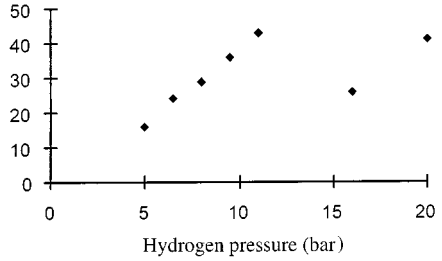
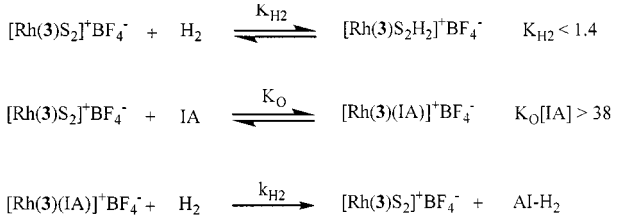


Figure 4. Dependency of the conversion of itaconic acid on H_2 pressure at 40 °C and [Rh] = 1.66 mM

sample of $[Rh(\mathbf{3})(IA)]^+BF_4^-$, generated in situ by mixing isolated $[Rh(\mathbf{3})(CH_3OH)_2]^+BF_4^-$ and 1 equiv. of itaconic acid, was charged in the HPNMR tube at 5 bar, to calculate k_{H2} by HPNMR (Scheme 4). However, the results are not conclusive because of the drop in pressure during the hydrogenation experiment.



Scheme 4. Individual steps of the catalytic cycle

From these results and the fact that the resting state observed by HPNMR at 5 bar is always complex **15**, we cannot conclude that the rate-determining step is not the addition of H_2 to the complex $[Rh(\mathbf{3})S_2]^+$, since it should have a negative order in the itaconic acid concentration. In spite of this, path B cannot be discarded because the same pattern in the rate law derived from mechanism A can be obtained from path B if the rate-determining step is the addition of IA to the complex $[Rh(\mathbf{3})S_2]^+$.

According to the improved conversion when a more basic diphosphite was used, the hydrogenation of itaconic acid with precursor **6** is in agreement with path A, where the rate-determining step is the oxidative addition after partial decoordination of IA to complex $[Rh(\mathbf{3})(IA)]^+$.

Conclusions

Complexes [M(diphosphite)(cod)]BF_4, M= Rh, Ir, with diphosphites derived from xylose, are active in the hydrogenation of some acrylic acid derivatives and achieve moderate enantioselectivities. The most basic hindered diphosphites provided better conversions and selectivities. Under the same conditions, the rhodium-catalysed hydrogenation achieved better enantioselectivities than the iridium-catalysed reaction. Kinetic studies of the Rh-catalysed hydrogenation of itaconic acid between 5 and 11 bar were consistent with a reaction rate which is zero-order in itaconic acid concentration, first-order in rhodium concentration and first-order in H_2 pressure. Despite the electronic differences between phosphanes and phosphites, the Rh-catalysed hy-

drogenation of itaconic acid with diphosphites seems to follow the same mechanism as the one proposed for diphosphanes in the hydrogenation of α-acetamidocinnamic acid.

Experimental Section

General Comments: All syntheses were performed by standard Schlenk techniques under nitrogen or argon. The complexes $[Rh(cod)_2]^+BF_4^-$,[16] $[Ir(cod)_2]^+BF_4^-$,[16] and the diphosphite ligands **1**, **2**, and **3**[2o] were prepared by previously described methods. Solvents were purified by standard procedures. All other reagents were used as commercially available. Elemental analyses were performed with a Perkin−Elmer 240 B instrument. ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR spectra were recorded with a Varian Gemini 300 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 and HETCOR spectra. Standard pulse sequences were employed for the ^{1}H-^{2}D-NOESY.[17] EI mass spectra were obtained with an HP 5989 A spectrometer. VG-Autospect equipment was used for FAB mass-spectral analyses. The matrix was *m*-nitrobenzyl alcohol. Optical rotations were measured at 25 °C with a Perkin−Elmer 241 MC polarimeter. Hydrogenation reactions at high pressure were carried out in a home-made 100-mL stainless steel autoclave. The reaction under 1 atm of H_2 was performed in a previously described hydrogen−vacuum line.[18] The molecular mechanics calculations were carried out with the program CERIUS2 developed by Molecular Simulations (MSI)[19]and the force field UFF developed by Rappe et al.[20] Electrostatic interactions were taken into account from atomic charges generated by the Qeq method.[21]

Preparation of Rhodium Complexes. − General Procedure: The diphosphite ligand (0.1 mmol) was added to a solution of $[Rh(cod)_2]BF_4$ (40.5 mg, 0.1 mmol) in dichloromethane (2 mL). After 10 min, the desired products were obtained by precipitation with hexane.

$[Rh(1)(COD)]^+BF_4^-$ (4): (76 mg, 83%) yellow solid. − MS; *m*/*z*: 829 [M^+]. − $C_{40}H_{40}BF_4O_9P_2Rh$: calcd. C 52.42, H 4.40; found C 51.99, H 4.51. − Major conformer (95% according to ^{31}P NMR): ^{31}P NMR (121.4 MHz, $CDCl_3$, 293 K): δ = 133.4 [dd, 1 P, ^2J(P,H) = 50.0 Hz, ^1J(P,Rh) = 259.2 Hz], 139.4 [dd, 1 P, ^2J(P,H) = 50.0 Hz, ^1J(P,Rh) = 253.1 Hz]; ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ = 1.19 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 2.35 (m, 8 H, CH_2), 4.01 [d, 1 H, H-2, ^3J(H2,H1) = 3.3 Hz], 4.57 (m, 1 H, H-4), 4.68 (m, 1 H, H-5′), 5.12 (m, 1 H, H-5), 5.32 (m, 1 H, H-3), 5.52 (m, 1 H, CH=), 5.69 (m, 1 H, CH=), 5.92 [d, 1 H, H-1, ^3J(H1,H2) = 3.3 Hz], 5.99 (m, 1 H, CH=), 6.04 (m, 1 H, CH=), 7.30−7.8 (m, 16 H, Ph); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 26.5 (CH_3), 26.9 (CH_3), 28.2 (CH_2), 29.9 (CH_2), 30.0 (CH_2), 30.4 (CH_2), 63.3 (C-5), 76.7 (C-4), 81.3 (C-3), 84.4 (C-2), 105.4 (C-1), 109.0 (m, CH=), 109.9 (m, CH=), 111.0 (m, CH=), 111.9 (m, CH=,), 113.0 (CMe_2), 121.8, 122.0, 122.5, 127.0, 127.5, 127.6, 127.7, 129.4, 129.7, 130.0, 130.6, 130.8, 130.9, 131.1, 131.3, 131.5 (Ph). − Minor conformer (5% according to ^{31}P NMR): ^{31}P NMR (121.4, $CDCl_3$, 293 K): δ = 118.2 [dd, 1 P, ^2J(P,P) = 54.0 Hz, ^1J(P,Rh) = 261.2 Hz], 139.4 [dd, 1 P, ^2J(P,P) = 54.0 Hz, ^1J(P,Rh) = 256.1 Hz].

$[Rh(2)(COD)]^+BF_4^-$ (5): (107 mg, 89%) yellow solid. − MS; *m*/*z*: 1173 [M^+]. − $C_{60}H_{80}BF_4O_{13}P_2Rh \cdot 1/2\ CH_2Cl_2$: calcd. C 55.75, H 6.27; found C 56.28, H 7.01. − ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ = 1.26 (s, 3 H, CH_3), 1.52 (m, 18 H, CH_3 *t*Bu), 1.66 (m, 21 H, CH_3, CH_3 *t*Bu), 2.35 (m, 8 H, CH_2), 3.03 (m, 1 H, H-2), 3.84 (s, 12 H, OMe), 3.92 (m, 2 H), 4.19 (m, 1 H), 4.73 (m, 1 H), 5.04 (m, 1 H, CH=), 5.29 (m, 1 H, CH=), 5.52 (m, 1 H, H-1), 6.02 (m, 2 H, CH=), 6.7−7.3 (m, 8 H, Ph). − Major conformer (80% according to ^{31}P NMR): − ^{31}P NMR (121.4 MHz, $CDCl_3$, 233 K): δ = 122.9 [dd, 1 P, $^2J_{(P,P)}$ = 52.2 Hz, $^1J_{(P,Rh)}$ = 208.2 Hz], 124.9 [dd, 1 P, ^2J(P,P) = 52.2 Hz, ^1J(P,Rh) = 214.3 Hz]. − Minor conformer (20% according to ^{31}P NMR): − ^{31}P NMR (121.4 MHz, $CDCl_3$, 233 K): δ = 114.8 [dd, 1 P, ^2J(P,P) = 27.5 Hz, ^1J(P,Rh) = 201.4 Hz], 116.9 [dd, 1 P, ^2J(P,P) = 27.5 Hz, ^1J(P,Rh) = 208.7 Hz].

$[Rh(3)(COD)]^+BF_4^-$ (6): (115 mg, 84%) yellow solid. − MS; *m*/*z*: 1277 [M^+]. − $C_{72}H_{104}BF_4O_9P_2Rh \cdot 1/2\ CH_2Cl_2$: calcd. C 61.91, H 7.52; found C 61.21, H 7.31. − ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ = 1.27 (s, 3 H, CH_3), 1.35 (m, 36 H, CH_3 *t*Bu), 1.55 (m, 18 H, CH_3 *t*Bu), 1.70 (m, 21 H, CH_3, CH_3 *t*Bu), 2.10 (m, 2 H, CH_2), 2.40 (m, 6 H, CH_2), 3.23 (m, 1 H, H-2), 4.16 (m, 2 H), 4.83 (m, 2 H), 5.22 (m, 1 H, CH=), 5.57 (m, 1 H, H-1), 6.03 (m, 1 H, CH=), 6.11 (m, 2 H, CH=), 7.0−7.8 (m, 8 H, Ph). − Major conformer (75% according to ^{31}P NMR): − ^{31}P NMR (121.4 MHz, $CDCl_3$, 293 K): δ = 121.4 [dd, 1 P, ^2J(P,P) = 36.6 Hz, 1J(P,Rh) = 225.6 Hz], 123.6 [dd, 1 P, ^2J(P,P) = 36.6 Hz, ^1J(P,Rh) = 231.1 Hz]; ^{1}H NMR (300 MHz, $CDCl_3$, 233 K): δ = 1.36 (m, 21 H, CH_3, CH_3 *t*Bu), 1.54 (m, 12 H, CH_3, CH_3 *t*Bu), 1.67 (m, 9 H, CH_3 *t*Bu), 2.05 (m, 2 H, CH_2), 2.34 (m, 4 H, CH_2), 2.57 (m, 2 H, CH_2), 3.05 [m, 1 H, H-2, ^3J(H2,H1) = 2.3 Hz], 4.09 (m, 2 H, H-4, H-5′), 4.77 (m, 1 H, H-3), 5.04 (m, 1 H, H-5), 5.28 (m, 2 H, CH=), 5.51 [d, 1 H, H-1, ^3J(H1,H2) = 2.3 Hz], 6.25 (m, 2 H, CH=), 7.0−7.8 (m, 8 H, Ph). − Minor conformer (25% according to ^{31}P NMR): − ^{31}P NMR (121.4 MHz, $CDCl_3$, 233 K): δ = 111.2 [dd, 1 P, ^2J(P,P) = 44.5 Hz, ^1J(P,Rh) = 218.2 Hz], 113.2 [dd, 1 P, ^2J(P,P) = 44.5 Hz, ^1J(P,Rh) = 227.5 Hz]; ^{1}H NMR (300 MHz, $CDCl_3$, 233 K): δ = 1.24 (s, 3 H, CH_3), 1.36 (m, 18 H, CH_3 *t*Bu), 1.54 (m, 9 H, CH_3 *t*Bu), 1.67 (m, 9 H, CH_3 *t*Bu), 1.72 (s, 3 H, CH_3), 2.05 (m, 2 H, CH_2), 2.34 (m, 4 H, CH_2), 2.57 (m, 2 H, CH_2), 3.56 [m, 1 H, H-2, ^3J(H2,H1) = 2.5 Hz], 4.56 (m, 2 H, H-4, H-5′), 4.77 (m, 1 H, H-3), 5.04 (m, 1 H, H-5), 5.28 (m, 2 H, CH=), 5.71 [d, 1 H, H-1, ^3J(H1,H2) = 2.5 Hz], 6.25 (m, 2 H, CH=), 7.0−7.8 (m, 8 H, Ph).

Preparation of Iridium Complexes. − General Procedure: The diphosphite ligand (0.1 mmol) was slowly added to a cooled (195 K) solution of $[Ir(cod)_2]BF_4$ (49.7 mg, 0.1 mmol) in dichloromethane (2 mL). The resulting solution was stirred and the temperature was increased to 273 K. After 2 min, the desired product was obtained by precipitation with diethyl ether.

$[Ir(1)(COD)]^+BF_4^-$ (7): (88 mg, 88%) as a white solid. − MS; *m*/*z*: 919 [M^+]. − $C_{40}H_{40}BF_4IrO_9P_2$: calcd. C 47.77, H 4.01; found C 47.82, H 4.32. − Major conformer (75% according to ^{31}P NMR): ^{31}P NMR (121.4 MHz, CD_2Cl_2, 293 K): δ = 105.3 (broad, 1 P), 104 (broad, 1 P). − Minor conformer (25% according to ^{31}P NMR): ^{31}P NMR (121.4 MHz, CD_2Cl_2): δ = 104.8 (broad, 1 P), 103.5 (broad, 1 P).

$[Ir(2)(COD)]^+BF_4^-$ (8): (75 mg, 60%) as a purple solid. − MS; *m*/*z*: 1263 [M^+]. − $C_{60}H_{80}BF_4IrO_{13}P_2 \cdot 1/2\ CH_2Cl_2$: calcd. C 54.36, H 6.71; found C 54.48, H 6.66. − Major conformer (90% according to ^{31}P NMR): ^{31}P NMR (121.4 MHz, CD_2Cl_2, 253 K): δ = 113.2 [d, 1 P, ^2J(P,P) = 48.4 Hz], 113.7 [d, 1 P, ^2J(P,P) = 48.4 Hz]; ^{1}H NMR (300 MHz, CD_2Cl_2, 253 K): δ = 1.34 (s, 3 H, CH_3), 1.54 (m, 21 H, CH_3, CH_3 *t*Bu), 1.59 (m, 18 H, CH_3 *t*Bu), 2.05 (m, 3 H, CH_2), 2.19 (m, 4 H, CH_2), 2.34 (m, 1 H, CH_2), 2.92 (m, 1 H, H-2), 3.82 (s, 12 H, OMe), 4.01 (m, 1 H), 4.15 (m, 2 H), 4.81 (m, 2 H, H, CH=), 5.01 (m, 1 H, CH=), 5.43 (m, 1 H, H-1), 6.08 (m, 2 H, CH=), 6.6−7.4 (m, 8 H, Ph). − Minor conformer (10% accord-

ing to ^{31}P NMR): ^{31}P NMR (121.4 MHz, CD_2Cl_2, 253 K): δ = 114.8 [dd, 1 P, ^2J(P,P) = 49.2 Hz], 116.9 [dd, 1 P, ^2J(P,P) = 49.2 Hz].

[Ir(3)(COD)]$^+$BF$_4^-$ (9): (115 mg, 72%) as a purple solid. − MS; *m/z*: 1365 [M^+]. − $C_{72}H_{104}BF_4IrO_9P_2$: calcd. C 59.45, H 7.21; found C 58.99, H 7.30. − ^1H NMR (300 MHz, C_7D_8, 293 K): δ = 1.20−1.40 (m, 39 H, CH_3, CH_3 *t*Bu), 1.45−1.70 (m, 39 H, CH_3, CH_3 *t*Bu), 2.10 (m, 8 H, CH_2), 3.48 (m, 1 H, H-2), 3.90 (m, 1 H), 4.15 (m, 2 H), 4.50 (m, 1 H, CH=), 4.71 (m, 1 H, CH=), 5.06 (m, 1 H), 5.71 (m, 1 H, H-1), 5.80 (m, 2 H, CH=), 6.8−7.8 (m, 8 H, Ph). − Major conformer (75% according to ^{31}P NMR): ^{31}P NMR (121.4 MHz, C_7D_8, 293 K): δ = 109.76 [d, 1 P, ^2J(P,P) = 46.1 Hz], 111.23 [d, 1 P, ^2J(P,P) = 46.1 Hz]. − Minor conformer (25% according to ^{31}P NMR): ^{31}P NMR (121.4 MHz, C_7D_8, 293 K): δ = 100.18 (m, 2 P).

[Rh(3)(C_7H_8)]$^+$BF$_4^-$ · C_7H_8 (13): A 100-mL vessel was filled with a solution of **6** (0.05 mmol) in toluene (10 mL) and placed into the autoclave. The autoclave was purged three times with hydrogen and pressurised to the appropriate pressure (5 bar). After a reaction time of 3 h at room temperature, the autoclave was depressurised. The product was then obtained as a yellow solid by concentration to dryness (70 mg, quantitative). − $C_{78}H_{108}BF_4O_9P_2Rh$: calcd. C 65.00, H 7.55; found C 64.65, H 7.67. − ^1H NMR (300 MHz, C_7D_8): δ = 1.00−1.40 (m, 42 H, CH_3, CH_3 *t*Bu), 1.60−2.00 (m, 36 H, CH_3 *t*Bu), 2.71 (s, Ph−CH_3), 3.62 [dd, 1 H, H-5′, ^2J(H5′,H5) = 8.8 Hz, ^3J(H5′,H4) = 6.1 Hz], 3.92 [d, 1 H, H-2, ^3J(H2,H1) = 3.3 Hz], 4.34 [dd, 1 H, H-5, ^2J(H5,H5′) = 8.8 Hz, ^3J(H5,H4) = 12.4 Hz], 4.45 (m, 1 H, H-4), 5.26 (m, 1 H, H-3), 5.78 [d, 1 H, H-1, ^3J(H1,H2) = 3.3 Hz], 7.0−8.0 (m, 18 H, Ph). − ^{31}P NMR (121.4 MHz, C_7D_8): δ = 128.88 [dd, 1 P, ^2J(P,P) = 49.8 Hz, ^1J(P,Rh) = 344.5 Hz], 129.62 [dd, 1 P, ^2J(P,P) = 49.8 Hz, ^1J(P,Rh) = 333.6 Hz].

[Rh(3)($CH_3OH)_2$]$^+$BF$_4^-$ (14): A 10-mL Schlenk flask was filled with a solution of **13** (0.05 mmol) in methanol (10 mL). After a reaction time of 30 min at room temperature, the product was obtained as a yellow-orange solid by concentration to dryness (62 mg, quant.). − $C_{66}H_{100}BF_4O_{11}P_2Rh$: calcd. C 60.00, H 7.63; found C 60.11, H 7.87. − ^1H NMR (300 MHz, CD_3OD): δ = 1.05 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.36 (s, 18 H, CH_3 *t*Bu), 1.38 (s, 18 H, CH_3 *t*Bu), 1.62 (s, 18 H, CH_3 *t*Bu),1.90 (s, 18 H, CH_3 *t*Bu), 2.32 (s, OH), 3.17 [d, 1 H, H-2, ^3J(H2,H1) = 3.3 Hz], 3.48 (s, CH_3−O), 4.09 (m, 2 H, H-5, H-5′), 4.56 (m, 1 H, H-4), 4.74 (m, 1 H, H-3), 5.52 [d, 1 H, H-1, ^3J(H1,H2) = 3.3 Hz]. − ^{31}P NMR (121.4 MHz, CD_3OD): δ = 132.32 [dd, 1 P, ^2J(P,P) = 50.3 Hz, ^1J(P,Rh) = 341.9 Hz], 133.07 [dd, 1 P, ^2J(P,P) = 50.3 Hz, ^1J(P,Rh) = 332.1 Hz].

[Rh(3){CH_2=C(CH_2COOH)(COOH)}]$^+$BF$_4^-$ (15): Itaconic acid (6.1 mg, 0.05 mmol) was added to a solution of **14** (62 mg, 0.05 mmol) in [D_4]methanol (1 mL). After 1 h, the NMR tube was filled and the mixture analysed. − ^1H NMR (300 MHz, CD_3OD): δ = 1.04 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.35 (s, 18 H, CH_3 *t*Bu), 1.37 (s, 18 H, CH_3 *t*Bu), 1.61 (s, 18 H, CH_3 *t*Bu),1.88 (s, 18 H, CH_3 *t*Bu), 3.18 [d, 1 H, H-2, ^3J(H2,H1) = 3.6 Hz], 3.30 (s, 2 H, CH_2), 4.08 (m, 2 H, H-5, H-5′), 4.43 (m, 1 H, H-4), 4.75 (m, 1 H, H-3), 5.52 [d, 1 H, H-1, ^3J(H1,H2) = 3.6 Hz], 5.72 (m, 1 H, CH=), 6.27 (m, 1 H, CH=). − ^{13}C NMR (75.4 MHz, CD_3OD): δ = 27.1 (CH_3), 27.5 (CH_3), 32.3 (CH_3 *t*Bu), 32.4 (CH_3 *t*Bu), 32.9 (CH_3 *t*Bu), 33.2 (CH_3 *t*Bu), 33.6 (CH_3 *t*Bu), 33.8 (CH_3 *t*Bu), 38.8(CH_2), 65.2(d, C-5, *J*(C,P) = 5.8 Hz), 78.2 (dd, C-4, *J* = 10.0 Hz, *J* = 6.3 Hz), 81.4 (d, C-3, *J*(C,P) = 9.5 Hz), 84.7 (C-2), 107.9 (C-1), 114.4 (CMe_2), 129.1 (d, CH_2=, *J* = 30.6 Hz). − ^{31}P NMR (121.4 MHz, CD_3OD): δ = 138.59 [dd, 1 P, ^2J(P,P) = 79.1 Hz, ^1J(P,Rh) = 329.5 Hz], 139.86 [dd, 1 P, ^2J(P,P) = 79.1 Hz, ^1J(P,Rh) = 334.5 Hz].

Hydrogenation Experiments: The reactions were performed in a home-made autoclave. The autoclave was purged three times with H_2. In a typical run, catalytic precursor (0.02 mmol) and substrate (2 mmol) were dissolved in the appropriate mixture of solvents (12 mL) and introduced in the purged autoclave. After pressurising to the desired pressure with hydrogen and heating the autoclave to the reaction temperature, the reaction mixture was stirred. During the reaction, a number of samples were taken and analysed by NMR. After the desired reaction time, the autoclave was cooled to room temperature and depressurised. The solvent was evaporated.

Workup of the Hydrogenation Product: The following procedures were used to isolate the hydrogenation product. For 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 a little water. The ethereal phase was dried with sodium sulfate and concentrated to dryness. The extent of conversion was measured by ^1H-NMR spectroscopy. The enantiomeric excesses were determined by polarimetry.[22] For *N*-acetylalanine methyl ester, gas chromatography analyses were performed in a Hewlett−Packard 5890A instrument (fused silica capillary column 25 m × 0.25 mm permabond L-Chirasil-Val).

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[1] [1a] *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), VCH, Weinheim, **1993**. − [1b] *Asymmetric Catalysis in Organic Synthesis* (Ed.: R. Noyori), John Wiley Sons, New York, **1994**. − [1c] *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Hermann), VCH, Weinheim, **1996**.

[2] [2a] S. Gladiali, J. C. Bayón, C. Claver, *Tetrahedron: Asymmetry* **1995**, *6*, 1453−1474 and references cited therein. − [2b] J. E. Babin, G. T. Whiteker, WO 93/03839, US 911, 518, **1992** (around 90% *ee*). − [2c] E. Fernández, A. Ruiz, C. Claver, S. Castillón, A. Polo, J. F. Piniella, A. Alvarez Larena, *Organometallics* **1998**, *17*, 2857−2864. − [2d] A. van Rooy, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Organomet. Chem.* **1997**, *535*, 201−207. − [2e] J. R. Johnson, G. D. Cuny, S. L. Buchwald, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1760−1761. − [2f] G. D. Cuny, S. L. Buchwald, *Synlett* **1995**, 519−522. − [2g] G. D. Cuny, S. L. Buchwald, *J. Am. Chem. Soc.* **1993**, *115*, 2066−2068. − [2h] B. Moasser, W. L. Gladfelter, D. C. Roe, *Organometallics* **1995**, *14*, 3832−3838. [2i] B. Moasser, W. L. Gladfelter, *Inorg. Chim. Acta* **1996**, *242*, 125−136. [2j] G. J. H. Buisman, E. J. Vos, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton Trans.* **1995**, 409−417. − [2k] A. van Rooy, J. N. H. Debruijn, K. F. Roobek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Organomet. Chem.* **1996**, *507*, 69−73. − [2l] A. van Rooy, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, N. Veldman, A. L. Spek, *Organometallics* **1996**, *15*, 835−847. − [2m] G. J. H. Buisman, L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1997**, *16*, 5681−5687. − [2n] G. J. H. Buisman, L. A. van der Veen, A. Klootwijk, W. G. J. de Lange, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, *Organometallics* **1997**, *16*, 2929−2939. − [2o] G. J. H. Buisman, M. E. Martin, E. J. Vos, A. Klootwijk, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Tetrahedron: Asymmetry* **1995**, *6*, 719−738. − [2p] S. Cserépi-Suzcs, I. Tóth, L. Párkányi, J. Bakos, *Tetrahedron: Asymmetry* **1998**,

9, 3135−3142. − [2q] Y. Jiang, S. Xue, Z. Li, J. Deng, A. Mi, A.S.C. Chan, *Tetrahedron: Asymmetry* **1998**, *9*, 3185−3189.

[3] [3a] M. J. Baker, P. G. Pringle, *J. Chem. Soc., Chem. Commun*. **1991**, 1292−1293. − [3b] M. J. Baker, K. N. Harrison, A. G. Orpen, G. Shaw, P. G. Pringle, *J. Chem. Soc., Chem. Commun.* **1991**, 803−804.

[4] [4a] D. J. Wink, T. J. Kwok, A. Yee, *Inorg. Chem*. **1990**, *29*, 5006−5008. − [4b] A. J. Sivak, E. L. Mutterties, *J. Am. Chem. Soc*. **1979**, *101*, 4878−4887. − [4c] L. S. Stuhl, M. Rakovski Dubois, F. J. Hirsekorn, J. R. Bleeke, A. E. Stevens, E. L. Mutterties, *J. Am. Chem. Soc*. **1978**, *100*, 2405−2410. − [4d] E. L. Mutterties, J. R. Bleeke, *Acc. Chem. Res.* **1979**, *12*, 324−331. − [4e] L. W. Grosser, *Inorg. Chem*. **1975**, *14*, 1453−1456. − [4f] H. K. A. C. Coolen, R. J. M. Nolte, P. W. N. M. van Leeuwen, *J. Organomet. Chem*. **1995**, *496*, 159−168. − [4g] R. Kadyrov, D. Heller, R. Selke, *Tetrahedron: Asymmetry* **1998**, *9*, 329−340. − [4h] R. B. Berdford, S. Castillón, P. A. Chaloner, C. Claver, E. Fernández, P. B. Hitchcock, A. Ruiz, *Organometallics* **1996**, *15*, 3990−3997. − [4i] M. T. Reetz, T. Neugebauer, *Angew. Chem. Int. Ed*. **1999**, *38*, 179−181. − [4j] H. Brunner, W. Pieronczyk, *J. Chem. Res. (S)* **1980**, 76.

[5] [5a] P. C. Nirchio, D. J. Wink, *Organometallics* **1991**, *10*, 336−340. − [5b] P. M. Lorz, W. Bertleff, M. Roeper, D. Koeffer, Eur. Pat. EP 472071, **1993**.

[6] L. H. Pignolet, *Homogeneous Catalysts with Metal Phosphine Complexes*, Plenum, New York, **1983**.

[7] [7a] R. Selke, H. G. Pracejus, *J. Mol. Catal.* **1986**, *37*, 213. − [7b] R. Selke, M. Ohff, A. Riepe, *Tetrahedron* **1996**, *52*, 15079−15102. − [7c] T. V. RajanBabu, T. A. Ayers, G. A. Halliday, K. K. You, J. C. Calabrese, *J. Org. Chem*. **1997**, *62*, 6012−6028 and references therein. − [7d] Industrial application for L-Dopa synthesis: W. Vocke, R. Hänel, F.-U. Flöter, *Chem. Tech. (Leipzig)* **1987**, *39*, 123.

[8] O. Pàmies, G. Net, A. Ruiz, C. Bo, J. M. Poblet, C. Claver, *J. Organomet. Chem*. **1999**, *586*, 125−137.

[9] [9a] *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis. Organic Compounds and Metal Complexes* (Eds.: J. V. Verkade, Louis D. Quin), VCH, **1987**. − [9b] J. Scherer, G. Huttner, M. Büchner, J. Bakos, *J. Organomet. Chem.* **1996**, *520*, 45−58.

[10] [10a] P. L. Bodgan, J. J. Irwin, B. Bosnich, *Organometallics* **1989**, *8*, 1450−1453. − [10b] J. M. Brown, P. A. Chaloner, G. A. Morris, *J. Chem. Soc., Chem. Commun.* **1983**, 664−666. − [10c] N. W. Alcock, J. M. Brown, A. E. Derome, A. R. Lucy, *J. Chem. Soc., Chem. Commun.* **1985**, 575−578. − [10d] D. G. Allen, S. B. Wild, D. L. Wood, *Organometallics* **1986**, *5*, 1009−1015. − [10e] J. M. Brown, P. J. Maddox, *J. Chem. Soc., Chem. Commun*. **1987**, 1278−1280. − [10f] J. M. Brown, P. A. Chaloner, G. A. Morris, *J. Chem. Soc., Perkin Trans. 2* **1987**, 1583−1588. − [10g] C. R. Landis, J. Halpern, *J. Am. Chem. Soc.* **1987**, *109*, 1746−1754. − [10h] J. M. Brown, P. L. Evans, *Tetrahedron* **1988**, *44*, 4905−4916. − [10i] B. M. McCulloch, J. Halpern, M. R. Thompson, C. R. Landis, *Organometallics* **1990**, *9*, 1392−1395. [10j] J.M. Brown, *Chem. Soc. Rev.* **1993**, *22*, 25−41. − [10k] C. R. Landis, T. W. Brauch, *Inorg. Chim. Acta* **1998**, *270*, 285−297. − [10l] B. F. M. Kimmich, E. Somsook, C. R. Landis, *J. Am. Chem. Soc*. **1998**, *120*, 10115−10125.

[11] [11a] E. L. Mutterties, J. R. Bleeke, E. J. Bucherer, T. A. Albright, *Chem. Rev.* **1982**, *82*, 499−525. − [11b] R. G. Gastinger, K. J. Klabunde, *Transition Met. Chem*. **1979**, *4*, 1−13. − [11c] R. Uson, L. A. Oro, C. Foces-Foces, F. H. Cano, S. García-Blanco, M. Valderrama, *J. Organomet. Chem*. **1982**, *229*, 293−304. − [11d] E. L. Mutterties, J. R. Bleeke, A. C. Sievert, *J. Organomet. Chem.* **1979**, *178*, 197−216. − [11e] R. Uson, L. A. Oro, C. Foces-Foces, F. H. Cano, A. Vegas, M. Valderrama. *J. Organomet. Chem*. **1981**, *215*, 241−253. − [11f] L. A. Oro, C. Foces-Foces, F. H. Cano, S. García-Blanco, *J. Organomet. Chem*. **1982**, *236*, 385−394. − [11g] R. Uson, L. A. Oro, D. Carmona, M. A. Esteruelas, C. Foces-Foces, F. H. Cano, S. García-Blanco, A. Vázquez de Miguel, *J. Organomet. Chem*. **1984**, *273*, 111−128. − [11h] R. Giernoth, P. Huebler, J. Bargon, *Angew. Chem. Int. Ed.* **1998**, *37*, 2473−2475.

[12] J. Halpern, *Inorg. Chim. Acta* **1981**, *50*, 11−19.

[13] R. Uson, L. A. Oro, D. Carmona, M. A. Esteruelas, C. Foces-Foces, F. H. Cano, S. García-Blanco, *J. Organomet. Chem*. **1983**, *254*, 249−260.

[14] [14a] J. Halpern, D. P. Riley, A. S. C. Chan, J. J. Pluth, *J. Am. Chem. Soc*. **1977**, *99*, 8055−8057. − [14b] D. A. Slack, I. Greveling, M. C. Baird, *Inorg. Chem*. **1979**, *8*, 3125−3132. − [14c] J. M. Brown, P. A. Chaloner, A. G. Kent, B. A. Murrer, P. N. Nicholson, D. Parker, P. J. Sidebottom, *J. Organomet. Chem*. **1981**, *216*, 263−276.

[15] [15a] J. M. Brown, D. Parker, *J. Chem. Soc., Chem. Commun.* **1980**, 342−344. − [15b] K. Achiwa, P. A. Chaloner, D. Parker, *J. Organomet. Chem.* **1981**, *218*, 249−260. − [15c] J. M. Brown, D. Parker, *J. Org. Chem*. **1982**, *47*, 2722−2730.

[16] M. Green, T. A. Kuc, S. H. Taylor, *J. Chem. Soc., A* **1971**, 2334−2337.

[17] D. J. States, R. A. Haberkorn, D. J. Ruben, *J. Magn. Reson.* **1982**, *48*, 286−292.

[18] C. Cativiela, J. Fernandez, J.A. Mayoral, E. Melendez, R. Usón, L. A. Oro, M. J. Fernandez, *J. Mol. Catal.* **1982**, 16, 19−25.

[19] *CERIUS2*, version 3.5, Molecular Simulations Inc., San Diego, USA, **1997**.

[20] [20a] L. A. Castonguay, A. K. Rappé, *J. Am. Chem. Soc*. **1992**, *114*, 5832−5842. − [20b] A. K. Rappé, C. J. Casewit, K. S. Colwell, W. A. Goddard III, W. M. Skiff, *J. Am. Chem. Soc*. **1992**, *114*, 10024−10035. − [20c] A. K. Rappe, K. S. Colwell, C. J. Casewit, *Inorg. Chem*. **1993**, *32*, 3438−3363.

[21] A. K. Rappé, W. A. Goddard-III, *J. Phys. Chem.* **1991**, *95*, 3358−3363.

[22] D. Lafont, D. Sinou, G. Descotes, *J. Organomet. Chem.* **1979**, *169*, 87−95.

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