Amidophosphine−Phosphinites: Synthesis and Use in Rhodium-Based Asymmetric Hydrogenation of Activated Keto Compounds. Crystal Structure of Bis[(*μ*-chloro)((*S*)-2-((diphenylphosphino)oxy)-2-phenyl-*N*-(diphenylphosphino)-*N*-methylacetamide)rhodium(I)]

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Received January 9, 1996[⊗]

Amidophosphine−phosphinite ligands (AMPP) derived from (*S*)-*N*-benzylmandelamide ((*S*)-R,R′-benzylmandelNOP (*S*)-**1** (R = R′ = phenyl) and (*S*)-**7** (R = phenyl, R′ = cyclopentyl)), (*S*)-*N*-methylmandelamide ((*S*)-R,R′-methylmandelNOP (*S*)-**2** (R = R′ = phenyl) and (*S*)-**8** (R = phenyl, R′ = cyclopentyl)), (*S*)-*N*-methyllactamide ((*S*)-R,R′-methyllactaNOP (*S*)-**3** (R = R′ = phenyl) and (*S*)-**9** (R = phenyl, R′ = cyclopentyl)), and (*S*)-2-(hydroxymethyl)-2-pyrrolidinone ((*S*)-R,R′-oxoProNOP (*S*)-**4**−**6** and (*S*)-**10** (R, R′ = phenyl, cyclohexyl, cyclopentyl)) have been prepared in high yields (60−94%) and reacted with rhodium precursors to prepare neutral "Rh{AMPP}" complexes **11**−**26** of general formula $[Rh\{AMPP\}X]_2$, where X = Cl, I, $OCOCH_3$, $OCOCF_3$, and $OCOC_3F_7$. The crystal structure of $[Rh\{(S)\text{-Ph,Ph-methylmandelNOP}\}Cl]_2$ (**12**) has been determined. The rhodium atom has a *cis* square-planar coordination, and the seven-membered chelate ring has a boat conformation with the nitrogen atom in the mean plane RhP_2. Complexes **11**−**26** have been used as catalyst precursors for the asymmetric hydrogenation of dihydro-4,4-dimethyl-2,3-furandione (**27**) and *N*-benzylbenzoylformamide (**29**) giving the corresponding optically active hydroxy compounds **28** and **30** in high yields and low to high enantiomeric excesses (28−98.7% ee and 13−87% ee, respectively). Catalytic activities (turnover frequency at 50% conversion at room temperature up to 3300 h^{-1}) as well as the enantioselectivities depended strongly on the nature of the substituents on phosphorus as well as on the nature of the non chiral ligands. Catalyst precursor $[Rh\{(S)\text{-Cp,Cp-oxoProNOP}\}OCOCF_3]_2$ afforded (*R*)-pantolactone in 98.7% ee.

Introduction

The asymmetric hydrogenation of prochiral compounds catalyzed by chiral transition-metal complexes has seen widespread use in stereoselective organic synthesis.[1] As such, some processes have found industrial applications.[2] As a prerequisite, the access to chiral ligands was essential for the development of new catalytic systems exhibiting high efficiency and enantioselectivity. In particular, several classes of chiral phosphines have been described, and, when associated with rhodium and ruthenium in catalytic precursors, conduct to date almost complete enantioselectivity for the hydrogenation of olefins and ketones.[1,2] In general, the most successful chiral ligands used in asymmetric hydrogenation are rigid chelating diphosphines possessing a C_2 symmetry axis thus reducing the number of diastereomeric transition states.[1,3] In addition, most of them bear at least two aryl substituents on their phosphorus atoms. Among these bis(phosphines), BINAP type ligands have been extensively studied with rhodium, ruthenium, and recently iridium because of their outstandingly high ability to induce almost complete enantioselectivity in hydrogenation, isomerization, and hydroformylation reactions.[2,4] Mechanisms of enan-

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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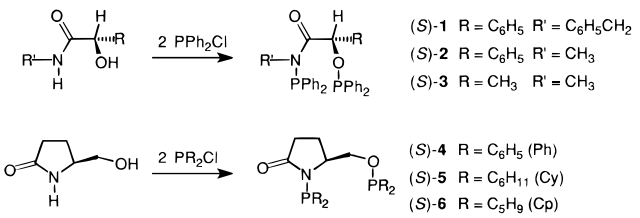
S0276-7333(96)00012-X CCC: $12.00

tioselection of the asymmetric hydrogenation of alkenes have been studied in details[5] and can depend upon either the substrate binding event or subsequent H_2-addition and hydride-transfer steps. Similar considerations are also relevant to product stereogenesis in hydrogenation of other substrates.[6] The structural origin of chirality induced during the hydrogenation reaction using many of these phosphines has frequently been correlated to the ligand backbone chirality (conformation) depending on the specific "face−edge" array of the phenyl rings on both phosphorus.[7] Furthermore, the phenyl substituents present in most chiral diphosphines render the phosphorus atoms and thus the attached metal center relatively electron poor. Although equally interesting properties are expected from more electron-rich diphosphines, relatively few reports have presented so far the capabilities of such ligands in asymmetric hydrogenation of ketones and olefins.[8]

We have conducted an extensive study of the synthesis of new chiral diphosphines in order to apply them in asymmetric catalysis. For that purpose, special efforts have been devoted toward the synthesis of easily accessible ligands based on natural amino acids and amino alcohols.[9] Accordingly, the synthesis of several chiral aminophosphine− and amidophosphine−phosphinite ligands (abbreviated AMPP) bearing either identical or different substituents at their phosphorus atoms has been presented. These ligands have been applied with success in asymmetric catalysis like C−C bond formation,[10] hydroformylation,[11] and hydrogenation of olefins and ketones.[12] Among these bis(phosphines), we have shown that mixed ligands were the most active and selective for the hydrogenation of activated ketones.[12f,h] Also we proposed that the reaction rate and the enantioselectivity of the hydrogenation were both controlled by the aminophosphine moiety.[12a] Hence, we set out to explore the synthesis and application of new closely related bis(phosphines) and their corresponding rhodium complexes exhibiting specific constrains and electronic properties in order to improve

Scheme 1



both activities and selectivities of the hydrogenation reactions. Such a concept of electronic tuning has already been presented and when associated with steric tuning has lead to optimized ligands for asymmetric catalysis.[13]

In this paper, we report (1) the ready synthesis of new AMPP ligands, (2) the synthesis of their corresponding rhodium complexes and a crystal structure of complex $[Rh\{(S)\text{-Ph,Ph-methylmandelNOP}\}Cl]_2$ (**12**), and (3) their subsequent application in asymmetric hydrogenation of ketones. Parts of this work have been previously communicated.[14]

Results and Discussion

1. Synthesis and Characterization of Amidophosphine−Phosphinite Ligands. Symmetrically substituted aminophosphine−phosphinite ligands are generally synthesized by reaction of an amino alcohol with the appropriate chlorophosphine.[9a] Accordingly, the amidophosphine−phosphinite ligands were synthesized by following an analogous procedure. The starting amido alcohols (*S*)-*N*-benzylmandelamide, (*S*)-*N*-methylmandelamide, and (*S*)-*N*-methyllactamide were obtained from the corresponding optically active acids (*i.e.* L-(+)-mandelic and L-(−)-lactic acid) through standard procedures (see Experimental Section). Then under nitrogen, in separate experiments, the three previous amido alcohols and commercial (*S*)-5-(hydroxymethyl)-2-pyrrolidinone were reacted with 2.2 equiv of chlorodiphenylphosphine in diethyl ether (room temperature, NEt_3 excess, 48−120 h) to give after workup the corresponding ligands (*S*)-Ph,Ph-benzylmandelNOP, (*S*)-**1**, (*S*)-Ph,Ph-methylmandelNOP, (*S*)-**2**, (*S*)-Ph,Ph-methyllactaNOP, (*S*)-**3**, and (*S*)-Ph,Ph-oxoProNOP, (*S*)-**4**, in 72−90% yields (Scheme 1). Similarly, amido alcohol (*S*)-5-(hydroxymethyl)-2-pyrrolidinone was reacted with chlorodicyclohexylphosphine or chlorodicyclopentylphosphine (see Experimental Section for an optimized synthesis) (2.2 equiv, NEt_3 excess, THF reflux, 64−120 h) to give respectively the peralkylated ligands (*S*)-Cy,Cy-oxoProNOP, (*S*)-**5**, and (*S*)-Cp,Cp-oxoProNOP, (*S*)-**6**, in 81% yield (Scheme 1).

Next, unsymmetrically substituted ligands were sought. An efficient route to this class of ligands has

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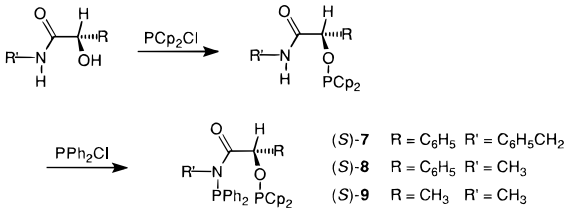
Scheme 2



Scheme 3

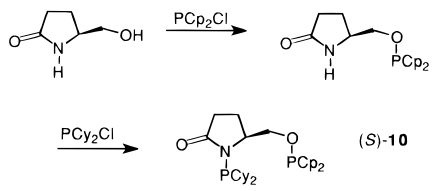


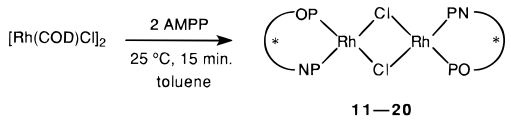
Table 1. Yields and $^{31}P\{^1H\}$ NMR Data for the AMPP Ligands

ligand	no.	yield (%)	δ(P−N)	δ(P−O)
(*S*)-Ph,Ph-benzylmandelNOP	**1**	72	50.8	114.7
(*S*)-Ph,Ph-methylmandelNOP	**2**	90	49.2	114.4
(*S*)-Ph,Ph-methyllactaNOP	**3**	77	51.8	112.6
(*S*)-Ph,Ph-oxoProNOP	**4**	80	36.0	116.9
(*S*)-Cy,Cy-oxoProNOP	**5**	80	58.1	150.4
(*S*)-Cp,Cp-oxoProNOP	**6**	81	60.9	146.5
(*S*)-Ph,Cp-benzylmandelNOP	**7**	94	50.4	146.2
(*S*)-Ph,Cp-methylmandelNOP	**8**	85	49.1	146.3
(*S*)-Ph,Cp-methyllactaNOP	**9**	76	49.4	141.0
(*S*)-Cy,Cp-oxoProNOP	**10**	60	58.3	145.6

been developed recently.[12f] Accordingly, the syntheses of the ligands bearing different phosphino groups at their nitrogen and oxygen atoms were conducted in two steps and monitored by ^{31}P NMR spectroscopy. Thus, under nitrogen, in separate experiments, the amido alcohols were placed in diethyl ether at room temperature along with an excess of NEt_3 and 1 equiv of chlorodicyclopentylphosphine. When all the starting amido alcohols were converted to the corresponding amino−phosphinites (NH−OP) (1−7 days), 1 equiv of chlorodiphenylphosphine was added and the medium was stirred again at room temperature for several days (1−4 days). After workup, (*S*)-Ph,Cp-benzylmandelNOP, (*S*)-**7**, (*S*)-Ph,Cp-methylmandelNOP, (*S*)-**8**, and (*S*)-Ph,Cp-methyllactaNOP, (*S*)-**9**, were isolated in 76−94% yields (Scheme 2). The mixed ligand (*S*)-Cy,Cp-oxoProNOP, (*S*)-**10**, was synthesized by following an identical procedure with sequential phosphinylation of (*S*)-5-(hydroxymethyl)-2-pyrrolidinone (Scheme 3).

The ligands are white air-sensitive powders and were characterized by microanalysis, mass spectrometry, and NMR (^1H, ^{13}C, ^{31}P) spectroscopies (Experimental Section) (Table 1). Their NMR properties resemble those described earlier for the corresponding aminophosphine−phosphinite ligands.[12f] Thus, ligands (*S*)-**1**−**10** exhibited two ^{31}P resonances that were assigned on the basis of chemical shifts trends established earlier (Table 1).[9a] Generally, for amidophosphine−phosphinites, the chemical shifts of the PN (36−60.9 ppm) and PO moieties (114.4−150.4 ppm) were downfield from those of the analogous aminophosphine−phosphinite ligands. Namely, the PN and PO resonances in (*S*)-**5** were at 60.9 and 146.5 ppm as compared to 57 and 142 ppm in the corresponding (*S*)-Cp,Cp-ProNOP ligand.[12f] An exception was the PN resonance of ligand (*S*)-**4** (36 ppm as compared to 46 ppm for (*S*)-Ph,Ph-ProNOP). The

Scheme 4



11—20

ligands ^1H and ^{13}C resonance patterns were complex because of strongly coupled systems.[15] However, complete assignment of almost all resonances was possible on the basis of ^2D NMR (^1H,^1H and ^{13}C,^1H COSY) (see Experimental Section). These ligands were stable on the time scale of months in their solid state at low temperature (−20 °C).

The mechanism of formation of the ligands is assumed to be identical to that already reported.[12f] The presence of three products, as assayed by ^{31}P NMR monitoring of the reaction, *i.e.* amido−phosphinite (NH−OP), amidophosphine−alcohol (NP−OH), and amidophosphine−phosphinite (NP−OP), was taken as evidence for such a mechanism. The reactions of amido alcohols are markedly slower than that of the amino alcohols because of the rather small nucleophilicity of the amido function. Thus, the times and temperatures requested by the reactions to go to completion are longer and higher. As a consequence, byproducts were present in greater amounts and the purification through filtration or selective precipitation was sometimes hampered by the identical solubilities of the ligands and the byproducts. In those cases, attempts to circumvent this problem by adjusting the reactant stoichiometry were unsuccessful in terms of reproducibility.

2. Synthesis of Rhodium−AMPP Precursors. As a consequence of observations relative to the best "Rh{AMPP}" precursors for the hydrogenation of activated ketones, optically active neutral rhodium precursors of general formula $[Rh\{AMPP\}Cl]_2$ were sought. Thus, in separate experiments, the dimeric $[Rh(COD)Cl]_2$[16] and 2.2 equiv of ligands (*S*)-**1**−**10** were reacted (toluene, room temperature, 15 min) leading to the corresponding complexes **11**−**20** (Scheme 4). The crude solutions of the precursors were analyzed by ^{31}P NMR, and their spectroscopic properties, summarized in Table 2, showed unambiguously the chelating character of the AMPP ligands. A careful examination of the ^{31}P NMR spectra showed the presence of additional resonances in some samples (**11**, **14**−**17**). Unfortunately, the nature of the corresponding rhodium species could not be determined so far. Nonetheless, the chemical shift patterns presented are typical of rhodium complexes bearing chelated diphosphines, suggestive of some dynamic phenomenon.[17]

The full characterization of complex $[Rh\{(S)\text{-Cy,Cy-oxoProNOP}\}Cl]_2$ (**15**) as well as the crystallographic characterization of complex **12** described below showed the dimeric nature of the catalyst precursors in the solid state (see Experimental Section). Importantly, crude and purified reaction mixtures of the catalysts precur-

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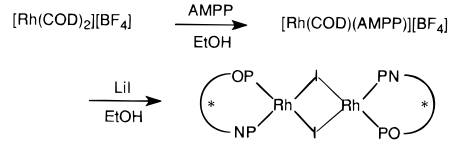
(17) Such an observation has already been reported in ref 12f. Rhodium chloro phosphine complexes have the potential for several types of dynamic behavior. The nature of the two rhodium species is unknown. Nevertheless, the fact that this behavior is observed only for the neutral dimeric species suggests that it is a *syn*-dimer/anti-dimer isomerization equilibrium.

Table 2. $^{31}P\{^1H\}$ NMR Data for the [Rh{AMPP}Cl]$_2$ Complexes

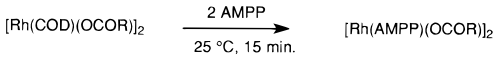
ligand	compd	δ(P−N)	δ(P−O)	J(P−P) (Hz)	J(Rh−P(N)) (Hz)	J(Rh−P) (Hz)
(*S*)-Ph,Ph-benzylmandelNOP	**11**	103.0	149.4	39	222	220
(*S*)-Ph,Ph-methylmandelNOP	**12**	100.2	151.2	37	222	216
(*S*)-Ph,Ph-methyllactaNOP	**13**	96.9	148.9	43	221	210
(*S*)-Ph,Ph-oxoProNOP	**14**	93.4	131.4	47	222	209
(*S*)-Cy,Cy-oxoProNOP	**15**	123.2	163.3	35	228	209
(*S*)-Cp,Cp-oxoProNOP	**16**	122.6	164.7	35	226	211
(*S*)-Ph,Cp-benzylmandelNOP	**17**	112.4	189.6	30	230	206
(*S*)-Ph,Cp-methylmandelNOP	**18**	103.4	186.1	28	235	210
(*S*)-Ph,Cp-methyllactaNOP	**19**	102.5	180.1	32	236	208
(*S*)-Cy,Cp-oxoProNOP	**20**	126.0	162.4	35	229	211

Scheme 5



AMPP : (*S*)-Cy,Cy-oxoProNOP **21**
: (*S*)-Cp,Cp-oxoProNOP **22**

Scheme 6



R : CH_3CO_2	AMPP : (*S*)-Cp,Cp-oxoProNOP	**23**
: CF_3CO_2	: (*S*)-Cy,Cy-oxoProNOP	**24**
	: (*S*)-Cp,Cp-oxoProNOP	**25**
: $C_3F_7CO_2$	: (*S*)-Cy,Cy-oxoProNOP	**26**

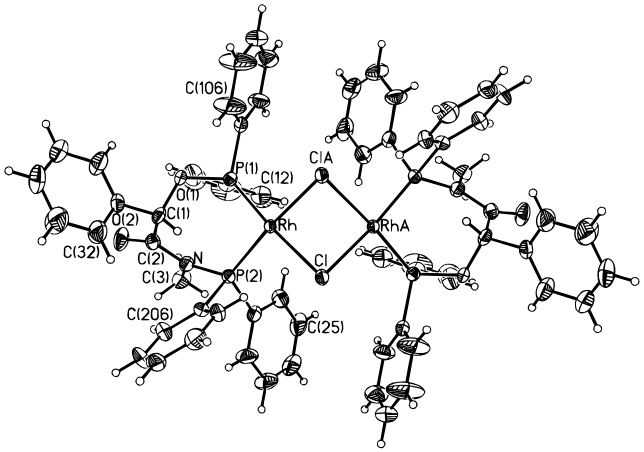


Figure 1. Structure of the dimer [Rh{(*S*)-Ph,Ph-methylmandelNOP}Cl]$_2$ (**12**).

sors gave identical activities and enantioselectivities (*vide infra*). Hence, for the hydrogenations, efforts to purify systematically the catalyst precursors prior to catalysis were useless. Similar observations were made with respect to the purity of the ligands involved. This is very helpful in the cases were the access to highly pure ligands was not systematically possible as mentioned above. These observations provide a further support for the generalization of the *in situ* generation of the rhodium catalysts precursors with this class of ligands.[18]

Next, we sought to study rhodium complexes that would have other non chiral ligands instead of chloride within the coordination sphere in order to evaluate their catalytic performances. Thus, the iodorhodium complex [Rh{(*S*)-Cp,Cp-oxoProNOP}I]$_2$ (**21**) was generated in two steps (Scheme 5). First, cationic [Rh(COD)$_2$]BF$_4$[19] was reacted with 1.1 equiv of (*S*)-Cp,Cp-oxoProNOP, (*S*)-(**5**) (EtOH, room temperature, 45 min), to give [Rh(COD)-{(*S*)-Cp,Cp-oxoProNOP}]BF$_4$. Second, 1.1 equiv of lithium iodide was added to the crude reaction mixture giving complex **21** as assayed by ^{31}P NMR spectroscopy. Complex [Rh{(*S*)-Cy,Cy-oxoProNOP}I]$_2$ (**22**) was synthesized by following an analogous procedure. Complexes **21** and **22** were isolated after filtration and used for catalysis without further purification. Acetate and perfluorocarboxylate complexes were accessible starting from [Rh(COD)(OCOR)]$_2$ (R = CH_3, CF_3, C_3F_7) obtained through reported procedures.[20] Complexes [Rh(COD)-(OCOR)]$_2$ were reacted with 2.2 equiv of the appropriate ligand in toluene (Scheme 6). The resulting red solutions were stirred at room temperature for 15 min and used for catalysis. Accordingly, [Rh{(*S*)-Cp,Cp-oxoProNOP}(OCOCH$_3$)] (**23**), [Rh{(*S*)-Cy,Cy-oxoProNOP}-(OCOCF$_3$)] (**24**), [Rh{(*S*)-Cp,Cp-oxoProNOP}(OCOCF$_3$)] (**25**), and [Rh{(*S*)-Cp,Cp-oxoProNOP}(OCOC$_3$F$_7$)] (**26**) were prepared. The rhodium iodo and carboxylato complexes presented ^{31}P NMR trends analogous to the chloro complexes described above (see Experimental Section).

3. Crystal Structure of [Rh{(*S*)-Ph,Ph-methylmandelNOP}Cl]$_2$ (12). In order to provide support for the solid-state structure of the precursors and to gain information concerning the conformation of the metallacycle, complex **12** was characterized crystallographically. The refinement procedure described in the Experimental Section, along with X-ray data collection, yielded the structure shown in Figure 1, which presents a view of a single dimeric molecule in a direction normal to the central {Rh$_2$Cl$_2$} portion. Important bond distances and bond angles are summarized in Table 3.

The dimer has crystallographically-imposed C_2 symmetry about this viewing direction. Thus, the two phosphinite phosphorus atoms [P(1) and P(1A)] are arranged mutually *trans* across the central portion, as are the two amidophosphine phosphorus atoms [P(2) and P(2A)]. The coordination sphere at rhodium is approximately square-planar (mean atomic deviation = 0.04 Å), and the two such planes are hinged about the Cl···ClA vector to subtend a dihedral angle of 54.0°, clearly evident from Figure 2. This structural arrangement is similar to that observed in [Rh{P(CF$_2$CF$_3$)$_2$CH$_2$-CH$_2$P(CF$_2$CF$_3$)$_2$}Cl]$_2$[21] (dihedral angle 52.1°) but dis-

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Table 3. Important Interatomic Distances (Å) and Angles (deg) for 12, with Estimated Standard Deviations in Parentheses[a]

Rh−P(1)	2.163(3)	Rh−P(2)	2.189(2)
Rh−ClA	2.400(2)	Rh−Cl	2.408(2)
P(1)−O(1)	1.638(6)	P(1)−C(101)	1.787(6)
P(1)−C(11)	1.818(6)	O(1)−C(1)	1.456(12)
C(1)−C(31)	1.474(11)	C(1)−C(2)	1.516(14)
C(2)−O(2)	1.198(13)	C(2)−N	1.371(14)
N−C(3)	1.495(14)	N−P(2)	1.731(9)
P(2)−C(21)	1.825(6)	P(2)−C(201)	1.829(6)
P(1)−Rh−P(2)	92.29(10)	P(1)−Rh−Cl	174.87(9)
P(1)−Rh−ClA	93.75(9)	P(2)−Rh−Cl	91.53(9)
P(2)−Rh−ClA	173.90(10)	Cl−Rh−ClA	82.50(10)
Rh−Cl−Rh	84.82(8)	O(1)−P(1)−C(101)	96.6(4)
O(1)−P(1)−C(11)	101.8(4)	C(101)−P(1)−C(11)	105.2(4)
O(1)−P(1)−Rh	117.6(3)	C(101)−P(1)−Rh	119.3(3)
C(11)−P(1)−Rh	113.6(3)	C(16)−C(11)−P(1)	122.6(5)
C(12)−C(11)−P(1)	117.4(5)	C(106)−C(101)−P(1)	117.9(4)
C(102)−C(101)−P(1)	122.1(4)	C(1)−O(1)−P(1)	120.5(5)
O(1)−C(1)−C(31)	108.5(7)	O(1)−C(1)−C(2)	106.0(9)
C(31)−C(1)−C(2)	113.6(8)	C(36)−C(31)−C(1)	121.4(7)
C(32)−C(31)−C(1)	118.6(7)	O(2)−C(2)−N	123.9(11)
O(2)−C(2)−C(1)	120.2(10)	N−C(2)−C(1)	115.6(8)
C(2)−N−C(3)	113.2(9)	C(2)−N−P(2)	123.2(8)
C(3)−N−P(2)	123.4(8)	N−P(2)−C(21)	101.6(4)
N−P(2)−C(201)	98.5(4)	C(21)−P(2)−C(201)	103.2(3)
N−P(2)−Rh	119.9(3)	C(21)−P(2)−Rh	114.2(3)
C(201)−P(2)−Rh	116.7(2)	C(26)−C(21)−P(2)	117.3(4)
C(22)−C(21)−P(2)	122.7(4)	C(206)−C(201)−P(2)	120.7(4)
C(202)−C(201)−P(2)	119.3(4)		

[a] Symmetry transformations used to generate equivalent (A) atoms: $-x, -y, z$.

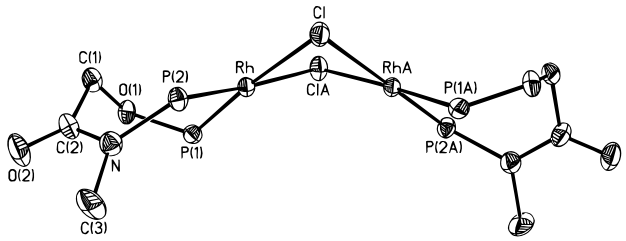

Figure 2. Partial structure of the dimer [Rh(*S*)-Ph,Ph-methylmandelNOP}Cl]$_2$ (**12**). All the phenyl rings have been omitted.

similar to that observed in $[Rh(PPh_3)_2Cl]_2$,[22] which has a planar central portion with a crystallographically-imposed dihedral angle of 0°. These two structure types differ mainly in respect of the angle at μ-Cl (*ca.* 85° in the hinged forms and *ca.* 100° in the planar form) and Rh···Rh distances (*ca.* 3.22 and *ca.* 3.66 Å, respectively). In the title compound, the two independent Rh-Cl distances are almost equal, but Rh−P(N) is significantly longer than Rh−P(O), $D = 0.026(4)$ Å, a general phenomenon in transition metal complexes of chelating aminophosphine−phosphinite ligands.[23] A small widening of the P(N)−Rh−P(O) bond angle (92.24(8)°) is observed. Usually, the opening of this angle is larger for complexes having a seven-membered chelating diphosphine as for example in [Rh(COD){(*S*)-Ph,Ph-ProNOP}]$^+$ (93.0(1)°) and in [Rh(acac){(*S*)-Cy,Cy-ProNOP}] (94.8(1)°).[12f] The P(N)−Rh (2.1635(20) Å) and P(O)−Rh (2.1856(21) Å) bonds are shorter than in the other aminophosphine−phosphinite complexes of Ru, Pd, Pt, and Rh that are 2.209(3)−2.300(4) and 2.188(3)−2.278 (3) Å, respectively.[11b,12f,23] The seven-membered chelate ring has a boat conformation as in other previously reported complexes. However, the nitrogen atom is located in the plane P(N)−Rh−P(O) contrary to the other complexes where the oxygen atom is in that plane.

4. Asymmetric Hydrogenation of Activated Keto Compounds with Neutral Rh(I)−AMPP Complexes. The asymmetric hydrogenation of dihydro-4,4-dimethyl-2,3-furandione (**27**) and *N*-benzylbenzoylformamide (**29**) using the above catalyst precursors (**11**−**26**) was investigated, and the results are shown in Tables 4 (entries 1−19) and 5 (entries 20−31) (Scheme 7).

Asymmetric hydrogenations were carried out in toluene at a temperature ranging from room temperature to 50 °C under hydrogen from 1 to 50 atm. The substrates were hydrogenated quantitatively in up to 98.7% ee to the corresponding optically active hydroxy compounds (Scheme 7). Generally, the catalytic activities of chloro complexes are greatly affected by the nature of the substituents at the phosphorus atoms of the ligands. Thus, the chlororhodium precursors bearing diphenylphosphino-substituted ligands were less active (entries 1−4, 16−18, 20−22, and 28−30) and needed higher temperatures and pressures to progress at reasonable rates. The use of cycloalkyl-substituted ligands allowed the hydrogenation reaction to proceed under mild conditions (1 atm of hydrogen, room temperature) (entries 5, 9, 19, 24, 26, 31). Thus, the best catalytic activities were observed for the hydrogenation of **27** in the presence of (*S*)-Cy,Cy-oxoProNOP and (*S*)-Cp,Cp-oxoProNOP ligands ($TOF_{50\%} = 103$ and 353 h^{-1}, respectively) (entries 5 and 9). These two ligands are also the more efficient ones in the hydrogenation of **29** (entries 24 and 26). All chloro complexes chelated by "linear" amidophosphine−phosphinites required heating and pressure of hydrogen for the hydrogenation reaction to go to completion. Interestingly, these ligands present diphenylphosphino substituents at their nitrogen atom and this property suggested, as it has already been reported,[12f] that the catalytic activity was under the control of the aminophosphine moiety. A spectacular effect on activities measured during the hydrogenation of **27** was observed when changing the nonchiral ligand from Cl to $OCOCF_3$. For example, the activity increased about ten times in going from chloro precursor **16** to trifluoroacetato precursor **25** ($TOF_{50\%} = 353$ and 3333 h^{-1}, respectively) (entries 9 *vs* 14). That enhancement of activity was also encountered for the hydrogenation of **29** ($TOF_{50\%} = 200$ h^{-1} for **16** and 750 h^{-1} for **25**) (entries 24 *vs* 25 and entries 26 *vs* 27).

The best enantioselectivities were achieved during the hydrogenation of the rigid substrate **27**. For example, 96% ee was reached with ligand (*S*)-Cp,Cp-oxoProNOP (entry 9). This value was increased when using complex **25**. Namely, the use of a trifluoroacetato instead of a chloro ligand induced an increase of enantioselectivity from 96 to 98.7% ee (entry14 *vs* 9). To the best of our knowledge, this is the highest ee reported to date for that substrate. The same trend was observed in the presence of ligand (*S*)-Cy,Cy-oxoProNOP for the hydro-

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Table 4. Asymmetric Hydrogenation of Dihydro-4,4-dimethyl-2,3-furandione (27)[a]

entry	compd	chiral ligand	X	$t_{1/2}$[b] (min)	time[c] (h)	ee[d] (%) (conf)
1[e]	**11**	(*S*)-Ph,Ph-benzylmandelNOP	Cl	nd[f]	16	55 (*S*)
2[e]	**12**	(*S*)-Ph,Ph-methylmandelNOP	Cl	nd[f]	30	35 (*S*)
3[e]	**13**	(*S*)-Ph,Ph-methyllactaNOP	Cl	nd[f]	23	28 (*S*)
4[e]	**14**	(*S*)-Ph,Ph-oxoProNOP	Cl	nd[f]	48	52 (*R*)
5	**15**	(*S*)-Cy,Cy-oxoProNOP	Cl	58	18	96.6 (*R*)
6	**21**	(*S*)-Cy,Cy-oxoProNOP	I	22	4	98.0 (*R*)
7	**24**	(*S*)-Cy,Cy-oxoProNOP	CF_3CO_2	nd[f]	1	97.7 (*R*)
8[g]	**24**	(*S*)-Cy,Cy-oxoProNOP	CF_3CO_2	nd[f]	48	96.0 (*R*)
9	**16**	(*S*)-Cp,Cp-oxoProNOP	Cl	17	1.2	96.0 (*R*)
10[h]	**16**	(*S*)-Cp,Cp-oxoProNOP	Cl	nd[f,i]	2[h]	95.6 (*R*)
11[j]	**16**	(*S*)-Cp,Cp-oxoProNOP	Cl	nd[f]	18	95.0 (*R*)
12	**22**	(*S*)-Cp,Cp-oxoProNOP	I	45	18	98.0 (*R*)
13	**23**	(*S*)-Cp,Cp-oxoProNOP	CH_3CO_2	28	1.5	97.7 (*R*)
14	**25**	(*S*)-Cp,Cp-oxoProNOP	CF_3CO_2	1.8	6 min	98.7 (*R*)
15	**26**	(*S*)-Cp,Cp-oxoProNOP	$C_3F_7CO_2$	2.2	5 min	98.0 (*R*)
16[e]	**17**	(*S*)-Ph,Cp-benzylmandelNOP	Cl	nd[f]	20	90 (*S*)
17[e]	**18**	(*S*)-Ph,Cp-methylmandelNOP	Cl	nd[f]	5	81 (*S*)
18[e]	**19**	(*S*)-Ph,Cp-methyllactaNOP	Cl	nd[f]	20	86 (*S*)
19	**20**	(*S*)-Cy,Cp-oxoProNOP	Cl	nd[f]	3.5	96.3 (*R*)

[a] Hydrogenations were carried out in a 200 mL-flask in toluene at room temperature under 1 atm of hydrogen unless otherwise stated. Substrate/Rh = 200. See Experimental Section for typical procedure. [b] Time for 50% conversion. [c] Reaction times were not necessarily optimized; in every case, total conversion of **27** was observed. [d] Enantiomeric excess was determined by GC analysis (FS-Cyclodex β-I/P 25 m × 0.32 mm column, 130 °C) and controlled on the basis of the optical rotation value of **28** (*c* 2.05, H_2O) in comparison with the reported one $[\alpha]_D^{25} = -50.7$.[35] [e] Reaction conducted in a 100 mL stainless-steel autoclave at 50 °C under 50 atm H_2. [f] The half-reaction time was not determined. [g] S/Rh = 70 000, T = 40 °C, $P(H_2)$ = 40 atm. [h] S/Rh = 1000; T = 20 °C, $P(H_2)$ = 60 atm. [i] 97% conversion after 15 min of reaction. [j] S/Rh = 10 000; T = 70 °C, $P(H_2)$ = 50 atm.

Table 5. Asymmetric Hydrogenation of *N*-Benzylbenzoylformamide (29)[a]

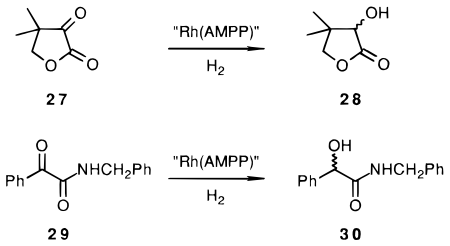
entry	compd	chiral ligand	X	$t_{1/2}$[b] (min)	time[c] (h)	ee[d] (%) (conf)
20[e]	**11**	(*S*)-Ph,Ph-benzylmandelNOP	Cl	nd[f]	96	13 (*R*)
21[e]	**12**	(*S*)-Ph,Ph-methylmandelNOP	Cl	nd[f]	90	22 (*R*)
22[e]	**13**	(*S*)-Ph,Ph-methyllactaNOP	Cl	nd[f]	48	43 (*R*)
23[e]	**14**	(*S*)-Ph,Ph-oxoProNOP	Cl	nd[f]	19	47 (*S*)
24	**15**	(*S*)-Cy,Cy-oxoProNOP	Cl	58	18	87 (*S*)
25	**24**	(*S*)-Cy,Cy-oxoProNOP	CF_3CO_2	10	1.5	61 (*S*)
26	**16**	(*S*)-Cp,Cp-oxoProNOP	Cl	30	2.3	80 (*S*)
27	**25**	(*S*)-Cp,Cp-oxoProNOP	CF_3CO_2	8	0.5	67 (*S*)
28[e]	**17**	(*S*)-Ph,Cp-benzylmandelNOP	Cl	nd[f]	17	53 (*R*)
29[e]	**18**	(*S*)-Ph,Cp-methylmandelNOP	Cl	nd[f]	24	51 (*R*)
30[e]	**19**	(*S*)-Ph,Cp-methyllactaNOP	Cl	nd[f]	24	70 (*R*)
31	**20**	(*S*)-Cy,Cp-oxoProNOP	Cl	nd[f]	3.2	84 (*S*)

[a] Hydrogenations were carried out in a 200 mL-flask in toluene at room temperature under 1 atm of hydrogen unless otherwise stated. Substrate/Rh = 200. See Experimental Section for typical procedure. [b] Time for 50% conversion. [c] Reaction times were not necessarily optimized; in every case, total conversion of **29** was observed. [d] Enantiomeric excess was determined on the basis of the optical rotation value (*c* 1.09, $CHCl_3$) in comparison with the reported one $[\alpha]_D^{26} = +82.2$.[12b] [e] Reaction conducted in a 100 mL stainless-steel autoclave at 50 °C under 50 atm H_2. [f] The half-reaction time was not determined.

genation of **27** (entry 7 *vs* 5). For the hydrogenation of **29**, although the activity was enhanced when using **25** in place of **16**, an overall simultaneous drop in ee was observed from 80 to 67% ee (entry 26 *vs* 27). This phenomenon was even more marked with the trifluoroacetato complex of (*S*)-Cy,Cy-oxoProNOP (entries 24 *vs* 25). An explanation for that loss in selectivity is a need for chelation of that more flexible substrate. Such a chelation is accessible through hydrogen bonding between the chloride ligand on rhodium and the NH function of the amide.[12b] An inversion of configuration of the hydrogenated product is observed in going from cyclic to linear ligands (entries 1−3 *vs* 4−14 for example).

The effect of temperature was studied on three catalyst precursors (**14**−**16**) during the hydrogenation of **27** (Table 6). As expected, an increase of temperature led to higher activities. For example, at 20 °C, 50% conversion was observed in 17 min ($TOF_{50\%}$ = 353 h^{-1}) whereas, at 70°C, the same amount was converted in 2.5 min ($TOF_{50\%}$ = 2400 h^{-1}) (Table 6, entries 9 and 37). The effect of the temperature on the selectivity was negligible except for ligand (*S*)-Ph,Ph-oxoProNOP, where a net increase could be obtained between 20 to 50 °C from 21 to 52% ee (entry 32 *vs* 4).

Scheme 7



Next, when the substrate to rhodium molar ratio was increased up to 10 000, the enantioselectivity remained the same within the experimental error (entry 11 *vs* 9). During the hydrogenation of **27**, ligand (*S*)-Cy,Cy-oxoProNOP, (*S*)-**5**, has been evaluated also at a much higher substrate/Rh molar ratio under technically relevant conditions (substrate/Rh = 70 000, toluene, 40 atm H_2, 40 °C, 48 h) with an *in situ* prepared catalyst **24** (entry 8). In such conditions the conversion was complete and the enantiomeric excess was 96%.

Table 6. Asymmetric Hydrogenation of Dihydro-4,4-dimethyl-2,3-furandione (27): Temperature Effects[a]

entry	compd	chiral ligand	T (°C)	$t_{1/2}$[b] (min)	time (h)[c]	ee[d] (%) (conf of **28**)
4[e]	**14**	(*S*)-Ph,Ph-oxoProNOP	20	nd	216	21 (*R*)
32[e]			50	nd	48	52 (*R*)
33[e]			70	nd	48	52 (*R*)
5	**15**	(*S*)-Cy,Cy-oxoProNOP	20	58	18	96.6 (*R*)
34			50	15	2	95.4 (*R*)
35			70	12	1.2	94.8 (*R*)
9	**16**	(*S*)-Cp,Cp-oxoProNOP	20	17	1.2	96.0 (*R*)
36			50	4	0.7	96.0 (*R*)
37			70	2.5	0.5	96.9 (*R*)

[a] Conditions and notes: see Table 4.

We did not conduct a detailed study of the effect of the hydrogen pressure on both activities and selectivities. However, as an example, the hydrogenation of **27** at a pressure of 60 atm of hydrogen with ligand (*S*)-Cp,Cp-oxoProNOP provided 97% conversion after 3 min as compared to a half time of reaction of 17 min at 1 atm (entry 9). The optical yields were independent of hydrogen pressure over the 1−60 atm range. This suggests that oxidative addition of hydrogen to rhodium species is the rate-determining step, but not the enantiodetermining step. It is noteworthy that we did not observe a variation of the enantiomeric excess with the conversion contrary to what we observed with ruthenium catalysts.[24]

In the course of their studies in the hydrogenation of activated ketones, Ojima and Achiwa observed a loss in enantioselectivity when the reactions were conducted in alcohols rather than in benzene or THF[25] in the presence of neutral precursors for the hydrogenation of **27** and other activated ketones as well. In the same way, Tani[26,8a] and Miyashita[27] observed that neutral rhodium complexes in toluene or THF were more enantioselective than cationic precursors for the hydrogenations of **29**. No conclusions were given related to the nature of the catalytic species for the neutral precursors as if the chloride could be or not on the rhodium during the catalysis. As the catalytic reactions are conducted in toluene, it is likely that the chloride remains coordinated to the metallic center all through the catalysis. This hypothesis is reinforced by the dependence of enantioselectivity upon the nature of the nonchiral ligand (Cl, I, OCOR, Tables 4 and 5)[14b,28] and also by the fact that cationic complexes are bad precursors for the two substrates **27** and **29**.[25] These observations associated to the above mentioned relative to the control of the activity and enantioselectivity by the amino(amido)phosphine moiety are in agreement with our earlier hypothesis.[12b]

In summary, the preceding data establish that amidophosphine−phosphinite ligands can be readily prepared in high yields. However, the reaction times are lengthy and heating becomes necessary when compared to the synthesis of related aminophosphine−phosphinite ligands.[12f] We have demonstrated that an alkyl-substituted phosphino group is required on the nitrogen atom of the ligand to enhance activities as the hydrogenations could be carried out under 1 atm of hydrogen and at room temperature. Accordingly, we can conclude that the amidophosphine moiety of the ligands controls the activity of the resulting rhodium catalysts as did the aminophosphine residue presented in earlier reports. Finally, some amidophosphine−phosphinite−rhodium complexes exhibit higher activities and selectivities than their aminophosphine−phosphinite counterparts.[12f,14b]

Experimental Section

General Methods. Nuclear magnetic resonance [^{1}H (300 MHz), ^{13}C (75 MHz), and ^{31}P (121 and 32 MHz) NMR] spectra were recorded on Bruker AM-300 and Bruker WP-80 spectrometers. Proton and carbon chemical shifts were referenced internally using the residual solvent resonances relative to tetramethylsilane (δ 0 ppm). Phosphorus chemical shifts were referenced to external 85% H_3PO_4 in D_2O (δ 0 ppm). Mass spectra were recorded on a Finnigan MAT 311 A (70 eV) and on a Kratos Concept II H-H (FAB$^+$, 3-nitrobenzyl alcohol/1,3,5-trichlorobenzene 80/20 v/v matrices) spectrometers. The compositions of the catalytic reaction mixtures were determined by GC analysis with a Delsi 30 gas instrument equipped with a flame ionization detector using a 25 m × 0.32 mm FS-Cyclodex β-I/P capillary column. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Elemental analyses were performed by Laboratories Wolff (Clichy, France) and by the Chemistry Department of the University of Lille. All melting points were not corrected. Basic alumina (grade 1) was obtained from Woelm Co., dried under vacuum, and stored at 80 °C prior to use. All reactions involving air- and moisture-sensitive compounds were carried out under a dry dinitrogen atmosphere using standard Schlenk techniques. Toluene, THF, and diethyl ether were distilled from sodium benzophenone ketyl. Ethanol was dried over magnesium alkoxide. Triethylamine was dried over potassium hydroxide and distilled in the presence of 2% phenyl isocyanate. Dried solvents were degassed by 3 freeze−thaw cycles prior to use.

Materials. (*S*)-5-(hydroxymethyl)-2-pyrrolidinone was obtained from Aldrich Chemical Co. and used as received. The other amido alcohols were prepared according to the method previously described.[12b]

(*S*)-(+)-*N*-Benzylmandelamide. Yield: 51% from (*S*)-(+)-mandelic acid. Mp: 136 °C. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.34; H, 6.06; N, 5.71. ^{1}H NMR (acetone-d_6, ethanol): δ 4.5 (d, 2H, CH_2, J = 7 Hz), 5.2 (s, 1H, CH), 7.35 (s, H phenyl), 7.6 (m, H phenyl), 8.0 (s broad, 1H, NH). $[\alpha]_D^{26}$ (*c* 1.09, $CHCl_3$) = +82.2.

(*S*)-(+)-*N*-Methylmandelamide. Yield: 99% from (*S*)-(+)-mandelic acid. Mp: 104−105 °C. Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 64.85; H, 6.39; N, 8.17. ^{1}H NMR ($CDCl_3$): δ 2.8 (d, 3H, CH_3, J = 5 Hz), 3.45 (s, 1H, OH), 5.0 (s, 1H, CH), 7.35 (s, 5H, H phenyl), 8.0 (s broad, 1H, NH). ^{13}C{^{1}H} NMR: δ 26.0 (CH_3), 74.7 (CH), 126.7−139.6 (C phenyl), 173.1 (CO). $[\alpha]_D^{20}$ (*c* 1, $CHCl_3$) = +106.5.

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(*S*)-(−)-*N*-Methyllactamide. Yield: 93% from methyl (*S*)-(−)-lactate. Bp: 93 °C/0.5 mmHg. Anal. Calcd for $C_4H_9NO_2$: C, 46.59; H, 8.80; N, 13.58. Found: C, 46.43; H, 8.62; N, 13.35. ^{1}H NMR ($CDCl_3$−HDMSO): δ 1.35 (d, 3H, CH_3, J = 7 Hz), 3.9 (s, 1H, OH), 4.15 (q, 1H, CH, J = 7 Hz), 6.9 (s, 1H, NH). $[\alpha]_D^{25}$ (*c* 1, $CHCl_3$) = −22.4.

Chlorodicyclohexylphosphine and chlorodiphenylphosphine were purchased from Strem Chemical Inc. and used as received. Chlorodicyclopentylphosphine was prepared by adapting a reported method.[29]

Chlorodicyclopentylphosphine. In a 500 mL round-bottom flask containing magnesium chips (14 g, 0.58 mol), diethyl ether (150 mL), and cyclopentyl chloride (8 mL, 0.077 mol) was introduced methyl iodide (0.2 mL). After the reaction started, cyclopentyl chloride (52 mL, 0.5 mol) was added dropwise in *ca*. 60 min and the solution was heated under reflux for 90 min. The dark reaction mixture was cooled to room temperature and filtered on Celite (3 × 2 cm), and the filtrate was titrated with 1 N NaOH, thus indicating an 85% yield (0.49 mol) of cyclopentylmagnesium chloride. This solution was added dropwise under vigorous stirring, into a round-bottom flask containing phosphorus trichloride (21 mL, 0.23 mol) and ether (250 mL), while the temperature was maintained below −30 °C. The reaction mixture was stirred at room temperature for 15 h. After elimination of $MgCl_2$ through filtration and removal of ether under vacuum, the crude oil was distilled under reduced pressure (50 °C/0.3 mmHg) yielding PCp_2Cl as a colorless liquid. Yield: 37.5 g (80%). Anal. Calcd for $C_{10}H_{18}ClP$: C, 58.68; H, 8.86. Found: C, 58.52; H, 8.88. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 121.0. ^{1}H NMR ($CDCl_3$): δ 1.42−1.73 (m, 12H), 1.78−1.93 (m, 4H), 2.05−2.22 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.4 (d, ^2J(CP) = 5.7 Hz), 28.8 (d, ^3J(CP) = 15.6 Hz), 41.2 (d, CH, ^1J(CP) = 29.6 Hz).

Preparation of Bis(diphenylphosphino) AMPP Ligands ((*S*)-1−4). (*S*)-Ph,Ph-oxoProNOP, (*S*)-4. In a typical experiment, (*S*)-5-(hydroxymethyl)-2-pyrrolidinone (0.138 g, 1.2 mmol) was placed in a 200-mL Schlenk tube along with diethyl ether (30 mL) and triethylamine (5 mL) and was reacted with a solution of chlorodiphenylphosphine (0.586 g, 2.65 mmol) in diethyl ether (10 mL). The mixture was stirred at room temperature for 48 h. Then, the reaction mixture was concentrated under vacuum and excess chlorodiphenylphosphine, ammonium chlorhydrate, and phosphorus impurities were removed by filtration through basic alumina (1 × 5 cm) (washed with 3 × 10 mL of diethyl ether). The solvents were removed from the filtrate under reduced pressure to afford (*S*)−**4** as a white powder: 0.46 g, 80% yield. Slow recrystallization from a diethyl ether−triethylamine solution afforded analytically pure colorless crystals. Anal. Calcd for $C_{29}H_{27}NO_2P_2$: C, 72.04; H, 5.63; N, 2.90. Found: C, 72.33; H, 5.65; N, 2.95. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 36.0 (s, P(N)) and 116.9 (s, P(O)). ^{1}H NMR ($CDCl_3$): δ 2.0−2.25 (m, 2H, CHC*H*$_2$), 2.25−2.40 (m, 1H, C(O)C*H*H), 2.5−2.65 (m, 1H, C(O)CH*H*), 3.45−3.6 (m, 1H, OC*H*H), 3.6−3.75 (m, 1H, OCH*H*), 3.75−3.85 (m, 1H, NCH), 7.2−7.5 (m, 20H, H phenyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 24.0 (d, ^3J(CP) = 3 Hz), 31.3 (d, J(CP) = 1.5 Hz), 61.1 (dd, NCH, J(CP) = 9.5 and 9.7 Hz), 71.0 (dd, OCH_2, J(CP) = 3.8 and 18.3 Hz), 128.3−141.0 (m, C phenyl). MS (*m*/*z*, rel int): 483 (10%, M^+), 386 (75%), 298 (15%, $M^+ - PPh_2$), 262 (100%, PPh_3), 201 (85%, $OPPh_2$). $[\alpha]_D^{20}$ (*c* 0.39, toluene) = −81.

The amidophosphine−phosphinites (*S*)-**1**−**3** were prepared through a procedure similar to that given for (*S*)-Ph,Ph-oxoProNOP, (*S*)−**4**, starting from the corresponding amido alcohol (1.2 mmol).

(*S*)-Ph,Ph-benzylmandelNOP, (*S*)-1: 48 h, 72% yield, white powder. ^{31}P{^{1}H} NMR (toluene-d_8): δ 50.8 (s, P(N)) and 114.7 (s, P(O)). ^{1}H NMR ($CDCl_3$): δ 4.66 (dd, 2H, CH_2 benzyl, J(HH) = 15.3 Hz, J(HP) = 55 Hz), 6.46 (d, 1H, CH, J(HP) = 7 Hz), 6.8−7.6 (m, 30H, H phenyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 49.6 (d, CH_2 benzyl, J(CP) = 7.3 Hz), 78.6 (dd, CH, J(CP) = 21.4 and 26.2 Hz), 125.9−142.0 (m, C phenyl), 175.4 (dd, CO, J(CP) = 4.3 and 24.4 Hz). MS (*m*/*z*, rel int): 408 (7%, $M^+ - OPPh_2$), 386 (95%), 262 (100%, PPh_3).

(*S*)-Ph,Ph-methylmandelNOP, (*S*)-2: 48 h, 90% yield, white powder. ^{31}P{^{1}H} NMR (toluene-d_8): δ 49.2 (s, P(N)) and 114.4 (s, P(O)). ^{1}H NMR ($CDCl_3$): δ 2.71 (s, 3H, NMe), 6.7 (dd, 1H, CH, J(HP) = 5.9 and 8.8 Hz), 6.8−7.6 (m, 25H, H phenyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 32.0 (d, NMe, J(CP) = 8.0 Hz), 78.5 (dd, CH, J(CP) = 21.4 and 26.3 Hz), 128.1−142.0 (m, C phenyl), 175.4 (d, CO, J(CP) = 25.6 Hz). MS (*m*/*z*, rel int): 533 (0.3%, M^+), 492 (10%), 332 (65%, $M^+ - OPPh_2$), 214 (45%, $NMePPh_2$), 201 (100%, $OPPh_2$).

(*S*)-Ph,Ph-methyllactaNOP, (*S*)-3: 120 h, 77% yield, white powder. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.8 (s, P(N)) and 112.6 (s, P(O)). ^{1}H NMR ($CDCl_3$): δ 1.58 (d, 3H, C*H*$_3$CH, J(HH) = 6.6 Hz), 2.72 (d, 3H, NMe, J(HP) = 1.0 Hz), 5.84 (m, 1H, CH), 7.25−7.6 (m, 20H, H phenyl). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.7 (dd, *C*H$_3$CH, J(CP) = 3.7 and 7.3 Hz), 32.2 (d, NMe, J(CP) = 8.5 Hz), 73.2 (dd, CH, J(CP) = 20.8 and 26.2 Hz), 128.5−135 and 142−143 (m, C phenyl), 177.7 (dd, CO, J(CP) = 4.5 and 24 Hz). MS (*m*/*z*, rel int): 471 (0.2%, M^+), 325 (40%), 286 (10%, $M^+ - PPh_2$), 270 (60%, $M^+ - OPPh_2$), 201 (95%, $OPPh_2$), 185 (100%, PPh_2).

Preparation of Bis(dicycloalkylphosphino) AMPP ligands ((*S*)-5, (*S*)-6). (*S*)-Cy,Cy-oxoProNOP, (*S*)-5. In a typical experiment, in a 200-mL Schlenk tube, (*S*)-5-(hydroxymethyl)-2-pyrrolidinone (0.46 g, 4 mmol) dissolved in THF (40 mL) was reacted, in the presence of triethylamine (5 mL), with a solution of chlorodicyclohexylphosphine (2.04 g, 8.77 mmol) in THF (10 mL). The mixture was stirred at room temperature for 24 h and then under reflux for 40 h. Then, the reaction mixture was concentrated under vacuum and excess chlorodicyclohexylphosphine, ammonium chlorhydrate, and phosphorus impurities were removed by filtration through basic alumina (1 × 5 cm) (washed with 3 × 50 mL diethyl ether). The solvents were removed from the filtrate under reduced pressure to afford **5** as a white solid: 1.62 g, 80% yield. Anal. Calcd for $C_{29}H_{51}NO_2P_2$: C, 68.60; H, 10.12; N, 2.76. Found: C, 68.04; H, 9.91; N, 2.41. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 58.1 (s, P(N)) and 150.4 (s, P(O)). ^{1}H NMR ($CDCl_3$): δ 1.0−2.0 (m, 42H), 2.0−2.2 (m, 2H, C*H*$_2$CH), 2.2−2.35 (m, 1H, C*H*HCO), 2.4 (m, 1H, CH Cy), 2.4−2.55 (m, 1H, CH*H*CO), 2.6−2.75 (m, 1H), 2.6 (m, 1H, CH Cy), 3.5 (m, 1H, NCH), 3.65 (m, 1H, OC*H*H), 3.75−3.85 (m, 1H, OCH*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.3−32.0 (m, CH_2), 33.7 (d, CH Cy, J(CP) = 11.6 Hz), 34.9 (d, CH Cy, J(CP) = 14.6 Hz), 38.0 (d, CH Cy, J(CP) = 16.5 Hz), 38.1 (d, CH Cy, J(CP) = 17.1 Hz), 63.8 (dd, NCH, J(CP) = 9.2 and 22.6 Hz), 73.3 (dd, OCH_2, J(CP) = 6 and 18 Hz), 180.0 (d, CO, J(CP) = 10 Hz). MS (*m*/*z*, rel int): 507 (0.1%, M^+), 424 (75%, $M^+ - Cy$), 328 (50%), 245 (20%), 55 (100%). IR (CsI, ν, cm^{-1}): 2925 (s), 2852 (s), 1700 (s), 1447 (s).

(*S*)-Cp,Cp-oxoProNOP, (*S*)-6, was prepared through a procedure similar to that given for (*S*)-Cy,Cy-oxoProNOP ((*S*)-**5**) starting from chlorodicyclopentylphosphine (1.79 g, 8.77 mmol): 120 h, 81% yield, white powder. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 60.9 (s, P(N)) and 146.5 (s, P(O)). ^{1}H NMR ($CDCl_3$): δ 1.2−2.0 (m, 34H), 2.0−2.1 (m, 2H, CH_2CH), 2.2−2.3 (m, 1H, C*H*HCO), 2.4−2.55 (m, 1H, CH*H*CO), 2.8−2.95 (m, 1H, CH Cp), 2.95−3.1 (m, 1H, CH Cp), 3.6−3.7 (m, 2H, OC*H*H + NCH), 3.8−3.9 (m, 1H, OCH*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.3−31.5 (m, CH_2), 35.5 (d, CH Cp, J(CP) = 9.2 Hz), 36.0 (d, CH Cp, J(CP) = 11.4 Hz), 40.6 (d, CH Cp, J(CP) = 12.8 Hz), 40.8 (d, CH Cp, J(CP) = 13.7 Hz), 63.3 (dd, NCH, J(CP) = 9 and 20 Hz), 72.1 (dd, OCH_2, J(CP) = 6 and 16 Hz), 180.0 (d, CO, J(CP) = 8.6 Hz). MS (*m*/*z*, rel int): 382 (100%, $M^+ - Cp$), 282 (5%, $M^+ - PCp_2$).

Preparation of Mixed AMPP Ligands ((*S*)-7−10). General Procedure for the Synthesis of the (*S*)-Ph,Cp-Amidophosphine−Phosphinites Ligands ((*S*)-7−9). A solution of PCp_2Cl (0.77 g, 3.78 mmol) in diethyl ether (10 mL)

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was added to a solution of (*S*)-hydroxyamide (3.7 mmol) in diethyl ether (20 mL) in the presence of triethylamine (5 mL). The reaction mixture was stirred at room temperature for 24−168 h and monitored by $^{31}P\{^1H\}$ NMR (toluene-d_8) until only one signal remained: (*S*)-Cp-benzylmandelNHOP, 168 h, δ 150.6; (*S*)-Cp-methylmandelNHOP, 48 h, δ 151.4; (*S*)-Cp-methyllactaNHOP, 24 h, δ 143.7. To the crude reaction mixtures was directly added dropwise a solution of PPh_2Cl (0.82 g, 3.7 mmol) in diethyl ether (20 mL). The mixtures were stirred at room temperature for 24−96 h and monitored by $^{31}P\{^1H\}$ NMR until total conversion of the (*S*)-Cp-oxoNHOP derivatives. After removal of solvents under vacuum, the crude products were filtered through alumina to remove excess chlorodiphenylphosphine and triethylamine chlorhydrate and eluted with diethyl ether (30 mL). Evaporation to dryness of the filtrate afforded ligands (*S*)-**7**−**9** as white oily solids.

(*S*)-Ph,Cp-benzylmandelNOP, (*S*)-7: 96 h, 94% yield. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 50.4 (s, P(N)) and 146.2 (s, P(O)). ^1H NMR ($CDCl_3$): δ 1.1−2.3 (m, 18H, Cp), 4.65 (dd, 2H, CH_2 benzyl, J(HH) = 15.2 Hz, J(HP) = 27 Hz), 6.48 (d, 1H, CH, J(HP) = 7 Hz), 6.7−7.6 (m, 20H, H phenyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 26.3−29.1 (m, CH_2 Cp), 40.8 (d, CH Cp, J(CP) = 15 Hz), 41.0 (d, CH Cp, J(CP) = 15 Hz), 49.5 (d, CH_2 Br, J(CP) = 7 Hz), 80.2 (dd, CH, J(CP) = 21 and 26 Hz), 125.9−138.4 (m, C phenyl), 175.8 (dd, CO, J(CP) = 4.3 and 24 Hz).

(*S*)-Ph,Cp-methylmandelNOP, (*S*)-8: 24 h, 85% yield. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 49.1 (s, P(N)) and 146.3 (s, P(O)). ^1H NMR ($CDCl_3$): δ 1.1−2.2 (m, 18H, Cp), 2.70 (s, 3H, NMe), 6.66 (dd, 1H, CH, J(HP) ∼ 7 Hz), 6.8−7.6 (m, 15H, H phenyl). $\{^1H\}$ NMR ($CDCl_3$): δ 26.2−29.7 (m, CH_2 Cp), 32.0 (d, NMe, J(CP) = 8 Hz), 40.8 (d, CH Cp, J(CP) = 16 Hz), 41.0 (d, CH Cp, J(CP) = 15 Hz), 79.5 (dd, CH, J(CP) ∼ 25 Hz), 128.3−138.7 (m, C phenyl), 175.9 (d, CO, J(CP) = 4 Hz). MS (*m*/*z*, rel int): 448 (1%, M − Cp), 348 (1%, M − PCp_2), 332 (11%, M − PPh_2), 131 (100%).

(*S*)-Ph,Cp-methyllactaNOP, (*S*)-9: 36 h, 76% yield. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 49.4 (s, P(N)) and 141.0 (s, P(O)). ^1H NMR ($CDCl_3$): δ 1.1−2.2 (m, 18H, Cp) and δ 1.58 (d, 3H, C*H*$_3$-CH, J(HH) = 6.6 Hz)), 2.74 (s, 3H, NMe), 5.72 (dd, 1H, CH, J(HP) = 7 and 14 Hz), 7.2−7.6 (m, 10H, H phenyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.6−29.7 (m, CH_2 Cp), 32.0 (d, NMe, J(CP) = 8 Hz), 40.3−41.2 (m, CH Cp), 74.1 (dd, CH, J(CP) = 21.4 and 27 Hz), 128.3−135.2 (m, C phenyl), 178.4 (d, CO, J(CP) = 20 Hz).

(*S*)-Cy,Cp-oxoProNOP, (*S*)-10. This ligand was prepared in a slightly different manner than that described for (*S*)-**7**−**9**. A solution of PCp_2Cl (1.02 g, 5 mmol) in triethylamine (5 mL) was added to a solution of (*S*)-5-(hydroxymethyl)-2-pyrrolidinone (0.575 g, 5 mmol) in diethyl ether (40 mL). The reaction mixture was stirred at room temperature for 24 h and then under reflux for 40 h. $^{31}P\{^1H\}$ NMR monitoring (toluene-d_8) showed that only one signal remained: δ ∼ 146−147. To this crude reaction mixture was directly added dropwise a solution of PCy_2Cl (1.12 g, 4.8 mmol) in diethyl ether (20 mL). The mixture was stirred at room temperature and monitored again by $^{31}P\{^1H\}$ NMR until total conversion of (*S*)-Cp-oxoProNHOP (72 h). A similar treatment as that described above for (*S*)-**7**−(*S*)-**9** afforded (*S*)-**10** as a white powder: 1.44 g, 60% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 58.3 (s, P(N)) and 145.6 (s, P(O)). ^1H NMR ($CDCl_3$): δ 1.0−2.5 (m, 43H), 2.6−2.75 (m, 1H), 3.5−3.6 and 3.6−3.7 (m, 2 × 1H, OC*H*H + NCH), 3.75−3.9 (m, 1H, OCH*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.2−31.6 (m, CH_2), 33.7 (d, CH Cy, J(CP) = 11.3 Hz), 34.8 (d, CH Cy, J(CP) = 14.5 Hz), 40.6 (d, CH Cp, J(CP) = 15.8 Hz), 40.7 (d, CH Cp, J(CP) = 16.4 Hz), 63.9 (dd, NCH, J(CP) = 8 and 23 Hz), 72.0 (dd, OCH_2, J(CP) = 7 and 16 Hz), 180.1 (d, CO, J(CP) = 10 Hz). MS (*m*/*z*, rel int): 479 (0.1%, M^+), 410 (55%, M^+ − Cp), 396 (90%, M^+ − Cy), 382 (55%), 55 (100%).

Preparation of [Rh{AMPP}Cl]$_2$ Complexes (11−20). Typical Procedure for [Rh{(*S*)-Cy,Cy-oxoProNOP}Cl]$_2$ (15). To a yellow solution of $[Rh(COD)Cl]_2$[16] (0.246 g, 0.5 mmol) in toluene (10 mL) was slowly added a solution of (*S*)-Cy,Cy-oxoProNOP, (*S*)-**5** (0.557 g, 1.1 mmol), in toluene (15 mL). The solution quickly turned red-orange. After 15 min of stirring at room temperature, the solution was concentrated under reduced pressure and the resulting orange powder was washed with a small amount of ethanol to remove excess phosphine. Yield: 0.58 g, 90%. $^{31}P\{^1H\}$ NMR (toluene-d_8): see Table 2. Anal. Calcd for $C_{58}H_{102}N_2O_4P_4Cl_2Rh_2$: C, 53.92; H, 7.96; N, 2.48. Found: C, 54.14; H, 8.54; N, 2.36. MS (FAB$^+$; *m*/*z*): 1290 (M^+), 1064, 645 (M/2). IR (CsI, ν): 2931 (vs), 2854 (m), 1710 (s), 1617 (w), 1449 cm^{-1} (m).

Complexes **11**−**20** were prepared through a procedure similar to that given for [RhCl{(*S*)-Cy,Cy-oxoProNOP}]$_2$ using 1.0 equiv of $[Rh(COD)Cl]_2$ and 2.2 equiv of the adequate ligand. $^{31}P\{^1H\}$ NMR (306 K, toluene-d_8) data are reported in Table 2.

Preparation of [Rh{AMPP}I]$_2$ Complexes (21, 22). Typical Procedure for [Rh{(*S*)-Cy,Cy-oxoProNOP}I]$_2$ (21). A solution of (*S*)-Cy,Cy-oxoProNOP, (*S*)-**5** (0.168 g, 0.33 mmol), and $[Rh(COD)_2][BF_4]$[19] (0.122 g, 0.3 mmol) in ethanol (10 mL) was stirred at room temperature for 45 min. Ethanol was then removed under vacuum to yield the complex [Rh(COD){(*S*)-Cy,Cy-oxoProNOP}][BF_4] as an orange powder. IR (CsI, ν): 2933 (vs), 2854 (m), 1708 (s), 1625 (m), 1449 (m), 1060 cm^{-1} (vs). A solution of this crude complex (0.154 g, 0.19 mmol) in solution in ethanol (5 mL) was then added to LiI (28 mg, 0.21 mmol); the solution turned immediately dark red and a purple powder slowly precipitated. After 45 min of stirring at room temperature, ethanol was evacuated under vacuum, and toluene (3 mL) was added to the residue. The white precipitate formed during dissolution in toluene was removed by filtration, and the resulting solution was evaporated under vacuum to give a dark red powder. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 124.8 (dd, P(N)), 175.3 (dd, P(O)), J(PN−PO) = 14 Hz, J(Rh−P(N))= 220 Hz, J(Rh−P(O)) = 209 Hz.

[Rh{(*S*)-Cp,Cp-oxoProNOP}I]$_2$ (22) was obtained through a procedure similar to that given above by using (*S*)-Cp,Cp-oxoProNOP, (*S*)-**6**. $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 115.5 (dd, P(N)), 176.9 (dd, P(O)), J(PN−PO) = 12 Hz, J(Rh−P(N))= 217 Hz, J(Rh−P(O)) = 213 Hz.

***In Situ* Preparation of [Rh{AMPP}(OCOR)]$_2$ Complexes (23−26).** Complexes **23**−**26** were prepared *in situ* in a similar manner as that given for [Rh{AMPP}Cl]$_2$ by using 1.0 equiv of the corresponding [Rh(COD)(OCOR)]$_2$ complex (R= CH_3, CF_3, C_3F_7)[30] and 2.2 equiv of the appropriate ligand.[20] The resulting toluene solution was directly used for catalysis. The trifluoroacetato complexes of (*S*)-Cy,Cy-oxoProNOP and (*S*)-Cp,Cp-oxoProNOP could be isolated quantitatively as orange powders.

[Rh{(*S*)-Cy,Cy-oxoProNOP}(OCOCF$_3$)]$_2$ (24). Anal. Calcd for $C_{62}H_{102}F_6N_2O_8P_4Rh_2$: C, 51.46; H, 7.10; N, 1.94. Found: C, 52.8; H, 7.7; N, 2.1. IR (CsI, ν): 2933 (m), 2854 (m), 1709 (s), 1690 (s), 1451 cm^{-1} (m).

[Rh{(*S*)-Cp,Cp-oxoProNOP}(OCOCF$_3$)]$_2$ (25). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 130.8 (dd, P(N)), 168.7 (dd, P(O)), J(PN−PO) = 51 Hz, J(Rh−P(N)) = 235 Hz, J(Rh−P(O)) = 215 Hz.

Crystal Structure Determination of [Rh((*S*)-Ph,PhmethylmandelNOP)Cl]$_2$ (12). Slow recrystallization of **12** from toluene afforded yellow crystals which proved to be suitable for *X*-ray investigation. Table 7 gives details of the crystallographic study. The unit cell parameters and the orientation matrix for data collection were determined by the least-squares refinement of the setting angles of 25 strong, high-angle (2θ 24−28°) reflections. Regular remeasurement of the intensities of 2 check reflections revealed (CADABS[31]) no crystal decay over the *ca.* 52 h of *X*-ray exposure. The structure was solved without difficulty by direct methods

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Table 7. Crystallographic Data for 12[a]

cryst dimen/mm	0.3 × 0.3 × 0.2
formula	$C_{66}H_{58}Cl_2N_2P_4O_4Rh_2$
M_r	671.87
color	yellow
habit	blocks
cryst system	orthorhombic
space group (No.)	$P2_{1212}$ (18)
a/Å	21.441(4)
b/Å	19.438(4)
c/Å	8.768(6)
V/Å^3	3662.4(26)
Z	2 (C_2 symmetry imposed)
D_{calc}/g cm^{-3}	1.219
μ(Mo K_α)/cm^{-1}	6.5
F(000)/e	1368
2θ range/deg	2−50
T/K	292
no. of unique data collcd	3642
h range	0−25
k range	0−23
l range	0−10
R (all data)	0.0646
data observed ($F_o > 4\sigma(F_o)$]	3143
R (obsd data)	0.0472
wR^2	0.1803
S	1.231
Flack x param	−0.02(9)

[a] Data collected on an Enraf-Nonius CAD4 diffractometer operating in the $\omega-2\theta$ scan mode; graphite-monochromated Mo $K\alpha$ X-radiation, λ(bar) = 0.71073 Å. Refinement by full-matrix least-squares on F^2. $R = \sum||F_o| - |F_c||/\sum|F_o|$. w$R^2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n = no. of data and p = no. of variables.

(SHELXS86[32]), and refined by full-matrix least-squares (SHELXTL[33]). The absolute structure of the crystal chosen was confirmed by the Flack x text. Following isotropic convergence, an empirical absorption correction (DIFABS[34]) was applied to the data set. Phenyl rings were treated as regular, planar hexagons (C−C 1.39 Å), and all H atoms were set in idealized positions (C−H 0.93 Å for sp-hybridized C; 0.96 Å for sp^3-hybridized C) with isotropic displacement parameters riding at 1.2U(C). In the final stages of refinement data were weighted such that $w^{-1} = [\sigma^2(F_o^2) + (0.1156P)^2 + 1.47P]$ where $P = [\max(F_o^2 \text{ or } 0) + 2F_c^2]/3$. The largest peak and deepest hole in a final ΔF map were 0.77 and −0.51 e/Å^3. Final atomic positional parameters are available as Supporting Information.

(32) Sheldrick, G. M. SHELXS86. Program for crystal structure solution. University of Göttingen, Germany, 1986.
(33) SHELXTL PC version 5.0. Siemens Analytical Instruments Inc., Madison, WI, 1994.

Asymmetric Hydrogenation of Dihydro-4,4-dimethyl-2,3-furandione (27). A solution of dihydro-4,4-dimethyl-2,3-furandione (**27**, Aldrich Chemical Co., recrystallized in diethyl ether prior to catalysis) (0.512 g, 4 mmol) in toluene (10 mL) was degassed by 3 freeze−thaw cycles and then was transferred to a Schlenk tube containing **15** (12.9 mg, 0.01 mmol). The resulting solution was charged in a flask, hydrogen (1 atm) was introduced, and the reaction mixture was stirred at 25 °C for 18 h. Evolution of the reaction was monitored by the hydrogen rate consumption. After evaporation of the solvent, the resulting residue was dissolved in water. The catalyst was then removed by filtration through alumina and the filtrate was evaporated to dryness affording (*R*)-(−)-pantolactone ((*R*)-**28**) in a nearly quantitative yield. Enantioselectivity (96.6% ee) of the product was determined by GC analysis (FS-Cyclodex β-I/P, 130 °C) and controlled on the basis of the optical rotation value (*c* 2.05, H_2O) in comparison with the reported one ($[\alpha]_D^{25} = -50.7$).[35]

Asymmetric Hydrogenation of *N*-Benzylbenzoylformamide (29). This process was carried out under the same conditions as for dihydro-4,4-dimethyl-2,3-furandione (**27**) by starting from 0.957 g (4 mmol) of *N*-benzylbenzoylformamide (**29**). At the end of the reaction, after evaporation of the solvent, the resulting powder was washed with a small amount of cold ether and dried under vacuum to afford (*S*)-(+)-*N*-benzylmandelamide ((*S*)-**30**) as a white powder. Conversion of the substrate was controlled by ^{1}H NMR analysis. Enantioselectivity was determined on the basis of the optical rotation (*c* 1.09, $CHCl_3$) in comparison with the reported value ($[\alpha]_D^{26} = +82.2$).[12b]

Acknowledgment. This study was supported by the Centre National de la Recherche Scientifique and the Ministère de la Recherche et de la Technologie. We thank Dr. E. A. Broger at F. Hoffmann-La Roche Ltd., Basel, Switzerland, for attempts conducted under industrial technical conditions. We thank Dr. G. Ricart for his skillful assistance in obtaining mass spectrometry spectra.

Supporting Information Available: Tables of all refined atomic coordinates and U values and anisotropic thermal parameters for **12** (3 pages). Ordering information is given on any current masthead page.

OM960012M

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