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TETRAHEDRON: *ASYMMETRY*

New chiral aminophosphine carboxyphosphinite ligands (AMPCP). Synthesis and application in asymmetric hydrogenation and hydroformylation

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Abstract

The synthesis of the first three aminophosphine-carboxyphosphinite diphosphanes derived directly from α-amino acids is presented. These ligands were applied in the asymmetric hydrogenation of dihydro-2,4-dimethyl-2,3-furandione giving the corresponding pantolactone with up to 42% *ee*. They were also involved, in association with platinum, in the asymmetric hydroformylation of styrene giving the branched aldehyde with low *ee* (<5%).

1. Introduction

Chiral bisphosphines in which each of the two phosphorus atoms are bonded to three carbon atoms have so far been the most successful ligands for enantioselective hydrogenations.[1] They have also been of interest for application to other asymmetric catalytic processes.[1] Among these ligands, atropisomeric diphosphines of the BINAP type have found the more general applications and are now widely used in asymmetric catalysis (hydrogenation of C=O and C=C, isomerization, hydroformylation, etc.).[2] Nevertheless, other C_2-symmetric diphosphines also exhibit fascinating properties with practical applications in rhodium and ruthenium based enantioselective C=C, C=O, and C=N hydrogenation, i.e. the bis(phospholane)[3] and biphenyl based bisphosphines.[4] In addition, some studies were aimed at synthesizing ligands with the phosphorus atoms bonded to one or more heteroatoms that could be either O or N. An interesting advantage was that some ligands were synthesized in a few steps from diols or amino alcohols. They found use, for example, in asymmetric hydrogenation[5] as well as in asymmetric hydroformylation.[6] For the latter reaction, much interest has also been devoted to the use of diphosphanes in platinum and rhodium based catalysis.[6]

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Table 1
^{31}P NMR properties of ligand **5** and of the corresponding complexes

Ligand or Complex[a]	δ PO (ppm)	δ PN (ppm)	JPP (Hz)	JPO-M (Hz)	JPN-M (Hz)
5	106.0	35.6	-	-	-
8[b]	111.3	89.4	48.0	200	192
10a	145.4	94.1	10.0	-	-
10b	164.7	98.4	31.0	-	-
12[c]	92.9	50.7	11.8	3883	3938
12 + $SnCl_2$[c]	87.4	54.2	13.1	3330	3909

[a] $^{31}P\{^1H\}$RMN CD_2Cl_2 ; referenced to external H_3PO_4 85% in D_2O. [b] M = Rh. [c] M = Pt.

In earlier reports, we described the easy synthesis of non-C_2-symmetric chiral diphosphanes, the aminophosphine-phosphinites (AMPP) derived from α-amino alcohols and α-amido alcohols, as well as their successful application in asymmetric processes.[7,8] We anticipated that diphosphanes derived directly from amino acids may be as easily accessible and prove effective in asymmetric processes. We describe here the synthesis of the first homochiral aminophosphine-carboxyphosphinites (AMPCP) and their involvement as ligands in asymmetric hydrogenation and hydroformylation.

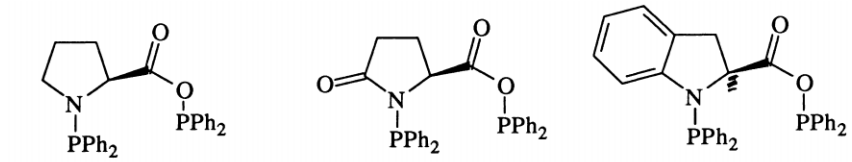
2. Results and discussion

2.1. Synthesis and characterization of the ligands

Among the several AMPP ligands synthesized so far, those with a cyclic chiral skeleton derived from proline, pyroglutamic acid and indoline carboxylic acid have been the most successfully applied to asymmetric hydrogenation.[7] Therefore, we chose to use such types of chiral backbones for the synthesis of the first AMPCP ligands. The quite general procedure developed earlier involving the reaction of a chlorophosphine with the organic precursor was applied for the syntheses. Thus, commercial (*S*)-proline **1**, (*S*)-2-pyrrolidinone-5-carboxylic **2**, and (*S*)-indoline-2-carboxylic acid **3** were reacted with chlorodiphenylphosphine as detailed in the experimental section. The end of the reaction was monitored by ^{31}P NMR and was observed with complete disappearance of the chlorophosphine involved. The only signals remaining in the spectrum were two singlets corresponding to the PO and PN residues of the diphosphanes. The general workup, i.e. alumina column chromatography in order to eliminate $Et_3N\cdot HCl$ and both some undesirable phosphine oxides and an eventual excess of chlorophosphine, led to a decomposition of the ligand. Thus, workup was performed with only a single filtration through a fritted glass funnel. Accordingly, and because of the equimolar stoichiometry between reagents, care had to be taken to be under rigorously deoxygenated conditions in order to avoid phosphine oxide formation. The diphosphanes (*S*)-Ph,Ph-ProliNOP **4**, (*S*)-Ph,Ph-oxoProliNOP **5**, and (*S*)-Ph,Ph-IndoliNOP **6** (Scheme 1, Table 1) were isolated in 91–95% yields and characterized as reported in the experimental section.

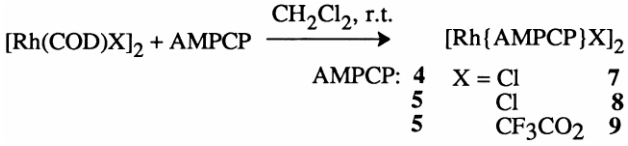
2.2. Synthesis and characterization of the catalyst precursors

Following our best results in asymmetric hydrogenation in the presence of rhodium– and ruthenium–AMPP complexes[7] and in asymmetric hydroformylation with platinum–AMPP catalysts,[8] we sought to synthesize analogous AMPCP complexes. The complexes of rhodium



Scheme 1.

[Rh{(*S*)-Ph,Ph-ProliNOP}Cl]$_2$ (**7**), [Rh{(*S*)-Ph,Ph-oxoProliNOP}Cl]$_2$ (**8**), and [Rh{(*S*)-Ph,Ph-oxoProliNOP}(OCOCF$_3$)]$_2$ (**9**) were prepared in situ prior to catalysis starting from the corresponding rhodium complexes, i.e. [Rh(COD)Cl]$_2$ and Rh(COD)(OCOCF$_3$)]$_2$ (Scheme 2, Table 1).[9]



Scheme 2.

The ruthenium precatalyst bearing ligand **5** was synthesized next. For this purpose, Ru(COD)(2-methylallyl)$_2$[10] was reacted with **5** in dichloromethane at reflux for 2 h (Scheme 3). After workup, Ru{(*S*)-Ph,Ph-IndoliNOP}(2-methylallyl)$_2$ (**10**) was isolated as a pale yellow powder in 70% yield. However, efforts to isolate pure complex **10** were unsuccessful and the latter could only be isolated as a spectroscopically pure species and characterized by ^{31}P NMR (Table 1). The ^{31}P NMR spectra presented two AB systems of equal intensities attributed to two diastereomeric complexes (**10a**/**10b**) in an approximate 50:50 ratio resulting from different configurations at ruthenium.[11] In the ^{1}H and ^{13}C NMR spectra, the resonances patterns were excessively complex, especially because of the presence of the two diastereomers rendering chemical shift and coupling constants difficult to assign unambiguously.

Scheme 3.

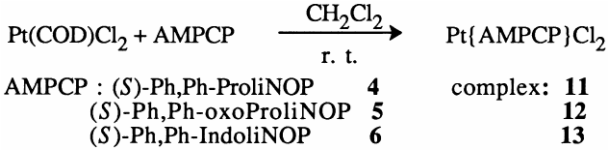
Next, platinum complexes were obtained easily and quantitatively through reaction of Pt(COD)Cl$_2$[12] with the ligands **4**–**6** in dichloromethane at room temperature (Scheme 4). After workup, complexes Pt{(*S*)-Ph,Ph-ProliNOP}Cl$_2$ (**11**), Pt{(*S*)-Ph,Ph-oxoProliNOP}Cl$_2$ (**12**), and Pt{(*S*)-Ph,Ph-IndoliNOPNOP}Cl$_2$ (**13**) were isolated as white solids and characterized as outlined in the experimental section. Their ^{31}P NMR properties were identical to the trends generally observed for Pt{AMPP}Cl$_2$ complexes (Table 1),[8] i.e. a pattern of two sets of signals. The two doublets of major intensities were assigned, respectively, to the $-$NPPh$_2$ (most upfield) and $-$OPPh$_2$ moieties (downfield signal) with coupling between the two *cis* phosphorus atoms in the 11.8–12.8 Hz range. These signals are flanked by two doublets of minor intensity constituting the ^{195}Pt satellites. Interestingly, because of the neighbouring carbonyl group, the OP signals were downfield from those of the corresponding AMPP ligands (ca. $\Delta\delta$=10 ppm). Also, contrary to the free ligands, platinum complexes in the solid state are much more stable and can be handled in air. The ^{31}P NMR properties of the PtCl(SnCl$_3$) (**5**), obtained from reaction of the platinum complex **12** with one equivalent of SnCl$_2$ in dichloromethane at room temperature, are also given in Table 1. The tin complex shows an analogous ^{31}P NMR pattern. Interestingly, while the J_{Pt-PN} coupling remained almost unchanged when compared to the parent complex (3909 vs 3938 Hz), the J_{Pt-PO} decreased significantly (3330 vs 3883 Hz). Such a variation is attributed to a *trans* effect resulting from the coordination of the SnCl$_3$ species *trans* to the PO

Table 2
ν_{CO} Infrared properties of ligand **5** and of the corresponding complexes[a]

Compound	$\nu_{C=O}$(amide) (cm^{-1})	$\nu_{C=O}$(COO) (cm^{-1})
pyrroglutamic acid	1720	1630
5	1730	1704
12	1777	1731
12 + $SnCl_2$	1779	1738

[a]KBr pellets.

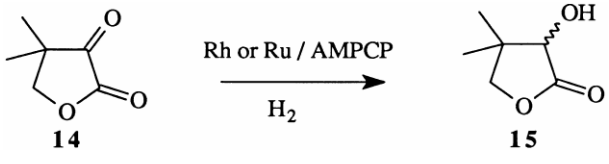
moiety.[13] The ν_{CO} infrared properties of the series of species related to ligand **5** are presented in Table 2. The presence of the phosphorus atoms and, further, the coordination of the ligands to the platinum, induced an overall shift of $\Delta\nu_{CO}$=77 cm^{-1} and 101 cm^{-1} for the amide and carboxyphosphinite C=O, respectively when compared to the starting organic precursor (Table 2). More, the presence of the $SnCl_3$ residue after reaction of **12** with $SnCl_2$ induced a further 7 cm^{-1} increase in the ν_{CO} of the carboxyphosphinite C=O corroborating the *trans* position of the tin species as already deduced from the ^{31}P NMR properties described earlier.



Scheme 4.

3. Asymmetric catalysis

The asymmetric hydrogenation of our test substrate dihydro-2,4-dimethyl-2,3-furandione (**14**) leading to the corresponding hydroxy compound (**15**) (Scheme 5), in the presence of the above rhodium and ruthenium precatalysts, was investigated and the key results are presented in Table 3. For comparison purposes, selected results obtained earlier with rhodium and ruthenium catalysts are also given.



Scheme 5.

The rate and enantioselectivity of the AMPCP based rhodium catalysts resemble those of the corresponding AMPP complexes with a general lower chiral induction. Namely, the reaction needs a pressure of hydrogen and heating to progress at reasonable rates. The highest enantiomeric excess was obtained with ligand **5** (precatalyst **9**; run 6). With the catalyst precursor **10**, the hydrogenation was complete with no chiral induction (run 7). This result could be attributed to a hydrogenolysis of the P–O bond. Such reactions have been reported already elsewhere.[16] We also carried out the synthesis of (*S*)-Cy,Cy-oxoProliNOP.[17] The hydrogenation reaction performed with that ligand in conditions identical to those described earlier for run 5 led to a complete conversion into pantolactone with no asymmetric induction. Here again, a decomposition of the OCOP moiety is highly expected.

Table 3
Asymmetric hydrogenation of **14** in the presence of rhodium and ruthenium catalysts[a]

Run	Ligand (P_2)	Precatalyst	T (°C)	P_{H2} (atm)	Time (h)	Conv.[b] (%)	ee (%)[c] Config.
1	(*S*)-Ph,Ph-ProNOP[d]	$[Rh(P_2)Cl]_2$	30	40	20	100	45 (*R*)
2	(*S*)-Ph,Ph-oxoProNOP[e]	$[Rh(P_2)Cl]_2$	20	50	48	100	51.8 (*R*)
3	(*S*)-Ph,Ph-oxoProNOP[f]	$Ru(P_2)(2\text{-meth})_2$[g]	20	50	18	100	79 (*R*)
4	**4**	$[Rh(P_2)Cl]_2$ **7**	50	50	17		20 (*R*)
5	**5**	$[Rh(P_2)Cl]_2$ **8**	50	50	17	30	34 (*R*)
6	**5**	$[Rh(P_2)(O_2CCF_3)]_2$ **9**	20	50	17		42 (*R*)
7	**5**	$Ru(P_2)(2\text{-meth})_2$ **10a/10b**	20	rt / 50	17	100	0

[a]Reactions were carried out by using 6 mmol of recrystallized substrate in 30 mL of dry degassed dichloromethane. Substrate/Rh or Ru: 200/1. [b]The conversions were determined by GC. [c]Determined by GC analysis (FS-cyclodextrine.β-I/P 25 m x 0.32 mm column, 130 °C. [d]Taken from reference 14. [e]Taken from reference 15. [f]Taken from reference 11. [g]2-meth: 2-methylallyl.

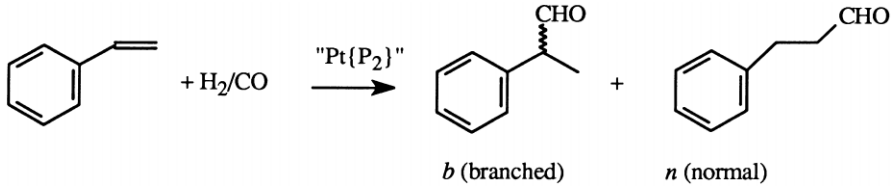
Table 4
Hydroformylation of styrene in the presence of $Pt\{AMPP\}Cl_2$ an $Pt\{AMPCP\}Cl_2$ catalyst precursors[a]

run	Ligand	Solvent	Time (h)	Conv.[b] (%)	PhEt (%)	*b*/*n*[c]	ee[d] (%) (conf.)
8	(*S*)-Ph,Ph-ProNOP[f]	$PhCH_3$	36	100	2	40/60	42 (*S*)
9	*S*)-Ph,Ph-ProliNOP **4**	CH_2Cl_2	112	73	3	66/34	2 (*S*)
10	(*S*)-Ph,Ph-oxoProNOP[f]	$PhCH_3$	16	100	3	30/70	40 (*S*)
11	(*S*)-Ph,Ph-oxoProNOP	CH_2Cl_2	16	98	5	33/67	38 (*S*)
12	(*S*)-Ph,Ph-oxoProliNOP **5**	CH_2Cl_2	16	93	7	65/35	5 (*S*)
13	(*S*)-Ph,Ph-IndoNOP[g]	$PhCH_3$	45	100	7	43/57	36 (*S*)
14	(*S*)-Ph,Ph-IndoliNOP **6**	CH_2Cl_2	16	55	3	65/35	< 1

[a]Reactions were carried out in a 50 ml autoclave in the mentioned solvent (10 mL), at 50 °C, initial pressure 135 bar, H_2 / CO = 1.5, Pt = 0.06 mmole ; Pt / Sn / Styrène = 1 / 1 / 100. [b] Total conversion. [c]*b*/*n* [d]Determined by GC analysis (FS-cyclodextrine.β-I/P 25 m x 0.32 mm column) on the corresponding alcohols [f]Taken from reference 8c. [g]See reference 18.

Next, the platinum precursors **11**–**13** were applied, in the presence of $SnCl_2$ as a cocatalyst, in the hydroformylation of styrene (Scheme 6, Table 4). Results obtained with the corresponding AMPP ligands are also given for comparison. The solvent used generally for AMPP based complexes, toluene, could not be used here because of the rather low solubility of the catalyst precursor. Accordingly, dichloromethane has been used. The reactions (Table 4) gave the expected aldehyde mixtures of the branched (β, 2-phenylpropanal) and the normal (n, 3-phenylpropanal) regioisomers (Scheme 6). Moderate branched to normal aldehyde ratios (β/n) were obtained. These selectivities are higher than those usually obtained with platinum catalysts and have the opposite regiochemistry to that usually obtained in the reaction. Hydrogenation to ethylbenzene occurred as a competing reaction to an extent of 11%. The presence of the 5-oxo moiety in the pyrrolidine cycle had a beneficial effect on the catalytic activity, as a reasonable

rate could be reached (run 11 vs 9). However, in the best case, the enantioselectivity induced in the branched product remained very low (5% *ee*). The effect of the aromatic ring of ligand **6** presented an intermediate effect on the rate of the hydroformylation reaction (run 14 vs 12 and 9). The presence of the higher electron-withdrawing carboxyphosphinite moiety when compared to the corresponding phosphinite residues of the AMPPs induced an increase in the regioselectivity of the system (run 12 vs 11). Thus, for an identical chiral skeleton, the effect of the electron-deficient diphosphanes related to solely their carboxyphosphinite residues is quite interesting in terms of regioselectivities. Nevertheless, the reaction is impracticable as a dramatic decrease in the activities and enantioselectivities is observed.



Scheme 6.

4. Conclusion

The aminophosphine-carboxyphosphinite ligands are easily accessible directly from the corresponding α-amino acids. However, they are exceedingly sensitive and unstable leading to rapid decomposition. The performances presented by these new ligands are very close to the related phenyl substituted AMPP ligands for the hydrogenation of dihydro-2,4-dimethyl-2,3-furandione with close asymmetric inductions. Unfortunately, when applied in the hydroformylation of styrene they proved to be impracticable, presenting low enantioselectivities, although with an interesting selectivity towards the branched aldehyde nevertheless.

5. Experimental section

All reactions were carried out under nitrogen by using standard Schlenk techniques. Solvents were dried under nitrogen by standard procedures, distilled before use, and stored under nitrogen. The transition-metal complexes $[Rh(COD)Cl]_2$, $Rh(COD)(OCOCF_3)]_2$,[9] $Ru(COD)(2\text{-methylallyl})_2$,[10] and $Pt(COD)Cl_2$[12] and the two ligands (*S*)-Ph,Ph-ProNOP[7] and (*S*)-Ph,Ph-oxoProNOP[7] were prepared according to reported procedures. ^1H, ^{13}C and ^{31}P spectra were recorded on Bruker AC 300 and AC 200 spectrometers. ^1H and ^{13}C NMR chemical shifts were reported relative to TMS. ^{31}P NMR chemical shifts were reported relative to external 85% H_3PO_4 in D_2O, with downfield values taken as positive. IR spectra are expressed in wavenumbers (cm^{-1}). The elemental analyses were performed by Wolff Laboratories, Clichy, France. For the hydrogenation product, evaluation of conversions and *ee*s during the course of the catalytic reactions were determined using a Delsi Série 30 gas chromatograph, on a Chrompack FS-CYCLODEX BETA-I/P capillary column (25 m×0.32 mm, film depth 0.25 mm). The determination of the optical purity of the alcohol obtained from the reduction of the branched aldehyde was performed on the same chiral column.

5.1. Synthesis of (S)-Ph,Ph-ProliNOP **4**

In a Schlenk tube under nitrogen, the organic precursor (*S*)-proline (**1**) (0.289 g, 2.5 mmol) was suspended in a mixture of diethyl ether (40 ml) and triethylamine (5 ml, 36 mmol). Then, under vigorous stirring, a solution containing $ClPPh_2$ (1.1 g, 5 mmol, 2.02 equiv.) in diethyl ether (15 ml) was added dropwise over a period of 15 min. The stirring was maintained and the reaction was monitored by ^{31}P NMR. The end of the reaction was observed with the complete disappearance of the chlorophosphine (average of 24 h). The ligand (*S*)-Ph,Ph-ProliNOP (**4**) was isolated, via a single filtration through a fritted glass funnel followed by evaporation of the solvent under reduced pressure and drying under vacuum, as a white air sensitive gum in 95% yield (1.15 g). IR (KBr, cm^{-1}): ν_{CO} 1729. Anal. calcd for $C_{29}H_{27}NO_2P_2$: C, 72.04; H, 5.62; N, 2.89. Found: C, 71.59; H, 5.74; N, 2.89. ^1H NMR (CD_2Cl_2, δ, ppm): 7.62 (m, 20H, Ph), 3.27 (m, 1H, CHN), 3.03 (m, 1H), 2.28 (m, 2H), 2.19 (m, 1H), 1.98 (m, 1H), 1.83 (m, 1H). $^{13}C(^1H)$ NMR (CD_2Cl_2, δ, ppm): 175.2 (s, CO), 132.9–128.9 (m, Ph), 66.6 (d, J_{CP}=35 Hz, *C*HCO), 47.7 (d, J_{CP}=6 Hz, N*C*HH), 31.9 (d, J_{CP}=6 Hz, NCHH*C*HH), 26.2 (s, NCH*C*HH). $^{31}P(^1H)$ NMR (CD_2Cl_2, δ, ppm): 101.4 (s, PO), 49.9 (s, PN).

5.2. Synthesis of (S)-Ph,Ph-oxoProliNOP **5**

The organic precursor (*S*)-pyroglutamic acid (**2**) (0.3 g, 2.3 mmol) and chlorodiphenylphosphine (1.04 g, 4.7 mmol, 2.03 equiv.) were reacted following a procedure identical to that described for **4**. An analogous workup gave (*S*)-Ph,Ph-oxoProliNOP **5** as a white powder in 91% yield (1.05 g). Anal. calcd for $C_{29}H_{25}NO_3P_2$: C, 70.02; H, 5.06; N, 2.82. Found: C, 70.53; H, 5.31; N, 2.75. ^1H NMR (CD_2Cl_2, δ, ppm): 7.45 (m, 20H, Ph), 4.17 (m, 1H, NCH), 2.42 (m, 3H, C*HH*C*H*H), 2.09 (m, 1H, CHHCH*H*). $^{13}C(^1H)$ NMR (CD_2Cl_2, δ, ppm): 179.8 (d, J_{CP}=4 Hz, NCO), 175.2 (s, COO), 135–128 (m, Ph), 62.54 (s, NCH), 31.2 (s, OC*C*HH), 26.2 (s, NCH*C*HH).

5.3. Synthesis of (S)-Ph,Ph-IndoliNOP **6**

The organic precursor (*S*)-indoline-2-carboxylic acid (**3**) (0.32 g, 1.96 mmol) and chlorodiphenylphosphine (0.874 g, 3.96 mmol, 2.02 equiv.) were reacted following a procedure identical to that described for **5**. An analogous workup gave (*S*)-Ph,Ph-IndoliNOP **6** as a white gum in 93% yield (0.97 g). IR (KBr, cm^{-1}): ν_{CO} 1726. Anal. calcd for $C_{33}H_{27}NO_2P_2$: C, 74.57; H, 5.12; N, 2.63. Found: C, 74.02; H, 4.93; N, 2.42. ^1H NMR (CD_2Cl_2, δ, ppm): 7.50 (m, 24H, Ph), 4.90 (m, 1H, CH), 3.75 (dd, J_{HH}=10.8 and 6.21 Hz, C*H*H), 3.24 (m, 1H, CH*H*). $^{13}C(^1H)$ NMR (CD_2Cl_2, δ, ppm): 174.3 (s, CO), 152.2 (s, NC(C)C), 137.7–113.3 (m, Ph), 66.93 (m, NCH), 37.19 (d, J_{CP}=Hz, CHH). $^{31}P(^1H)$ NMR (CD_2Cl_2, δ, ppm): 102.3 (s, PO), 43.5 (s, PN).

5.4. Synthesis of Ru{(S)-Ph,Ph-oxoProliNOP}(2-methylallyl)$_2$ **10**

In dichloromethane, under stirring, a solution containing the precursor Ru(COD)(2-methylallyl)$_2$[10] (0.167 g, 0.5 mmol) and (*S*)-Ph,Ph-oxoProliNOP (0.271 g, 0.56 mmol) was heated at reflux for 2 h. After cooling to room temperature, the crude reaction mixture was filtered through a pad of Celite (1×1 cm). After concentration of the mixture under reduced pressure (1–2 ml), hexane (10 ml) was added to precipitate a yellow–brown powder which was collected by filtration, washed with hexane (2×5 ml) and dried under vacuum. Complex **12** was isolated in 70% yield (0.276 g) with a spectroscopic purity of 90% as determined by ^{31}P NMR.

5.5. Synthesis of Pt{(S)-Ph,Ph-ProliNOP}Cl_2 **11**

Under nitrogen, the platinum complex Pt(COD)Cl_2[12] (0.166 g, 0.45 mmol) was reacted with **4** (0.215 g, 0.46 mmol) in dichloromethane (40 ml) under stirring for 3 h at room temperature. After removal of the solvent from the colorless solution and drying under reduced pressure, complex **11** was isolated in quantitative yield as a white solid (0.33 g). IR (KBr, cm^{-1}): ν_{CO} 1777. Anal. calcd for $C_{29}H_{27}Cl_2NO_2P_2Pt$: C, 46.50; H, 3.63; N, 1.87. Found: C, 45.90; H, 3.9; N, 1.73. ^{1}H NMR (CD_2Cl_2, δ, ppm): 7.53 (m, 20H, Ph), 5.61 (dd, 1H; *J*=5.5, *J*=7.5 Hz, CHN), 2.53 (m, 6H, C*H*$_2$C*H*$_2$C*H*$_2$). ^{13}C(^{1}H) NMR (CD_2Cl_2, δ, ppm): 165.9 (d, J_{CP}=6 Hz, CO), 134.9–127.8 (m, Ph), 64.77 (m, NCH), 49.9 (s, NCH_2), 28.1 (d, J_{CP}=5.8 Hz, NCH*C*H$_2$), 27.1 (d, J_{CP}=4.4 Hz, NCH$_2$*C*H$_2$). ^{31}P(^{1}H) NMR (CD_2Cl_2, δ, ppm): 91.4 (d, J_{PP}=11.8 Hz, J_{PtP}=4014 Hz, PO), 53.0 (d, J_{PP}=11.8 Hz, J_{PtP}=3871 Hz, PN).

5.6. Synthesis of Pt{(S)-Ph,Ph-oxoProliNOP}Cl_2 **12**

The ligand **5** (0.15 g, 0.30 mol) and Pt(COD)Cl_2 (0.113 g, 0.30 mmol) were reacted following a procedure identical to that reported for **11**. An identical workup gave **12** as a white solid in 98% yield (0.225 g). Anal. calcd for $C_{29}H_{27}Cl_2NO_3P_2Pt$: C, 45.6; H, 3.30; N, 1.83. Found: C, 45.20; H, 3.30; N, 1.74. ^{1}H NMR (CD_2Cl_2, δ, ppm): 7.45 (m, 20H, Ph), 5.60 (dd, 1H, *J*=5.6, *J*=7.5 Hz, NH), 2.35 (m, 4H, CH_2CH_2). ^{13}C(^{1}H) NMR (CD_2Cl_2, δ, ppm): 176.1 (d, J_{Cp}=3 Hz, NCO), 164.4 (d, J_{Cp}=5 Hz, COO), 135.2–126.4 (m, Ph), 64.7 (m, NCH), 32.3 (s, NCH*C*H$_2$), 23.1 (s, NCO*C*H$_2$).

5.7. Synthesis of Pt{(S)-Ph,Ph-IndoliNOP}Cl_2 **13**

The ligand **6** (0.2 g, 0.38 mol) and Pt(COD)Cl_2 (0.14 g, 0.38 mmol) were reacted following a procedure identical to that reported for **11**. An identical workup gave **13** as a white solid in 97% yield (0.29 g). IR (KBr, cm^{-1}): ν_{CO} 1779. ^{1}H NMR (CD_2Cl_2, δ, ppm): ^{13}C(^{1}H) NMR (CD_2Cl_2, δ, ppm): 164.9 (s, CO), 135.0–123.4 (m, Ph), 46.7 (s, NCH), 31.5 (d, J_{PP}=35 Hz, NCH*C*H$_2$). ^{31}P(^{1}H) NMR (CD_2Cl_2, δ, ppm): 91.9 (d, J_{PP}=12.8 Hz, J_{PtP}=3933 Hz, PO), 49.7 (d, J_{PP}=12.8 Hz, J_{PtP}=3918 Hz, PN).

5.8. General procedure of hydrogenation

Reactions were carried out in a magnetically stirred and double-walled 50 ml stainless steel reactor by using 6×10^{-3} mol of recrystallized dihydro-2,4-dimethyl-2,3-furandione (**14**) and the M-AMPCP catalyst (substrate:M=200:1) dissolved in 30 ml of distilled dichloromethane. The mixture was charged in the stainless steel autoclave. Hydrogenations were carried out under the specified pressure of H_2 at the given temperature and for the times reported in the table. At the end of the reaction, the solvent was evaporated under reduced pressure and diethyl ether was added to precipitate the complexes. After filtration on silica gel (1×1 cm), diethyl ether was evaporated under vacuum and the products were analyzed by chiral capillary chromatography.

5.9. Procedure for hydroformylation

As for previous sections, all catalytic hydroformylations were performed in a magnetically stirred and double-walled 50 ml stainless steel reactor. In a typical experiment, a solution of the cocatalyst $SnCl_2\cdot2H_2O$ (0.1 mmol) and of the platinum complex (0.1 mmol) in dichloromethane (10 ml) was introduced in the reactor under dinitrogen. Then, styrene (10 mmol) and the internal standard (n-decane)

were introduced. The reactor was sealed, pressurized to 135 atm with $CO:H_2$ (2:3) and heated at 50°C. The reaction was monitored by GLC analysis of aliquots of the reaction mixture. When the reaction was stopped, the reactor was cooled to room temperature and depressurized. The pale-yellow solution was analyzed by GLC to determine the selectivities into hydroformylated (branched and normal) products and ethylbenzene. Pentane was added to the crude reaction mixture to precipitate the catalyst. The resulting solid was filtered off and the filtrate was concentrated under reduced pressure. Diethyl ether (20 ml) was added followed by an excess of $NaBH_4$. After stirring at room temperature for 30 min, water was slowly added to the reaction mixture (10 ml). The alcohols were extracted with diethyl ether and washed with water. After drying with $MgSO_4$ and filtration, the solution was analyzed by chiral capillary chromatography.

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References

1. (a) Takaya, H.; Ohta, T.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993, Chapter 1, p. 1. (b) Noyori, R. In *Asymmetric Catalysis in Organic Synthesis*; Noyori, R., Ed.; Wiley, New York, 1994, Chapter 2, p. 16. (c) Mashima, K.; Kusano, K.-H.; Sato, N.; Matsumura, Y.-I.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T.; Akutagawa, S.; Takaya, H. *J. Org. Chem*. **1994**, *59*, 3064. (d) Brunner, H.; Zettlmeier, W. In *Handbook of Enantioselective Catalysis with Transition Metal Compounds*, Vol. I and II, VCH: Weinheim, 1993.
2. (a) Akutagawa, S. *Appl. Catal*. **1995**, *128*, 171. (b) Noyori, R. *Acta Chem. Scand*. **1996**, *50*, 380.
3. (a) Burk, M. J.; Harper, T. G.; Kalberg, C. S. *J. Am. Chem. Soc*. **1995**, *117*, 4423. (b) Burk, M. J. *J. Am. Chem. Soc*. **1991**, *113*, 8518. (c) Burk, M. J.; Feaster, J. E. *J. Am. Chem. Soc*. **1992**, *114*, 6266. (c) Burk, M. J.; Gross, M. F.; Harper, G. P.; Kalberg, C. S.; Lee, J. R.; Martinez, J. P. *Pure & Appl. Chem*. **1996**, *68*, 37.
4. Schmid, R.; Broger, E.; Cereghetti, M.; Crameri, Y.; Foricher, J.; Lalonde, M.; Müller, R. K.; Scalone, M.; Schoettel, G.; Zutter, U. *Pure & Appl. Chem*. **1996**, *68*, 1.
5. (a) Hayashi, T.; Tanaka, M.; Ogata, I. *Tetrahedron Lett*. **1977**, *3*, 295. (b) Döbler, C.; Kreuzfeld, H.-J.; Krause, H. W.; Michalik, M. *Tetrahedron: Asymmetry* **1993**, *4*, 1833. (c) Cullen, W. R.; Sugi, Y. *Tetrahedron Lett*. **1978**, 1635. (d) Jackson, R.; Thompson, D. J. *J. Organomet. Chem*. **1978**, *159*, C29. (e) Oehme, G.; Paetzold, E.; Selke, R. *J. Mol. Catal*. **1992**, *71*, L1. (f) Bendayan, A.; Masotti, H.; Peiffer, G.; Siv, C. *J. Organomet. Chem*. **1993**, *444*, 41. (g) Kumar, A.; Oehme, G.; Roque, J. P.; Schwarze, M.; Selke, R. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 2197. (h) Yamagishi, T.; Ikeda, S.; Egawa, T.; Yamagushi, M.; Hida *Bull. Chem. Soc. Jpn*. **1990**, *63*, 281. (i) Cesarotti, E.; Chiesa, A.; Ciani, G.; Sironi, A. *J. Organomet. Chem*. **1983**, *250*, 79. (j) Agbossou, F.; Carpentier, J.-F.; Hapiot, F.; Suisse, I.; Mortreux, A. *Coord. Chem. Rev*., in press.
6. (a) Agbossou, F.; Carpentier, J.-F.; Mortreux, A. *Chem. Rev*. **1995**, *95*, 2485. (b) Gladiali, S.; Bayon, J. C.; Claver, C. *Tetrahedron: Asymmetry* **1995**, *6*, 1453. (c) Consiglio, G. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; pp. 273. (d) Nozaki, K.; Sakai, N.; Nanno, T.; Higashijima, T.; Mano, S.; Horiuchi, Takaya, H. *J. Am. Chem. Soc*. **1997**, *119*, 4413 and references therein.
7. (a) Roucoux, A.; Devocelle, M.; Carpentier, J.-F.; Agbossou, F.; Mortreux, A. *Synlett* **1995**, 358 and references cited therein. (b) Agbossou, F.; Carpentier, J.-F.; Hatat, C.; Kokel, N.; Mortreux, A.; Betz, P.; Goddard, R.; Krüger, C. *Organometallics* **1995**, *14*, 2480. (c) Pasquier, C.; Naili, S.; Pelinski, L.; Brocard, J.; Mortreux, A.; Agbossou, F. *Tetrahedron: Asymmetry* **1998**, *9*, 193.
8. (a) Mutez, S.; Mortreux, A.; Petit, F. *Tetrahedron Lett*. **1988**, *29*, 1911. (b) Pottier, Y.; Mortreux, A.; Petit, F. *J. Organomet. Chem*. **1989**, *370*, 333. (c) Naili, S.; Carpentier, J.-F.; Agbossou, F.; Mortreux, A.; Nowogrocki, G.; Wignacourt, J.-P. *Organometallics* **1995**, *14*, 401.
9. (a) Chatt, J.; Venanzi, L. M. *J. Chem. Soc*. **1957**, 4735. (b) Giordano, G.; Crabtree, R. H. *Inorg. Synth*. **1979**, *19*, 218. (c) Lahoz, F. J.; Martin, A.; Esteruelas, M. A.; Sola, E.; Serrano, J. L.; Oro, L. A. *Organometallics* **1991**, *10*, 1794.

10. (a) Schrock, R. R.; Johnson, B. F.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 951. (b) Powell, J.; Shaw, B. L. *J. Chem. Soc. (A)* **1968**, 159.
11. Hapiot, F.; Agbossou, F.; Méliet, C.; Mortreux, A.; Rosair, G. M.; Welch, A. J. *New J. Chem.* **1997**, *21*, 1161.
12. Drew, D.; Doyle, J. R.; Shaver, A. G. *Inorg. Synth.* **1972**, *13*, 47.
13. Naili, S.; Carpentier, J.-F.; Agbossou, F.; Mortreux, A. *New J. Chem.* **1997**, *21*, 919.
14. Karim, A.; Mortreux, A.; Petit, A. *J. Organomet. Chem.* **1986**, *317*, 93.
15. Roucoux, A.; Agbossou, F.; Mortreux, A.; Petit, F. *Tetrahedron: Asymmetry* **1993**, *4*, 2279.
16. Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84*, 577.
17. S. Naili, unpublished results.
18. Ligand **6** has been synthesized according to Ref. 7c.