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# Synthesis, Characterization, and Catalytic Activity of Rh(I) Complexes with (*S*)-*BINAPO*, an Axially Chiral Inducer Capable of Hemilabile P,O-Heterobidentate Coordination

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**Summary.** The reaction of dinuclear rhodium(I) derivatives of the formula $[Rh(DIOL)X]_2$ with the axially chiral phosphinyl phosphane 2-(diphenylphosphinyl)-2′-(diphenylphosphanyl)-1,1′-binaphthalene ((*S*)-*BINAPO*, **1**) leads to the formation of cationic complexes $[(BINAPO)Rh(DIOL)]^+$ where the ligand (*S*)-*BINAPO* consistently displays a P,O-chelate coordination which is mantained even in solvents of fair polarity. The mononuclear rhodium(I) complexes (*S*)-2-diphenylphosphanyl-2′-diphenylphosphinyl-1,1′-binaphthalene-(1,5-cyclooctadiene) rhodium tetrafluoroborate (**3b**) and (*S*)-2-diphenylphosphanyl-2′-diphenylphosphinyl-1,1′-binaphthalene-(1,4-norbornadiene) rhodium tetrafluoroborate (**3c**) with 1,5-cyclooctadiene (*COD*) and 2,5-norbornadiene (*NBD*) as the diolefin were isolated and characterized. Both show a fluxional behaviour in solution which is due to the mobility of the diolefin rather than to a displacement-recombination of the oxygenated arm of the ligand. The mobility of the 1,4-norbornadiene ligand in **3c** is extremely pronounced and the coordinated diolefin flexibility could be frozen only at about 200 K. These complexes are active but poorly stereoselective catalysts for the hydrogenation, hydroboration, and hydroformylation of alkenes.

**Keywords.** Axially chiral auxiliaries; Coordination chemistry; Hemilabile ligands; Homogeneous catalysis; Rhodium complexes.

## Introduction

Mixed ligands with a phosphorus and an oxygen atom as substitutionally inert and labile donors are the most common type of hemilabile ligands reported in the literature [1]. A large variety of transition metal complexes with these ligands have been prepared and extensively studied for their peculiar reactivity, dynamic properties, and catalytic behaviour [2]. A significant part of these investigations has dealt with rhodium as the metal centre because the relevant complexes are of interest for their catalytic activity in several processes.

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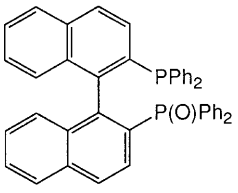
Hemilabile P,O-heterobidentate ligands apparently display a positive effect on the reaction rate and/or on the selectivity of some Rh-catalyzed hydrocarbonylation reactions. The activating properties of simple phosphane oxides in the hydroformylation of olefins by Rh-catalysts have been claimed in several patents [3]. The same holds for aminoalkylphosphane oxides, which perform better than the corresponding amino phosphanes in the hydroformylation of styrene [4]. The carbonylation of methanol proceeds at higher rate when Rh-complexes with diphosphane hemioxides [5] and hemisulfides [6] are used in the place of the conventional Monsanto catalyst.

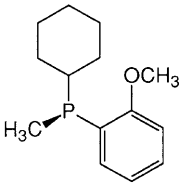
More recently, it has been shown that P,O-heterobidentate Rh(I)-complexes containing phosphane-phosphonates as hemilabile chelating ligands are quite active catalysts in the carbonylation of methanol to acetic acid [7]. Similar complexes are capable to hydroformylate styrene at a reasonable rate even at room temperature and moderate pressures, affording the branched aldehyde with excellent selectivity [8].

The catalytic applications of Rh-complexes of this type are not limited to the activation of carbon monoxide, but include also the activation of other small molecular entities such as hydrogen. For instance, in their extensive investigation on mixed ether-phosphane ligands, *Lindner et al.* have demonstrated the beneficial influence of the presence of a potentially chelating ether moiety on the performance of Rh complexes in the hydrogenation of simple alkenes [9].

In spite of the interesting results obtained in these catalytic reactions, to the best of our knowledge there are no reports on the use of Rh-complexes with chiral P,O-hemilabile ligands in enantioselective catalysis. It has been suggested that the unusual efficiency displayed in the Rh-catalyzed asymmetric hydrogenation of $\alpha,\beta$-unsaturated acids by some *ortho*-alkoxyphenyl substituted monophosphane such as cyclohexyl *o*-anisyl methyl phosphine (*CAMP* [10]) should be due to the temporary coordination of the oxygen donor, but no experimental evidence of chelate coordination to the metal of this type of ligand is yet available.




*BINAPO* (**1**)




*CAMP*

In recent papers we have shown that the axially chiral phosphinyl phosphane *BINAPO* (**1**, Fig. 1) easily available from 2,2′-dihydroxy-1,1′-binaphthalene (*BINOL*) in four steps, is an effective chiral inducer in the asymmetric hydrosilylation of styrene with *in situ* Pd catalysts ($ee > 70\%$) [11] and in the asymmetric hydroformylation of styrene with *in situ* Pt–Sn catalysts ($ee \sim 30\%$) [12].

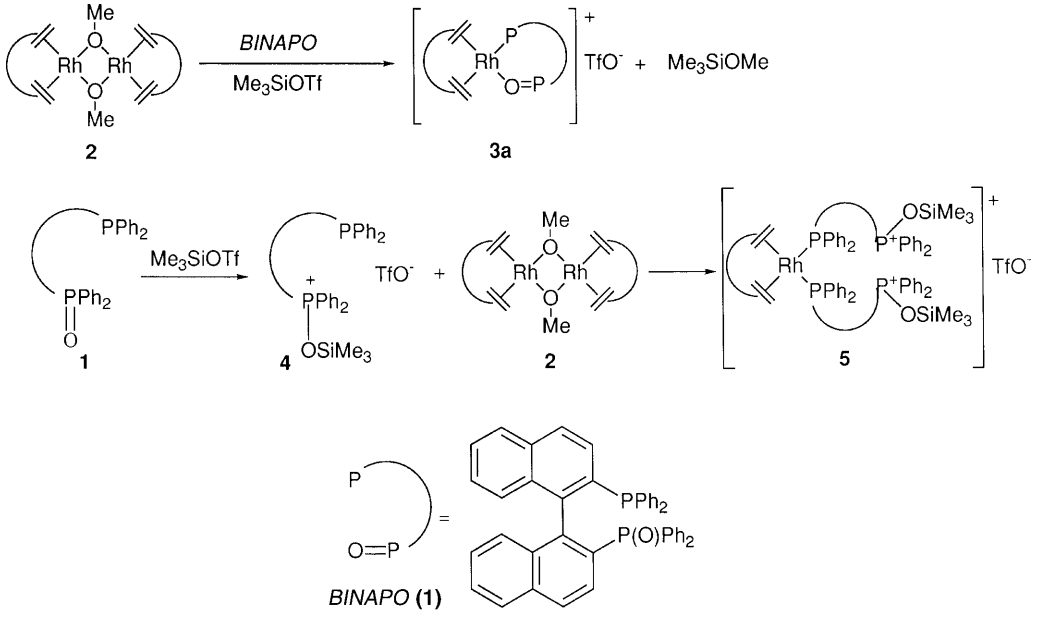
In the second case, we have provided evidences that *BINAPO* behaves as a hemilabile ligand towards the Pt(II) centre. Bidentate coordination affording an eight-membered P,O-chelate ring takes place in the absence of competitive donors, whereas cleavage of the chelate ring through displacement of the oxygenated arm is easily accomplished by donor solvents such as dimethylsulfoxide or by $\pi$-acidic

ligands such as CO [12]. We have also demonstrated that the insertion of tin(II)-chloride in the chelate complex, a crucial step for the production of the active hydroformylation catalyst, proceeds with complete positional selectivity into the Pt–Cl bond *trans* to the oxygen donor, thus affording a single Pt–$SnCl_3$ chelate complex [13].

These results encouraged us to expand the scope of the axially chiral hemilabile ligand (*S*)-*BINAPO* in asymmetric catalysis. Thus, we investigated in some detail the coordination chemistry of *BINAPO* towards Rh(I) centres with the aim to exploit the potential of the relevant complexes in some Rh-catalyzed enantioselective reactions. Here we report the results obtained in the course of this investigation.

## Results and Discussion

The first experiments were performed using [Rh(*COD*)($\mu$-OMe)]$_2$ (**2**; *COD* = 1,5-cyclooctadiene) and racemic *BINAPO* (**1**) as the starting materials and monitoring the progress of the reaction by $^{31}$P NMR spectroscopy. When two molar equivalents of **1** were added to a solution of **2** in $CDCl_3$ at room temperature, no reaction took place, and only the peaks of the free ligand at −14.7 and 27.7 ppm could be observed. The addition of two molar equivalents of trimethylsilyl triflate to this solution caused the immediate displacement of the bridging methoxo groups of **2** as evidenced by a pronounced downfield shift of both phosphorus resonances, resulting in a sharp singlet at 42.9 and a sharp doublet at 19.1 ppm ($J$ = 142.5 Hz). The shift to lower field of both resonances and the presence of a $^1J_{P,Rh}$ coupling demonstrated that chelate coordination of ligand **1** to the rhodium centre occurred through the oxygen donor of the phosphinyl group and the phosphanyl phosphorus affording **3a**.




**Scheme 1**

Complex **3a** did not show any coupling between the metal and the phosphinyl phosphorus. The same occurred in the case of the related derivatives **3b** and **3c** (*vide infra*). The absence of coupling between these nuclides contrasted with the results reported by other authors for phosphane-phosphinyl 5- and 6-membered chelate Rh complexes [5, 7], whereas it is in line with our previous observations on *BINAPO*-Pt complexes [12]. We may wonder whether magnetization exchange between phosphorus and rhodium is suppressed because of the larger size of the chelate ring in **3a**.

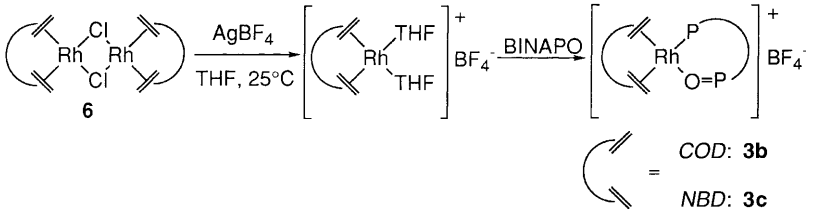
The $^1$H NMR spectrum of this sample showed four fairly broad signals in the range of the olefinic protons and two multiplets in the region of allylic protons which were assigned to the chemically nonequivalent protons of *COD* coordinated to the metal. No free *COD* was noticed in solution.

Trimethylsilyl triflate reacts as well with free *BINAPO*, giving a product featuring two singlets at −0.9 and 52.1 ppm in $^{31}$P NMR. The formation of this triflate adduct, tentatively identified as the trimethylsilyl phosphanyl oxonium triflate **4**, is fast and quantitative at room temperature. Addition of the dinuclear complex **2** to a $CDCl_3$ solution of **4** resulted in the formation of a new complex showing two peaks at 35.1 (d, $J = 169.2$ Hz) and 50.5 ppm (s) in the $^{31}$P NMR. These were attributed to the coordinated phosphanyl and to the uncoordinated phosphanyl oxonium group of complex **5** containing two monodentate ligands **4** with a *cis*-geometry. Apparently, monodentate coordination to the Rh(I) centre of two units of *BINAPO* takes place only when the ligand cannot chelate the metal.

The preparation of the enantiopure complexes **3b** and **3c** was accomplished by reacting the rhodium-*THF* adducts $[Rh(NBD)(THF)_2]^+BF_4^-$ (**6a**, *NBD* = 2,5-norbornadiene) and $Rh(COD)(THF)_2]^+BF_4^-$ (**6b**), respectively, with a stoichiometric amount of (*S*)-*BINAPO*. The required intermediate complexes **6** were prepared *in situ* from the corresponding chloro-bridged dimers and $AgBF_4$ according to Ref. [14]. The isolated yields of the pale yellow products **3b** and **3c** were in the range of 80–85%.

The $^{31}$P NMR spectrum of the isolated complex **3b** gave two sharp phosphorus resonances (42.9 (s) and 19.1 (d, $J = 142.5$ Hz) ppm) in accordance with the *in situ* experiments. Both the aromatic and the olefinic region in the $^1$H NMR (see experimental) clearly showed the presence of a single complex only. The coordinated *COD* gave four broad olefinic signals at 5.3, 4.7, 3.5, and 3.3 ppm and two broad multiplets at 1.8 and 2.2 ppm. Line broadening was indicative of a modest but not negligible fluxional behaviour of the complex at room temperature.

The $^{31}$P NMR spectrum of the norbornadiene complex **3c** showed the same pattern as that of **3b** (39.8 (s) and 16.6 (d, $J = 163.5$ Hz) ppm, sharp peaks). In the




**Scheme 2**

$^1$H NMR in $CDCl_3$, the protons of the norbornadiene moiety bound to rhodium appeared at 1.25, 3.67, 4.0, and 4.12 ppm, each integrating for 2H (see Experimental). The equivalent nuclei were assigned to the methylene bridge, the allylic, and the two pairs of vinylic protons, respectively. In the absence of any dynamic process, the *NBD* ligand bound to the metal should give eight separated resonances because all protons are diastereotopic. The observed proton averaging indicated that complex **3c** is highly fluxional at room temperature.

The chelate coordination of (*S*)-*BINAPO* in **3c** is confirmed in the IR spectrum by the shift of the P=O stretching band to lower wave numbers (from 1201 to 1162 $cm^{-1}$) as a consequence of the slight weakening of the P=O bond.

In acetone-$d_6$, the *NBD* olefinic protons of **3c** gave a single signal at 4.2 ppm, whereas the allylic and the methylene protons experienced only an almost negligible downfield shift. Whether this is due to an accidental isochronicity or to an additional dynamic process averaging all vinylic protons of the coordinated *NBD* could not be definitely clarified. Variable temperature measurements showed that the singlet of the olefinic protons became very broad at 248 K ($\nu_{1/2} \cong 60$ Hz) and practically disappeared in the noise at 233 K. Further lowering of the temperature down to 193 K resulted in the separation of four broad olefinic protons at 2.7, 3.7, 3.95, and 4.7 ppm.

Apparently, the slowing down of the internal motion of the norbornadiene ligand in **3c** at 193 K produced a situation similar to that observed for 1,5-cyclooctadiene in **3b** at 298 K. Taking into consideration the different solvents, from these data the difference in the activation energy for the dynamic processes of the two complexes could be estimated to lie in the range of 25–35 kJ/mol. Such a difference in the fluxionality of the two complexes **3b** and **3c** is exceptionally high and, to the best of our knowledge, it has no precedent in the case of other Rh-diolefin complexes with bidentate/heterobidentate chelating ligands.

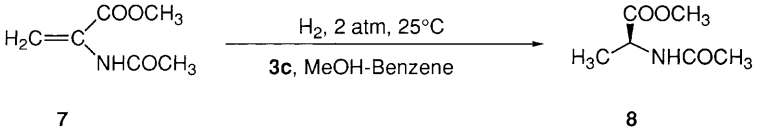
It is as well surprising that the *NBD* derivative appears definitely more fluxional than the *COD* species; in our experience, the opposite situation is more frequently encountered. It must be stressed that the fluxional behaviour noticed for **3b** and **3c** is apparently due to the mobility of the diolefin ligand rather than to a dissociation-recombination process of the oxygenated arm of the *BINAPO* ligand. This conclusion followed from the observation that even at room temperature the protons of the binaphtyl backbone showed no line broadening at all but mantained their very detailed pattern, whereas the diastereotopic protons of *NBD* were experiencing a fast dynamic process which made them equivalent pair by pair. The same occurred to the phosphorus resonances of the *NBD* complex which remained quite sharp over the entire range of temperature investigated, showing no evidence of the presence of traces of an uncoordinated P=O arm.

The preservation of the chelate coordination of **1** even in the presence of a coordinating solvent such as acetone was fairly surprising and contrasted with the behaviour observed for the same ligand in the coordination towards a Pt(II) centre as in the case of (*BINAPO*)$PtCl_2$ [12]. This fact is even more surprising because in Rh derivatives such as **3** the metal centre is located at the junction of both chelate rings, and we would expect that the interplay of the two different rings should result in an increase of the torsional strain to be accommodated in the *bis*-chelate structure.

We may wonder whether the different hemilabile character displayed by **1** towards rhodium and platinum may be ascribed to the different softness of the two metal centres, Pt(II) being probably softer than Rh(I) in spite of the presence of two hard chlorine ligands. As a matter of fact, literature contains several examples of chelating P,O-heterobidentate Rh(I) complexes which have been isolated and characterized, whereas the analogous Pt(II) derivatives are found much less frequently [1, 2].

With these Rh complexes at hand, we initiated a screening of their catalytic activity in some reactions of asymmetric addition to multiple bonds. These catalytic runs were carried out either using the preformed complexes **3b** and **3c** or by adding the required amount of ligand **1** to a suitable dinuclear Rh(I)-diolefin complex with the aim to generate the catalyst *in situ*.

The *NBD* complex **3c** displayed no catalytic activity in the H-transfer reduction of acetophenone from 2-propanol, but it was found to be a good catalyst for the hydrogenation of the carbon-carbon bond of methyl acetamidoacrylate (**7**, Scheme 3). The saturated product **8** (Scheme 3) was isolated in quantitative yield after 5 h of reaction in benzene-MeOH solution under 2 bar of hydrogen at room temperature at a substrate/metal ratio of 100:1. The reaction was basically devoid of stereoselectivity, and the alanine derivative **8** was almost racemic (4% *ee*; (*R*)-configuration).

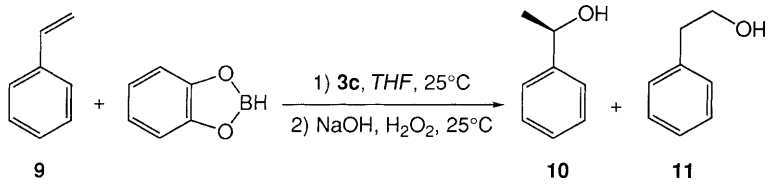



**Scheme 3.** Hydrogenation of methyl $\alpha$-acetamidoacrylate

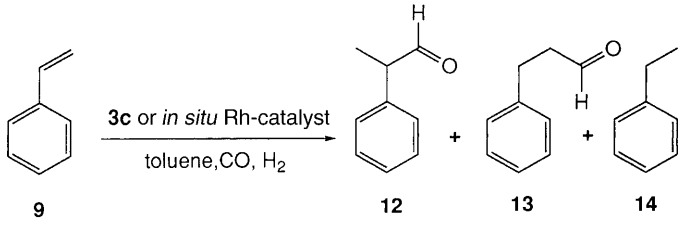
In order to gain some insight into this reaction, a $CDCl_3$ solution of complex **3c** was pressurized with 40 bar of hydrogen in a NMR high-pressure quartz tube, and the progress of the reaction was monitored by $^1H$ and $^{31}P$ NMR. Fast and complete hydrogenation of the coordinated *NBD* took place in a few seconds, and a complex mixture of Rh(III)-hydrides was generated. Even if we could not draw any sound conclusion about the structure of the main hydridic species present in solution from the NMR spectra, two of them were characterized by one doublet ($J = 193.4$ and 177 Hz, respectively) in the shift range of bound phosphanes and by one singlet in the region of a bound phosphane oxide group. This fact lent support to the view that chelate coordination of *BINAPO* can survive even under high hydrogen pressure, at least in part.

The asymmetric hydroboration of styrene (**9**) was run for 8 h at room temperature in *THF* solution using catecholborane as the reagent and **3c** as the catalyst at a substrate-to-metal ratio of 500:1 (Scheme 4). The reaction was analyzed by GC on a chiral phase after an oxidative work-up which converted the borane derivatives into the corresponding carbinols **10** and **11**. The conversion was as low as 22%, and the branched isomer **10** was formed in 73% yield with 40% *ee* ((*S*)-configuration).

The preformed complex **3c** was inspected for its catalytic acitivity in the hydroformylation of styrene, and its behaviour was compared with the catalyst




**Scheme 4.** Hydroboration of styrene




**Scheme 5.** Hydroformylation of styrene

prepared *in situ* by addition of the appropriate amount of ligand **1** to $[Rh(NBD)Cl]_2$ (Scheme 5).

The catalytic runs were carried out in toluene at a substrate-to-metal ratio of 4000:1 (or 2000:1) at 40–100°C under 80 bar of an equimolar mixture of CO and $H_2$. The reaction product consisted of a mixture of branched and linear aldehydes **12** and **13**. The amount of the hydrogenated product **14** was always below 1%. The most significant results are collected in Table 1.

The catalytic activity of the preformed complex **3c** was quite high, and quantitative conversions of styrene were obtained at 40°C in 15 h at a substrate-to-metal ratio of 2000 (Table 1, entry 6). The reaction rate was lower but still high when acetone was used as the solvent (Table 1, entry 7). These rates compare favourably with those observed in the hydroformylation of styrene with bidentate diphosphanes and diphosphites [15] or other chelating phosphorus donor ligands such as the mixed phosphane-phosphite *BINAPHOS* [16].

**Table 1.** Hydroformylation of Styrene by Rhodium/*BINAPO* Catalysts (2 $cm^3$ of styrene in 6 $cm^3$ of toluene; substrate:metal = 4000:1; initial pressure: 80 bar; $CO:H_2 = 1:1$)

| Entry | *T*/C° | *L*/Rh | *t*/h | Conv./% | Branched/% (*ee*) |
|---|---|---|---|---|---|
| 1[a] | 100 | 1 | 5 | 95 | 76 |
| 2[a] | 100 | 2 | 2 | 67 | 65 |
| 3[b] | 80 | 1.5 | 6 | 95 | 76 |
| 4[b] | 80 | 2 | 6 | 69 | 77 |
| 5[b] | 60 | 1.5 | 6 | 36 | 93 |
| 6[c] | 40 | 1 | 15 | >99 | 92 (6%, *R*) |
| 7[c,d] | 40 | 1 | 15 | 68 | 96 (4%, *R*) |

[a] Racemic *BINAPO* in the presence of $[Rh(NBD)Cl]_2$; [b] (*S*)-*BINAPO* (75% *ee*) in the presence of $[Rh(NBD)Cl]_2$; the chiral aldehyde was almost racemic; [c] preformed $[Rh(NBD)(S)\text{-}BINAPO]^+BF_4^-$ (**3c**) used as catalyst; substrate:metal = 2000:1; [d] solvent: acetone

Taking into account the temperatures and the higher substrate-to-metal loading (4000:1), the catalytic activity displayed by the *in situ* catalysts was definitely lower than that observed for **3c** (Table 1, entries 1–5). This was particularly evident in runs 1 and 2, where racemic rather than enantiopure *BINAPO* was used as the ligand. Apparently, ligands of different enantiomeric composition can produce catalysts of different activity. This may be the case if Rh complexes containing two *BINAPO* molecules as monodentate ligands play some role in the catalysis of the hydroformylation.

Increasing the ligand-to-metal ratio resulted in a further decrease of the reaction rate (compare entries 1/2 and 3/4 in Table 1) and in a lower selectivity for the branched aldehyde (compare entries 1/2). This result may as well point towards an active involvement in the catalysis of Rh-*BINAPO* species with two units of ligand for each metal atom.

As usual for Rh-catalyzed hydroformylation, the branched selectivity improved substantially upon lowering the reaction temperature. At 60°C, the ratio of the chiral aldehyde **12** was as high as 93% (Table 1, entry 5) and improved up to 96% at 40°C when the reaction was run in acetone (Table 1, entry 7).

In the enantioselective hydroformylation, the *in situ* catalysts prepared with a sample of (*S*)-*BINAPO* of 75% enantiomeric purity produced a practically racemic branched aldehyde. As these experiments were run at fairly high temperatures (Table 1, entries 3–5), with the aim to minimize the extent of racemization of the chiral aldehyde **12** in the course of the reaction, the following tests using the preformed complex **3c** containing the enantiopure (*S*)-ligand were run for 15 h at 40°C. Even under these mild conditions, however, the stereoselectivity of the reaction was low (*ee* $< 10\%$). Since in our experience under these conditions no racemization of **12** took place in the hydroformylation of styrene with other Rh-based catalysts, we can confidently assume that the same has occurred in the present case. This means that these low *ee*s reflect the real enantiodiscrimination ability of the catalyst and that they are not the consequence of stereochemical transformations which follow after the formation of the chiral aldehyde **12**.

In conclusion, in the asymmetric hydroformylation of styrene the catalytic system (*S*)-*BINAPO*/Rh is significantly more active but less stereoselective than the *BINAP*-based rhodium catalyst under similar conditions [17]. This fact may indicate that the catalytic species originating from (*S*)-*BINAPO* and (*S*)-*BINAP* may involve a different type of binding of the chiral ligand at the metal centre.

Together with the previous observations, this result provides further support that Rh complexes containing two *BINAPO* molecules as monodentate ligands may play an active role in the catalysis of the hydroformylation of styrene. Unfortunately, our attempts aiming at trapping such a species under CO pressure failed as the $^{31}$P NMR spectra recorded under CO pressure led to inconclusive results.

## *Conclusions*

It has been already shown in our previous work that the binaphthyl phosphinyl phosphane **1** shows a sharp preference for P,O-chelate coordination towards Pd(II) and Pt(II) centres [11, 12]. This tendency is even more pronounced in the case of

Rh(I) derivatives, which by reaction with **1** produce the chelate species **3** as the sole isolable products.

Unlike in the platinum case, no evidence for monodentate coordination of two equivalents of **1** to the Rh-centre through the phosphanyl donor was noted at any intermediate stage of this reaction. On the contrary, it seems that for this process to occur the reaction path leading to chelate coordination must be suppressed, as was shown in the case of the oxonium triflate **4**.

The hemilabile character of **1** towards rhodium is hard to be evidenced: the oxygenated arm of the ligand is not displaced by acetone, and the chelate coordination is apparently preserved even after the oxidative addition of hydrogen. The results obtained in the asymmetric catalytic reactions, however, are better explained if one assumes that the chelate structure is not preserved and that Rh complexes containing two monodentate *BINAPO* molecules are actively involved in catalysis.

Although we have no direct evidence that displacement of the oxygenated arm of *BINAPO* occurs during the hydroformylation, this possibility finds some support from the results observed which are more comfortably assessed if one assumes that two catalytic species, each one containing two monohapto *BINAPO* units around the Rh centre, are present during the reaction. The modest stereoselections, the significant differences of the reaction rates recorded in changing from the racemic to the enantiopure *BINAPO*-based catalyst, and the reversal of handedness observed with (*S*)-*BINAPO* as compared to (*S*)-*BINAP* [17] are all factors lending support to this view.

## Experimental

The $^{1}H$ and $^{31}P$ NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400 and 161.9 MHz. The $^{31}P$ chemical shifts are reported relative to external 85% $H_3PO_4$. The samples from the catalytic runs were analyzed with a Hewlet Packard 5890A gas chromatograph fitted with a 25 m capillary column coated with diethyl *tert*-butylsilyl-$\beta$-cyclodextrin PS 086 (i.d. 0.25 mm) from MEGA (Legnano, Italia) using He as the carrier (head pressure 60 kPa, split ratio 100). The elemental analyses were performed on a 1108 Carlo Erba apparatus. They agreed favourably with the calculated values (C,H). The optical rotation of 2-phenylpropanal was measured in benzene solution on a Perkin Elmer 241 polarimeter. (*S*)-*BINAPO* was prepared as described in Ref. [11].

*(S)-2-Diphenylphosphanyl-2′-diphenylphosphinyl-1,1′-binaphthalene(1,5-cyclooctadiene) rhodium tetrafluoroborate* (**3b**; $C_{52}H_{44}OBF_4P_2Rh$)

To a solution of 200 mg $[Rh(COD)Cl]_2$ (0.4 mmol) in 10 $cm^3$ of anhydrous *THF* under argon, 156 mg $AgBF_4$ (0.8 mmol) were added. After stirring for 1 h, the precipitate was filtered through celite. To the yellow solution of the rhodium-*THF* adduct, 510 mg (*S*)-*BINAPO* (0.8 mmol) were added. The colour of the solution changed to orange immediately. After stirring for 2 h the solvent was evaporated, and the resulting complex **3b** was obtained as orange solid.

Yield: 600 mg (80%); $^{1}H$ NMR ($CDCl_3$, $\delta$, 400 MHz): 1.8 (m, 4H), 2.2 (m, 4H), 3.3 (m, 1H), 3.5 (m, 1H), 4.7 (m, 1H), 5.3 (m, 1H), 6.5 (d, 1H), 6.7 (m, 5H), 6.9 (m, 7H), 7.1 (m, 1H), 7.35 (t, 1H), 7.6 (m, 11H), 7.85 (m, 2H), 8.05 (m, 2H), 8.3 (d, 1H) ppm; $^{31}P$ NMR ($CDCl_3$, $\delta$, 161.9 MHz): 42.9 (s), 19.1 (d, $^{1}J(^{103}Rh, ^{31}P) = 142.5$ Hz) ppm.

*(S)-2-Diphenylphosphanyl-2′-diphenylphosphinyl-1,1′-binaphthalene-(2,5-norbornadiene) rhodium tetrafluoroborate* (**3c**; $C_{51}H_{40}OBF_4P_2Rh$)

Following the same procedure as reported above, $[Rh(NBD)Cl]_2$ gave **3c** as an orange solid.

Yield: 590 mg (80%); $^1$H NMR ($CDCl_3$, $\delta$, 400 MHz): 1.25 (s, 2H), 3.67 (s, 2H), 4.0 (s, 2H), 4.12 (s, 2H), 6.2 (d, 1H), 6.4 (m, 2H), 6.6 (m, 4H), 6.8 (t, 1H), 6.9 (m, 4H), 7.1 (m, 2H), 7.3 (m, 2H), 7.45 (m, 2H), 7.6 (m, 8H), 7.8 (m, 2H), 8.1 (d, 1H), 8.3 (dd, 2H), 8.5 (d, 1H) ppm; $^{31}$P NMR ($CDCl_3$, $\delta$, 161.9 MHz): 39.8 (s), 16.6 (d, $^1J(^{103}Rh, ^{31}P) = 163.5$ Hz) ppm; IR (KBr): $\nu = 1162$ ($\nu$(P=O)) cm$^{-1}$.

*Hydroformylation of styrene*

In a typical experiment, 0.005 mmol of $[Rh(NBD)Cl]_2$ and 0.01 mmol of **1** were dissolved in 6 cm$^3$ toluene in a *Schlenk* tube under Ar, and 2 cm$^3$ styrene were added. The solution was transferred into a 100 cm$^3$ autoclave and pressurized by a $CO:H_2 = 1:1$ mixture (80 bar). The reaction mixture was thermostatted in an oil bath at the required temperature and agitated by a magnetic stirrer. At the end of the reaction the mixture was cooled to room temperature, vented, and immediately analyzed. Conversions as well as chemo-, regio-, and enantio selectivities were determined by means of GC analysis (initial temperature: 60°C, heating rate: 2°C/min, final temperature: 150°C; retention times: branched aldehyde 21 min (*S*) 21.5 min (*R*); linear aldehyde 26.7 min).

*Catalytic hydroboration of styrene*

Styrene (0.172 cm$^3$, 1.5 mmol) was added to a solution of 2.9 mg **3c** (0.003 mmol, 0.2 mol%) in 2 cm$^3$ *THF* under Ar. The solution was stirred for 5 min; then, 0.16 cm$^3$ catecholborane (1.5 mmol) was added. The mixture was stirred at room temperature for 12 h and then quenched with 0.4 cm$^3$ EtOH. 2 cm$^3$ NaOH (2 *M* in $H_2O$) and 0.2 cm$^3$ $H_2O_2$ were added; the mixture was stirred for 10 h, extracted with $Et_2O$, washed (2 *M* NaOH, $H_2O$, brine), and dried over $Na_2SO_4$. Conversions, regioselectivity and *ee* were determined by GC analysis at 105°C (retention times: 3.13 min substrate), 13.8 min ((*R*)-1-phenylethanol), 14.8 min ((S)-1-phenylethanol), 14.1 min (2-phenylethanol)).

*Asymmetric hydrogenation of methyl acetamidoacrylate*

Methyl acetamidoacrylate (143 mg, 1 mmol) and 9.5 mg **3c** (0.01 mmol) were placed in a pressure bottle. The flask was purged with $N_2$, 10 cm$^3$ solvent (benzene/methanol 1:1) were added by means of a syringe through a septum, and the bottle was connected to the $H_2$ reservoir of a *Parr* mid-pressure apparatus. $N_2$ was evacuated, and the vessel was purged twice with $H_2$. Then $H_2$ (2 bar) was applied, and the reaction mixture was shaken for 16 h at room temperature. Conversion and *ee* of methyl alaninate have been determined by GC analysis at 95°C using He (60 kpa) as the carrier (retention times: substrate, 13.7 min; (*S*)-methyl alaninate, 14.8 min; (*R*)-methyl alaninate, 19.1 min).

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