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Synthesis, characterization and use in enantioselective hydroformylation of (BINAPO)$PtCl_2$ (BINAPO = 2-diphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthalene), the first chiral catalyst with an atropisomeric hemilabile P,O-heterodonor ligand

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Abstract

Platinum(II) complexes with the axially chiral phosphinyl phosphine (*S*)-BINAPO (**1**) have been prepared and their behaviour in solution has been studied by ^{31}P-NMR spectroscopy. Reaction of $PtCl_2(PhCN)_2$ with **1** in benzene leads to the isolation of a neutral complex, **4**, which maintains the P,O-chelate coordination of the ligand even in solvents of low polarity. The hemilabile character of the ligand is apparent from the reactions with DMSO and with carbon monoxide which promote the cleavage of the chelate ring of **4** through displacement of the oxygenated arm. Insertion of tin(II) chloride into the Pt–Cl bond takes readily place at room temperature affording only one of the possible trichlorostannato derivatives (**6**) with complete selectivity. In the presence of $SnCl_2$, the platinum complex **4** originates a catalyst of remarkable regioselectivity which, in the hydroformylation of styrene, is able to produce in up to 30% e.e. the branched aldehyde as the prevalent product.

Keywords: Platinum complexes; Pt–Sn hydroformylation catalysts; Hemilabile coordination; Atropisomeric heterodonor ligands

1. Introduction

Bidentate heterodonor ligands, in which a soft phosphorus is flanked by a hard oxygen, albeit able of chelate binding to the metal, may easily undergo displacement of the oxygen donor providing a free coordination site. Due to this peculiar aptitude, these hemilabile ligands have found several useful applications in the design of those homogenous catalysts where dissociation–recombination processes are presumed to play an important role in the stabilization (or activation) of the catalysts.

This feature appears of particular significance in some metal-catalyzed carbonylation reac-

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tions. Several patents claim the activating properties of simple phosphine oxides in rhodium-catalyzed hydroformylation [1–5]. Rhodium complexes with diphosphine hemioxides [6] and hemisulfides [7] have been found more active than the classical Monsato catalyst in the carbonylation of methanol. Aminoalkylphosphine oxides are better activators than the relevant phosphines in the rhodium-catalyzed hydroformylation of styrene [8].

In a recent paper, we have reported the preparation of 2-diphenylphosphino-2′-diphenylphosphinyl-1,1′-binapthalene (BINAPO, **1**), the first example of a potentially hemilabile ligand with axial chirality [9]. This compound has been obtained from 1,1′-binaphtol (BINOL) through a four-step procedure involving the Pd-catalyzed sequential substitution of two homotopic triflate groups by diphenylphosphine oxide and is an effective chiral inducer in the Pd-catalyzed asymmetric hydrosilylation of styrene (e.e. > 70%). It acts as a bidentate ligand towards Pd(II) centres, affording P,O-chelate complexes which have been isolated in the solid state and are fairly stable even in solution.

These promising figures stimulated us to investigate the catalytic activity of the corresponding trichlorostannato platinum(II) complex in the hydrofomylation of styrene. In this paper, we report the results of this investigation and some aspects of the coordination chemistry of ligand **1** towards platinum(II) which are significant as to the catalytic process.

2. Experimental

2.1. General methods

The ^{1}H- and ^{31}P-NMR spectra were recorded in $CDCl_3$ on a Varian Unity 300 spectrometer at 300 and 121.4 MHz, respectively. The ^{31}P chemical shifts were reported relative to H_3PO_4. The samples from the catalytic runs were analysed with a Hewlett Packard 5890A gas chromatograph fitted with a 30 m cyclodex-β capillary column (J&W Scientific). The elemental analyses were performed on a 1108 Carlo Erba apparatus. The optical rotation of 2-phenylpropanal was measured in benzene solution on a Perkin Elmer 241 polarimeter.

2.2. Reagents

Commercial chemical reagents were used as received and solvents were dried by standard procedures and stored over molecular sieves under inert atmosphere. Styrene was freshly distilled before use. (*S*)-BINAPO (**1**) [9] and $[PtCl_2(PhCN)_2]$ [10] were synthesized as previously reported.

2.3. Synthesis of $[PtCl_2(\mathbf{1})]$

Some 0.25 mmol (118 mg) of $[PtCl_2(PhCN)_2]$ was dissolved in 12 ml refluxing benzene, and a solution of 0.25 mmol (159.7 mg) of **1** in 3 ml benzene was added. The mixture was refluxed for 2.5 h. A pale yellow powder-like solid was formed, which after cooling the mixture to room temperature, was filtered off. The product was washed with cold benzene and dried in vacuum.

Analysis calculated for $C_{44}H_{32}OCl_2P_2Pt$ (MW = 904.67): C, 58.42; H, 3.57; Cl, 7.84. Found: C, 58.30; H, 3.24; Cl, 8.08. Yield: 89%. The product was characterized by NMR, IR and Raman spectroscopy (Table 1).

Table 1
Selected NMR and IR data of **1** and its platinum complexes

	δ(P) [ppm]	δ(PO) [ppm]	^{1}J(Pt,P) [Hz]	ν(P=O) [cm^{-1}]	ν(Pt–Cl) [cm^{-1}]
1	−14.7	27.8		1201	
3	9.2[d]	26.5	ca. 3600		
4	7.5	52.6	3883	1161	351[a], 283[b]
5a	27.1	26.4	2640		
5b	26.0	26.5	2625		
6	16.7	48.3	3812[c]		
7	13.0[d]	26.7	ca. 3230		
8	22.7	25.3	3750		

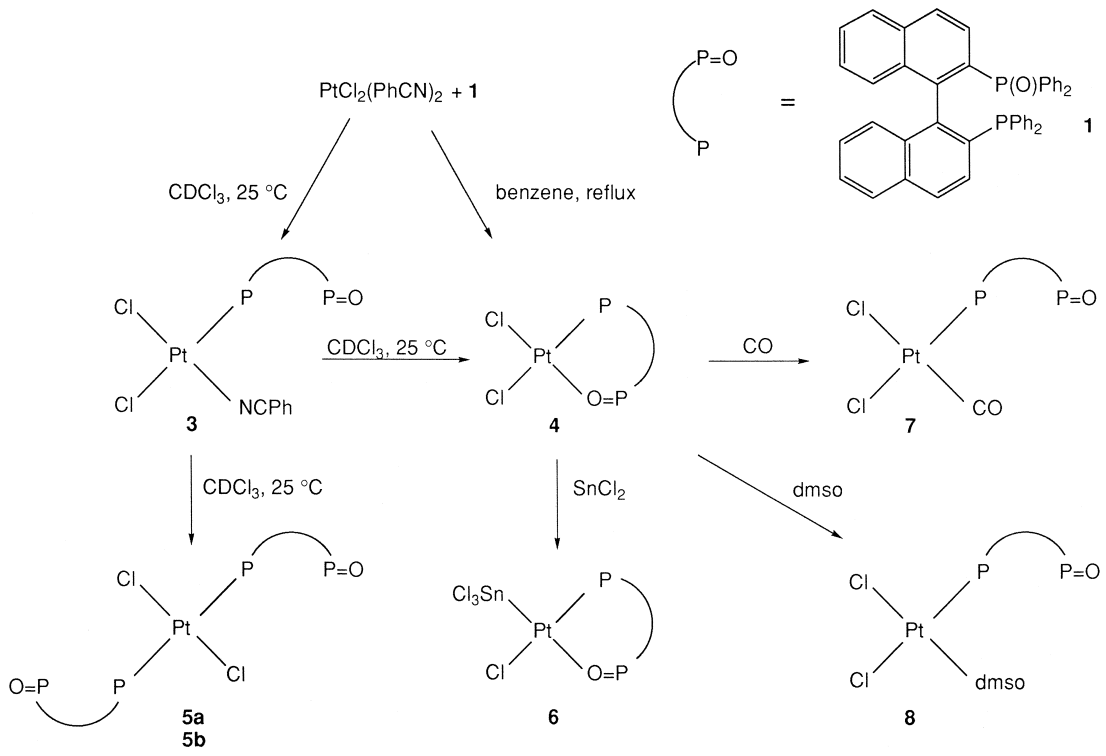
[a] Cl *trans* to P=O.
[b] Cl *trans* to P.
[c] P *cis* to $SnCl_3$ ($^{2}J(^{117,119}Sn,^{31}P) = 185$ Hz, ^{117}Sn and ^{119}Sn satellites coincide).
[d] Broad signal.

2.4. Hydroformylation experiments

In a typical experiment, a solution of 0.025 mmol of [$PtCl_2$(**1**)] and 0.05 mmol of $SnCl_2$ in 30 ml toluene containing 50 mmol of styrene was transferred under argon into a 150 ml stainless steel autoclave. The reaction vessel was pressurised to 80 bars total pressure (CO/H_2 = 1/1) and placed in an oil bath and the mixture was stirred with a magnetic stirrer. The pressure was monitored throughout the reaction. After cooling and venting, the solution was removed and conversion and composition of the reaction products were determined by GC (110°C). The enantiomer excess was determined in the same way on the corresponding carboxylic acids obtained by $KMnO_4$ oxidation [11] of a sample of the crude reaction mixture. Retention times (from 100° to 170° at 5°C/min) of (*S*)- and (*R*)-2-phenylpropanoic acid are 15.9 and 16.2 min, respectively.

3. Results and discussion

The synthesis of the [$PtCl_2$(**1**)] complex was carried out by reacting the appropriate amount of [$PtCl_2(PhCN)_2]_2$ with one equivalent of the racemic or enantiopure ((*S*)-configuration) ligand **1** in refluxing benzene (Scheme 1). It is clearly apparent from the IR and ^{31}P-NMR spectra of the isolated complex **4** that both ancillary benzonitrile ligands have been displaced and that P,O-bidentate coordination of the ligand **1** to the metal affording the neutral P,O-chelate complex **4** has taken place. The most significant spectroscopic data of complex **4** are collected in Table 1.



Scheme 1.

The 22.2 and 24.8 ppm downfield shifts observed in the ^{31}P-NMR for the PPh_2 and $P(O)Ph_2$ of complex **4** with respect to the free ligand provides a strong indication that both donor arms of the ligand **1** are bound to the metal. Further support comes from presence of $^1J(^{195}Pt,^{31}P) = 3883$ Hz, which indicates that the PPh_2 group is directly bound to platinum and occupies a position *trans* to a chloro ligand. On the contrary, the phosphinyl phosphorus does not exhibit any coupling with the metal. This fact is in keeping with previous observations that magnetization exchange between phosphorus and platinum is suppressed when an oxygen is interposed [12].

IR and Raman spectra are consistent with the chelate coordination of the ligand. Upon complexation the P=O stretching band undergoes a shift from 1201 to 1161 cm^{-1} as a consequence of the slight weakening of the P=O bond [6]. In the far IR region, the two separate bands at 351 and 283 cm^{-1} can be attributed to the Pt–Cl *trans* to oxygen and phosphorus, respectively.

The reaction of **2** with the enantiopure ligand (*S*)-**1** in $CDCl_3$ solution, monitored by ^{31}P-NMR, showed that in the early stages of the reaction, the concentration of the chelate complex **4** is quite low and that the prevailing products are two different species which contain either one or two moles of ligand **1** bound to the metal through the PPh_2 donor in a monodentate fashion.

At the very beginning, the main product shows a broad peak at 9.2 ppm with Pt-satellites (1–4–1 pattern; $^1J(^{195}Pt,^{31}P) \approx 3.600$ Hz) and a sharp singlet at 26.5 ppm, attributable to a bound PPh_2 and to a free $P(O)Ph_2$ groups, respectively. This NMR pattern suggests for this product the structure **3**, corresponding to the substitution of one ancillary PhCN by one equivalent of monodentate ligand **1**. The broadening of the first signal is most probably the consequence of the fast exchange experienced by the benzonitrile ligand of **3**.

The concentration of compound **3** decreases steadily at room temperature and within 1 h, it disappears completely, being mainly converted into the chelate complex **4**. At the same time another species is built up in solution at a lower rate and this one, at the end of the transformation, accounts for about the 30% of the whole product. In the ^{31}P-NMR, this complex shows two peaks at 27.1 and 26.4 ppm. It is readily apparent from these chemical shifts that only the PPh2 group of the ligand **1** is coordinated to the metal, while the phosphinyl group is not bound. The value of the $^1J(^{195}Pt,^{31}P) = 2640$ Hz indicates that the phosphorus of the PPh_2 group is opposed by a donor of strong *trans* influence. From these data this product can be attributed the structure **5a**, where two moles of ligand (*S*)-**1** are bound to the platinum with a *trans* geometry.

This attribution is confirmed by the result observed when the NMR experiment was performed on the same Pt-precursor using the ligand **1** in racemic form. In this case, one more species with chemical shifts and coupling constants quite similar to **5a** is present in solution (Table 1). This is due to the formation of the *meso*-complex **5b**, which contains two moles of ligand of opposite chiral notation. Notably, the coordination to platinum of the second unit of BINAPO takes place with a pronounced chiral recognition which leads to the preferential formation of the *meso*-compound **5b** with 70% diastereoselectivity.

In view of its use as hydroformylation catalyst, the reactivity of the chelate complex **4** towards tin(II) chloride and carbon monoxide in $CDCl_3$ solution has been followed by ^{31}P-NMR spectroscopy. At 25°C, complex **4** undergoes a smooth carbene-like insertion of $SnCl_2$, affording a poorly soluble derivative. The presence of the trichlorostannato ligand in complex **6** is evidenced by the characteristic tin satellites of the peak of the bound PPh_2 phosphorus. The value of these coupling constants is about 200 Hz and, as usual for $^2J_{cis}$(Sn,P), they are coincident for the ^{117}Sn and ^{119}Sn nuclides [13]. This provides convincing evidence that the insertion of $SnCl_2$ in **4** has occurred with complete posi-

tional selectivity into the Pt–Cl bond *trans* to the oxygen donor, leading exclusively to **6** (Scheme 1). The preference of the trichlorostannato ligand for the position *trans* to the harder donor is not unprecedented and seems to configure a general trend for the insertion of tin chloride into inequivalent Pt–Cl bonds [14].

When complex **4** is treated with carbon monoxide under pressure (25 bars) at 25°C in a high-pressure NMR tube, a complete and fast displacement of the P=O fragment takes place and some ligand (about 10%) is completely released from the metal. The ^{31}P-NMR shows a new peak at 13.0 ppm, $^{1}J(^{195}\text{Pt},^{31}\text{P}) = 3230$ Hz, attributable to the still bound PPh_2 arm. Under 25 bars of CO, this is rather broad ($\Delta\nu_{1/2} \approx 220$ Hz), probably due to the fast exchange of a carbonyl ligand in *cis* position, but becomes sharper when the pressure is reduced to 1 bar ($\Delta\nu_{1/2} \approx 120$ Hz). Even in these mild conditions, the phosphinyl oxygen is almost completely displaced, whereas no release of free ligand **1** is noticed. These NMR data and the presence in the IR spectrum of carbonyl stretching bands at 2108, 2022 and 1998 cm^{-1}, suggest that under CO pressure, the carbonyl complex **7** and some undefined dinuclear carbonyl complexes should be contextually present in solution (Scheme 1).

A similar set of experiments were run on complex **6**, but they led to inconclusive results, probably due to the low solubility of this derivative.

Easy displacement of the oxygenated arm of the ligand **1** resulting in the opening of the chelate ring is observed also when complex **4** is dissolved in solvent of high donicity such as DMSO. This results in the formation of a new complex (Table 1), most probably **8** (Scheme 1), where one DMSO has displaced the oxygen donor taking up the position *cis* to the PPh_2 group. Taken together with the previous results with carbon monoxide, this fact gives a measure of the lability of the P=O donor in ligand **1**.

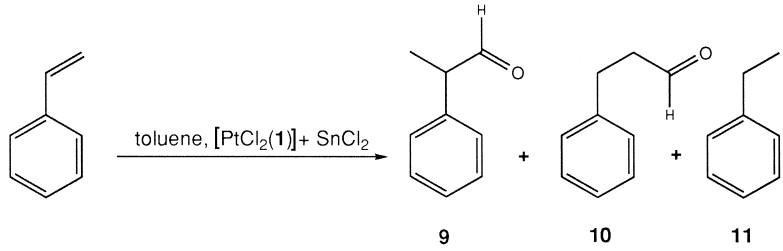
3.1. Catalytic hydroformylation of styrene promoted by $PtCl_2$(BINAPO) complex

The preformed complex **4** has been inspected for its catalytic activity in the hydroformylation of styrene (Scheme 2).

The catalytic reactions were run in toluene at a substrate-to-metal ratio 2000:1 in the presence of two equivalents of $SnCl_2$ as a promoter, at 70–100°C under 80–90 bars of an equimolar mixture of CO and H_2. The reaction product consisted of a mixture of branched and linear aldehydes, **9** and **10**, respectively, and some ethylbenzene **11** arising from hydrogenation of the substrate. The most significant results are collected in Table 2.

The catalytic activity of complex **4**, either alone or in the presence of additional free ligand **1**, is fairly low as compared to similar platinum-derived catalysts containing chelating diphosphines, such as BINAP [15], as chiral modifiers. Several hours of reaction were required to attain moderate conversions. The activity of the catalyst improved slightly after addition of one more equivalent of free ligand, but remained modest.

The chemoselectivity of the reaction was surely more satisfactory since the amount of ethylbenzene ranged between 2 and 15%, which



Scheme 2.

Table 2
Hydroformylation of styrene in the presence of **4** and $SnCl_2$ as in situ catalyst[a]

Run	Catalyst	Reaction time [h]	Temp. [°C]	Conv.[b] [%]	R_C^c [%]	R_R^d [%]
1	**4** + $SnCl_2$	22	90	6	82	59
2	**4** + **1** + $SnCl_2$	21	100	34	86	53
3	**4** + **1** + $SnCl_2$	43	100	57	85	52
4	**4** + $SnCl_2$[e]	21	100	9	90	53
5	$PtCl_2$(binap) + $SnCl_2$	7	100	21	93	41
6	$PtCl_2(PPh_3)_2$ + $SnCl_2$	23	100	51	94	41

[a] Reaction conditions: 0.025 mmol Pt-complex; 0.05 mmol $SnCl_2$; 50 mmol styrene; solvent: toluene; $p(CO) = p(H_2) = 40$ bar.
[b] mmol product/mmol initial substrate × 100.
[c] Chemoselectivity towards hydroformylation: **(9 + 10)**/**(9 + 10 + 11)** × 100.
[d] Regioselectivity towards branched aldehyde: **9**/**(9 + 10)** × 100.
[e] $p(CO) = 80$ bar; $p(H_2) = 40$ bar.

is quite acceptable and even better than usual for a platinum-catalyzed hydroformylation reaction. The most interesting feature of this catalyst, however, is related to the regioselectivity of the reaction. The branched isomer in this case is formed in an amount definitely higher than with the usual mono- and bidentate phosphorus ligands. In all but one of the experiments, the aldehyde **9** was, albeit for a neck, the main product of the reaction and its share was as high as 60% in the best run. This result is notable since a prevalence of the branched over the linear aldehyde has been never noticed in the hydroformylation of styrene with platinum–phosphine catalysts [16,17]. This is apparently the first time that a reversal of the usual selectivity is obtained in this reaction without making use of dibenzophosphole or structurally related derivatives as supporting ligands for the Pt-catalyst [18].

The enantioselective hydroformylation experiments have been carried out using the preformed complex **4** containing the enantiopure (*S*)-ligand in the presence of an additional equivalent of free (*S*)-**1** and two equivalents of $SnCl_2$ (Table 3). In a comparative experiment, run in the conditions of entry 3 of Table 1 with the enantiopure catalyst, a slight decrease of the branched selectivity was noticed (47% vs. 52%) and the e.e. was as low as 8% (*R*-configuration). In the aim to minimize the extent of racemization of the chiral aldehyde **9** in the course of the reaction, the experiments were run at a styrene-to-metal ratio as low as 200:1.

This resulted in a substantial reduction of the reaction times necessary for attaining a reasonable conversion and in improved chemoselectivities as the amount of ethylbenzene was limited to 2–4%. The branched isomer accounted for up to 60% of the aldehydes in the experiment run at 60°C, whereas, only 40% was obtained at 85°C. This latter value is definitely lower than the one observed under comparable conditions but at a lower catalyst concentration (Table 2, entry 2). It is our feeling that this decrease can be hardly ascribed solely to the difference of metal concentration, but that it may probably arise from the presence of two different diastereomeric catalytic species, each one featur-

Table 3
Asymmetric hydroformylation of styrene in the presence of (*S*)-**4** and $SnCl_2$ as in situ catalyst[a]

Run	Catalyst	*T* [°C]	Conv.[b] [%]	R_C^c [%]	R_R^d [%]	e.e.[e] [%]
1	(*S*)-**4** + **1** + $SnCl_2$	85	100	96	40	30
2	(*S*)-**4** + **1** + $SnCl_2$	60	59	98	60	28

[a] Reaction conditions: 0.025 mmol Pt-complex; 0.025 mmol (*S*)-**4**; 0.05 mmol $SnCl_2$; 5 mmol styrene; solvent: benzene 6 ml; $p(CO) = p(H_2) = 45$ bar; reaction time: 24 h.
[b] mmol product/mmol initial substrate × 100.
[c] Chemoselectivity towards hydroformylation: **(9 + 10)**/**(9 + 10 + 11)** × 100.
[d] Regioselectivity towards branched aldehyde: **9**/**(9 + 10)** × 100.
[e] In both cases, the configuration of the prevailing enantiomer is (*R*).

ing its own regoiselectivity, when using the racemic ligand **1**. This may provide a hint into the real structure of the catalyst(s) active under our conditions.

The prevailing enantiomer of the branched aldehyde is (*R*)-configured and its e.e. is modest (not higher than 30%) and poorly dependent on the reaction temperature. This means that the direction of the asymmetric induction is opposite to the one observed in the asymmetric hydroformylation of styrene with BINAP-based platinum catalysts under similar conditions [15] and that our catalytic system is significantly less stereoselective. Both these facts provide support to the assumption that the catalytic species originated from (*S*)-BINAPO and (*S*)-BINAP may involve a different type of binding of the chiral ligand at the metal centre.

4. Conclusions

It has been already shown previously that the binaphthyl phosphinyl phosphine **1** shows a sharp preference for P,O-chelate coordination to palladium(II) centres [9]. The same apparently occurs in the case of platinum(II) derivatives which, by reaction with **1**, produce the chelate species **4** as the main or the exclusive product. The hemilabile character of the ligand in complex **4** is, however, evident from the reactions with carbon monoxide and dmso, which readily afford products **7** and **8** where the entering ligand has taken up the position *cis* to the phosphorus vacated by the oxygen.

Monodentate coordination of two equivalents of **1** through the phosphino donor is noticed in the reaction of $[PtCl_2(PhCN)_2]$ with excess **1**. This constitutes a minor reaction path leading to **5**. This compound, however, shows a *trans* geometry and most probably its formation does not involve the intermediacy of **4**, but should take place directly from **3** via a stepwise substitution of the ancillary benzonitrile ligands. Competition for the substitution of the second PhCN ligand by the internal oxygen donor on the way to **4** or by an additional external phosphino donor on the way to **5** can be expected to occur at the intermediate stage on compound **3**. The intramolecular process should be favoured when the second benzonitrile to be displaced is in *cis* position (Scheme 1), but the intermolecular substitution should prevail if the leaving ligand is *trans* to **1**. We may then speculate that **5** can originate from a species such as **3** but with a *trans* geometry. This should be highly reactive towards substitution due to the labilizing effect of the phosphino donor on the *trans* PhCN leaving group. The lability of this species may well account for the fact that we were not able to collect any NMR evidence of its presence in the reacting mixture.

Complex **5** readily insert $SnCl_2$ affording the trichlorostannato derivative **6** in quantitative yield. The reaction is remarkable for its selectivity and this is a positive feature in view of the fact that **6** is the putative catalyst in the hydroformylation of styrene. We do not know, however, if the oxygen of the trichlorostannato species is displaced by CO under hydroformylation conditions as it occurs in the case of the dichloro complex **4**. Although we have no direct evidence of this process, this possibility finds some support from the results observed in the enantioselective reactions which are more comfortably assessed if one assumes that two catalytic species, each one containing two monohapto BINAPO units around the Pt-centre, are present during the reaction. The modest stereoselections, the significant differences of regioselectivity recorded going from the racemic to the enantiopure BINAPO-based catalyst and the reversal of handness observed with (*S*)-BINAPO as compared to (*S*)-BINAP are all factors which better support this view.

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