

Chiral Complexes of Rh^I Containing Binaphthalene-Core P,S-Heterobidentate Ligands – Synthesis, Characterization, and Catalytic Activity in Asymmetric Hydrogenation of α,β -Unsaturated Acids and Esters

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The enantiopure complexes **3a** and **3b** [Rh(NBD)(P,S)]⁺BF₄[−] [P,S = (S)-2-(diphenylphosphanyl)-2'-(methylthio)-1,1'-binaphthalene (**a**); (S)-2-(diphenylphosphanyl)-2'-(isopropylthio)-1,1'-binaphthalene (**b**)] have been prepared from [Rh(NBD)(THF)₂]⁺BF₄[−] by reaction with a stoichiometric amount of the appropriate P,S-heterobidentate ligand. Single-crystal X-ray analysis of the S-methyl derivative shows that the seven-membered chelate ring is locked in a boat-like conformation with the methyl group in the equator-

ial position. Variable-temperature NMR measurements confirm that this conformation is maintained in solution and that the dynamic behaviour displayed by the complex is due to pseudo-rotation of the diolefin. Complexes **3** have been tested in the asymmetric hydrogenation of α,β -unsaturated acids and esters. Enantioselectivities of up to 60% ee have been recorded.

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Introduction

The catalytic activity of transition metal complexes is largely dependent on the structure of the supporting ligands. The nature of the donor atoms is crucial because it affects substantially the electron density at the metal centre as well as the geometric properties of the corresponding complexes.

Owing to the presence of two donors of diverse ligating properties, bidentate P,X-heterodonor ligands, where the chelate coordination of a phosphanyl group (P) is supported by a different heteroatom (X), are sometimes endowed with a peculiar catalytic activity. Within the family of P,X-heterobidentate ligands, the P,S-pair deserves particular attention. When the sulfur atom is in a low oxidation state, as in sulfides, the softness of the S-donor is similar to that of the P-donor in a phosphane. Phosphanyl sulfides can be thus regarded as heterobidentate ligands that differ little in the ligating strength of the two donors. Consequently, such ligands are expected to have a fairly weak

hemilabile character and to show a strong propensity towards chelate coordination to the metal atom.^[1]

An additional interesting feature of the S-donor of a sulfide group is that upon coordination the S-centre becomes stereogenic. The stereochemistry at the S-binding site depends on the chiral backbone of the ligand and on the steric demand of the alkyl substituent at the S-centre. This results in the formation of diastereomeric complexes featuring either a matching or a mismatching combination of chiral elements; a fact that is expected to have a significant bearing on the use of these ligands in asymmetric catalysis.

Various chiral P,S-heterobidentate ligands have been reported recently. Phosphito sulfide derivatives based on the xylofuranose framework have been used in the Ir-catalysed asymmetric hydrogenation of itaconic acid (51% ee).^[2] Glucopyranose-substituted phosphanyl sulfides are able to stabilize otherwise elusive Pd⁰ complexes.^[3]

Bis(phosphinite) ligands with a tetrahydrothiophene backbone have been synthesised and used in rhodium-catalysed enantioselective hydrogenation of methyl acetamidocinnamate. A tridentate coordination of the ligand, forming thioether-bridged dinuclear species, has been proposed.^[4]

Novel P,S-bidentate ligands possessing an oxathiane ring condensed onto pulegone^[5] or norbornane^[6] moieties led to quite good enantioselectivity in the Co-catalysed asymmetric intramolecular Pauson–Khand reaction and in the Pd-catalysed asymmetric allylic substitution reaction, respectively.

Mixed phosphorus/sulfur ligands, where the thioether fragment is flanked by a diarylphosphinito^[7] or a diaryl-

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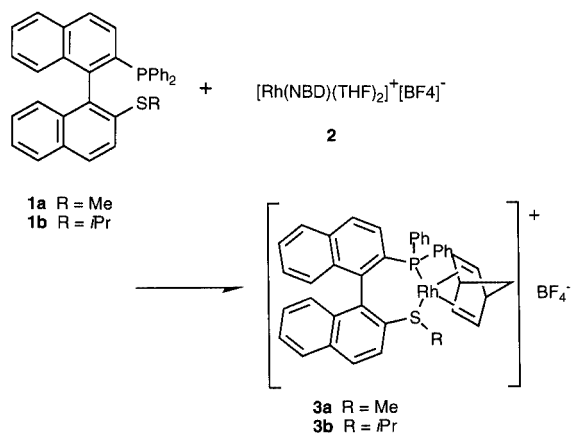
phosphanyl^[8] unit supported on chiral 1,2-disubstituted aliphatic backbones, proved to be highly efficient in Pd-catalysed enantioselective allylic substitution and in Rh-catalysed hydrogenation, respectively.

Atropisomeric 1,1'-binaphthyl-templated diphosphanes such as BINAP are among the most efficient chiral ligands for asymmetric hydrogenation. Recently, we reported on the synthesis of BINAPS,^[9] a heterobidentate version of BINAP in which one of the two diphenylphosphanyl substituents is replaced by an alkylthio group. BINAPS derivatives performed well in some Pd-catalysed asymmetric reactions, such as allylic alkylation^[10] and hydrosilylation,^[11] but were less satisfactory in Rh-catalysed processes such as hydroformylation and H-transfer reduction.^[11]

We report here on further investigations into the preparation, dynamic behaviour and utilization in enantioselective hydrogenation of such BINAPS-based Rh complexes.

Results and Discussion

The required ligands (*S*)-**1a** and (*S*)-**1b** were synthesised in enantiopure form as reported previously.^[11] The preparation of the enantiopure complexes **3a** and **3b** was accomplished as reported in Scheme 1 by treating the rhodium complex [Rh(NBD)(THF)₂]⁺BF₄[−] (**2**) (NBD = 1,4-norbornadiene) with a stoichiometric amount of (*S*)-**1a** and (*S*)-**1b**, respectively. The required intermediate adduct **2** was prepared in situ from the corresponding chloro-bridged dimer [Rh(NBD)Cl]₂ and AgBF₄.^[12] The isolated yields of the complexes **3a** and **3b** were in the range of 60–70%.



Scheme 1. Synthesis of complexes **3a** and **3b**

The molecular structure of the complex cation **3a** is depicted in Figure 1, together with the labelling scheme.

The Rh atom has a square-planar coordination geometry involving the double bonds of the norbornadiene ligand, the P atom and the stereogenic S-donor. The configuration at the newly created S-stereocentre is (*R*). The Rh–P and Rh–C bond lengths are comparable to those previously observed in [Rh(NBD)(BINAP)]⁺.^[13] The dihedral angle between the two naphthyl ligands (ca. 75°) is comparable to the 74.4° observed in the BINAP complex.

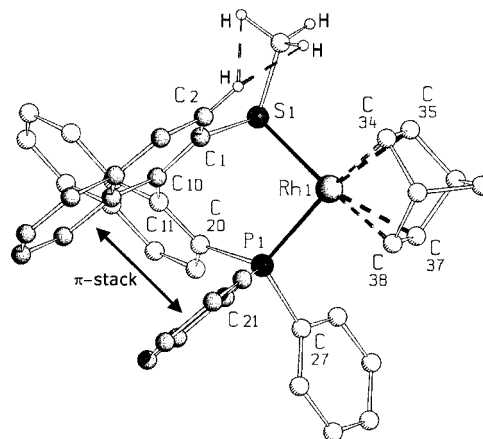


Figure 1. Ball-and-stick representation of the cationic complex in **3a**; selected structural parameters [Å]: Rh(1)–C(34) 2.200(5), Rh(1)–C(35) 2.216(5), Rh(1)–C(37) 2.181(5), Rh(1)–C(38) 2.144(6), Rh(1)–P(1) 3.290(1), Rh(1)–S(1) 2.343(1), P(1)–C(20) 1.838(4), S(1)–C(1) 1.793(4), C(34)–C(35) 1.385(7), C(37)–C(38) 1.356(9); the longest contacts involving H(2) and the H_{Me} atoms are shown by dotted lines; all remaining H atoms omitted for clarity

The H atom bound to C(2) is in close contact with the hydrogen atoms of the methyl group on the S atom; if free reorientation of the methyl group is assumed, the “dynamic” contacts between the H atoms range from 1.84 to 2.46 Å (assuming a normalised distance of 1.08 Å for the C_(by)–H group). One of the two extremes, with two equivalent H_{CH}...H_{Me} contacts of 2.46 Å, is shown in Figure 1.

Contrary to the BINAP complex, where the seven-membered chelate ring adopts a skew conformation in the solid state,^[13] the seven-membered ring in **3a** adopts a boat-like conformation (see Figure 2), with the Rh(1), P(1), C(10), and C(1) atoms constituting the flat part of the boat (maximum deviation from the average plane 0.05 Å). The sulfur and C_{methyl} atom elevations from this plane are 1.21 and 1.28 Å, respectively; thus, the methyl group bound to the sulfur atom is in an equatorial position with respect to the ring.

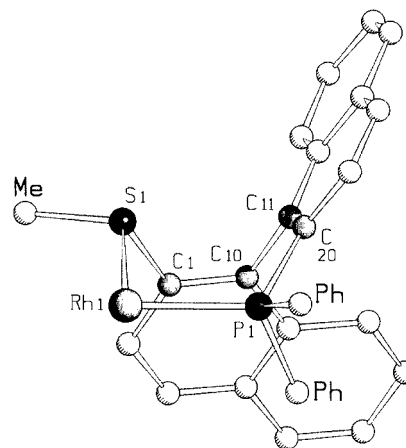


Figure 2. Boat-like conformation adopted by the seven-membered chelate ring in complex cation **3a**

Crystalline **3a** contains a stoichiometric amount of CHCl_3 solvent per formula unit. The H atom belonging to the solvent molecule interacts via bifurcated hydrogen bonding of the $\text{CH}\cdots\text{F}$ type with the BF_4^- anion (see Figure 3). The $(\text{C})\text{H}\cdots\text{F}$ distances (after normalisation of the C–H distance to the neutron value of 1.08 Å) are 2.26(1) and 2.24(1) Å, and compare well with the shortest $\text{CH}\cdots\text{F}$ interactions observed for organometallic salts containing BF_4^- or PF_6^- anions.^[14]

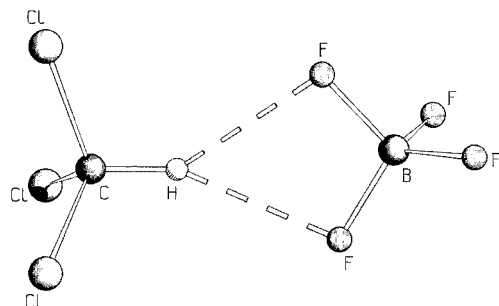


Figure 3. Bifurcated $\text{CH}\cdots\text{F}$ hydrogen bond interaction between the CHCl_3 solvent molecule and BF_4^- .

One of the phenyl substituents bound to the phosphorus atom and the portion of the binaphthyl moiety bound to S(1) are arranged in a π -stacking fashion, with an average distance between the two mean planes of ca. 3.5 Å (see Figure 1).

In the ^1H NMR spectrum of **3a** (CDCl_3 solution) four lines, each one accounting for two protons, can be observed for the coordinated NBD at 303 K (Figure 4). The signals of the allylic ($\delta = 4.04$ ppm) and the olefinic protons ($\delta = 4.40$ and 4.67 ppm) are broad singlets, while the bridging methylene group resonates as a sharp singlet ($\delta = 1.50$ ppm). When the temperature is lowered to 273 K, the olefinic protons' signal at $\delta = 4.67$ ppm undergoes line broadening, becoming extremely broad at 258 K and practically disappearing at 243 K. The second olefinic signal at $\delta = 4.40$ ppm also broadens, but at lower temperatures [$\nu(1/2) \approx 20$ Hz at 258 K], and practically disappears at 223 K. The allylic and the methylenic signals at $\delta = 4.04$ and 1.50 ppm, respectively, are still observable even at 223 K [$\nu(1/2) \approx 40$ Hz and 25 Hz, respectively]. From the NMR spectroscopic data it is apparent that a dynamic process is occurring in solution which averages the protons of the NBD ligand in the bound state.

The methyl peak appears at $\delta = 2.59$ ppm as a sharp doublet ($J = 1.5$ Hz). This is due to $^3J(\text{Rh},\text{H})$ coupling as demonstrated by a selective $^1\text{H}\{^3\text{P}\}$ decoupling. The shape, chemical shift and coupling constant of this signal remain unchanged over the whole temperature range investigated (303–203 K), suggesting that in this interval no dissociation of the S-donor from the metal atom occurs. Irradiation of this peak causes a significant NOE enhancement of the signal at $\delta = 7.67$ ppm which should be attributed to the naphthyl proton on the carbon atom adjacent to the S-substituted one. This is consistent with an equatorial

location of the S-methyl group and confirms that the solid-state structure is preserved in solution.

The pattern of the aromatic protons undergoes some minor variation with temperature, but the isolated peaks remain sharp and the coupling constants are substantially unchanged.

The protons were assigned to the corresponding carbon atoms by a ^1H - ^{13}C HSQC experiment. In the ^{13}C NMR spectrum all the carbon signals but those at $\delta = 81.61$, 71.25, and 66.50 ppm show sharp lines. These were assigned to the olefinic and the methylenic carbon atoms of norbornadiene, respectively. Finally, the sharp doublet in the ^{31}P NMR spectrum [$^1J(\text{Rh},\text{P}) = 161.7$ Hz] was not affected by the temperature variation.

The NOESY experiments show that the S- CH_3 group gives cross peaks with both olefinic signals at $\delta = 4.40$ and 4.67 ppm. This tells us that the two vinylic protons of the same double bond of NBD are not averaged and provides further evidence for the equatorial position of the methyl group. If the methyl group were axial, only one of the two protons on the same double bond would give a cross peak (Figure 5).

The NOESY spectra also show close contacts between the naphthyl proton adjacent to the S atom (signal at $\delta = 7.67$ ppm) and the olefinic proton of NBD (signal at $\delta = 4.67$ ppm). Thus, the more deshielded olefinic signal could confidently be assigned to the olefinic proton H^a (H^d) located below the average plane of the chelate ring (Figure 5).

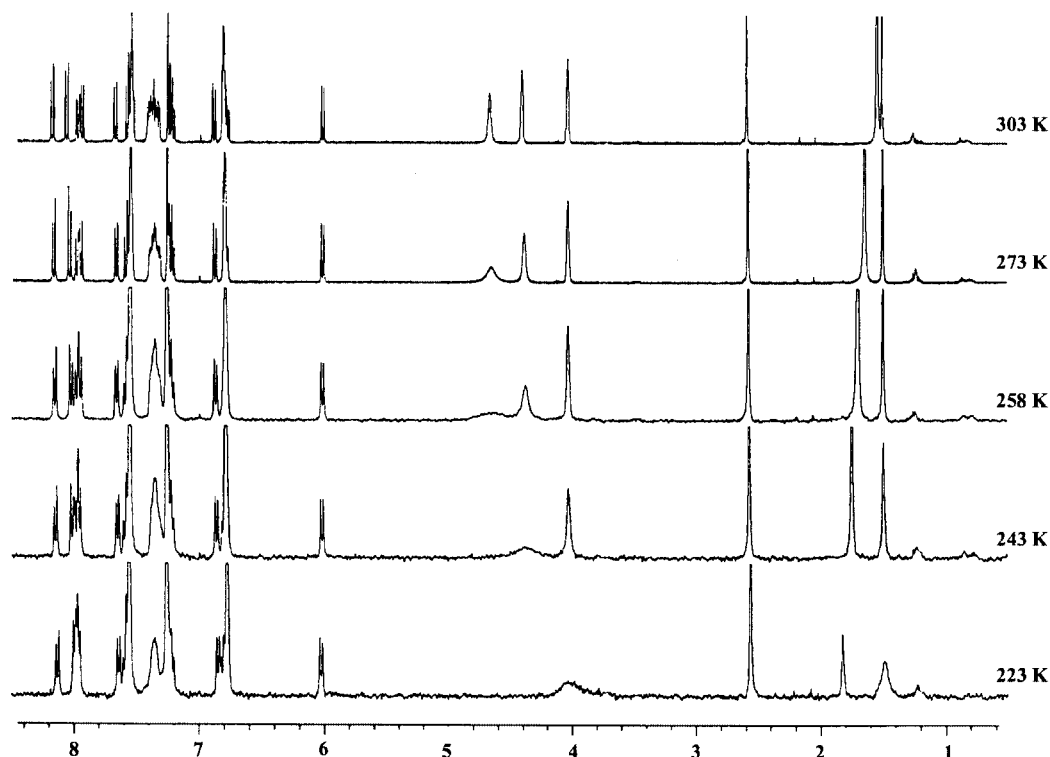
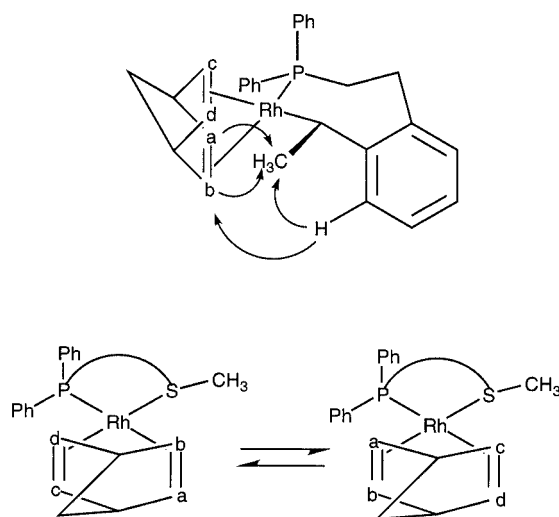
The olefinic protons (signals at $\delta = 4.40$ and 4.67 ppm) also show contacts with the *ortho* protons of the two different phenyl substituents of the PPh_2 unit (signals at $\delta = 7.38$ and 7.41 ppm).

These NMR experiments indicate that the dynamic process the complex experiences in solution results in averaging protons H^a with H^d and protons H^b with H^c (see Figure 5).

Dynamic behaviour of this type has been previously observed in cationic (diolefin)rhodium complexes with bidentate P,S- or P,N-ligands. This has been attributed to a mechanism involving $\text{Rh}-\text{S}^{[15,16]}$ or $\text{Rh}-\text{N}^{[16]}$ bond dissociation, followed by rotation around the remaining $\text{Rh}-\text{P}$ bond and subsequent recombination of the dissociated bond.

Although the S-stereocentre might be labilised more readily than the P-centre, the present NMR evidence indicates that the sulfur atom remains tightly bound to the metal atom throughout. Chemical shift, coupling constant and sharpness of the signal of the S-methyl group remain unchanged over the temperature range investigated. No shift of the methyl group towards that of the free ligand is observed; such a shift would be expected if the sulfur donor were displaced from the metal atom. Furthermore, the doublet at $\delta = 6.01$ ppm, regarded as diagnostic of the chelate coordination of the binaphthyl ligand, remains unchanged from 223 to 303 K.

All this evidence indicates that dissociation/inversion processes at the sulfur atom or conformational interconversions of the seven-membered ring do not take place. Instead, it appears that in solution both the chelate coordination of the P,S-ligand and the configurational integrity of

Figure 4. Variable-temperature ¹H NMR spectrum of **3a**Figure 5. Representation of NOE contacts in **3a**

the S-stereocentre in the bound state are preserved over the temperature range investigated.

An alternative plausible mechanism involves a Barry pseudo-rotation promoted by coordination of a donor at the fifth position of the metal atom. Such a reaction path has been proposed previously for a (1,5-cyclooctadiene)Rh complex containing 2-(diphenylphosphanyl)pyridine.^[17] However, this possibility was not substantiated as the ¹H NMR spectra registered in CDCl₃ after addition of donor solvents such as THF, or in [D₆]acetone, show no significant

change with respect to those registered in plain CDCl₃.

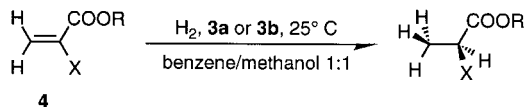
As it seems even more unlikely that the phosphorus atom is involved in a displacement/recombination process, the observed results should be ascribed to a dynamic process of the diolefin. This should proceed through an olefin pseudo-rotation, prompted by dissociation of one rhodium–olefin bond, followed by rotation through 180° around the remaining Rh–olefin bond and subsequent rebuilding of the chelate coordination of the diolefin. This conclusion fits better the experimental finding that the dynamic behaviour of the NBD protons is far more pronounced than that of the protons of the backbone of the P,S-ligand.

The isopropyl derivative **3b** shows in solution the same dynamic behaviour as **3a** as judged from the similar NMR pattern. The methylenic, allylic and olefinic protons of the norbornadiene ligand give rise to four broad singlets at $\delta = 1.49, 4.00, 4.48,$ and 4.61 ppm (2 H each), respectively. The signals of the diastereotopic methyl groups of the isopropyl group appear at $\delta = 1.18$ and 1.28 ppm. The chelating coordination of **1b** is confirmed by the presence of the aromatic doublet at $\delta = 5.95$ ppm.

Asymmetric Hydrogenation of α,β -Unsaturated Acids and Esters

Hydrogenation tests were performed on acrylic acid derivatives **4a–4c** (Scheme 2) at room temperature in methanol/benzene (1:1). A slight positive pressure of hydrogen was employed because at 1 bar the reaction was too sluggish. Even so, the catalytic activity of complexes **3a** and **3b** was rather low and fairly long reaction times were required

to attain a satisfactory conversion (Table 1). The two complexes exhibited comparable catalytic activity and both led to products of the same (*R*) configuration, although the methyl derivative **3a** was notably more efficient than the isopropyl counterpart **3b** and in all runs produced much higher *ees*.



Scheme 2. Asymmetric hydrogenation of α,β -unsaturated carboxylic acids and esters **4a–4c**

Under our reaction conditions, the acid **4b** was hydrogenated with 49% *ee* by **3a**. This is basically the same *ee* obtained with the Rh complex with BINAPP' [2-(Diphenylphosphanyl)-2'-(di-*o*-tolylphosphanyl)-1,1'-binaphthalene] (46% *ee*) and is much higher than the 13% *ee* we obtained with the corresponding Rh complex with BINAP.^[18]

The improvement over the chelate diphosphane-based catalysts was more pronounced with the methyl ester **4a** where *ees* obtained with BINAP (21%) and BINAPP' (40%)^[18] were outperformed by that obtained with complex **3a** (60%). This value is among the highest obtained in Rh-catalysed asymmetric hydrogenation using chiral P,S-heterodonor ligands. It is also close to that reported for the hydrogenation of the acid **4b** with a preformed [(*S*)-(BINAP)Rh(MeOH)₂]⁺ClO₄[−] complex (67% *ee*).^[19]

Both complexes **3a** and **3b** proved to be effective in hydrogenating dimethyl itaconate (**4c**), leading to high conversions (93 and 94%, respectively). Unfortunately, this activity was not matched by a high selectivity, and *ees* were decidedly poor both with **3a** and **3b** (8% and 2% *ee*, respectively).

In all these experiments the prevailing enantiomer showed the (*R*) configuration, the same as obtained with (*S*)-BINAP and (*S*)-BINAPP'. Therefore, the stereochemistry of the hydrogenation of these substrates is basically driven by the handedness of the chiral backbone; the stereogenicity at the sulfur plays a minor, albeit cooperative role, in the transfer of the chiral information.

Further work is in progress to determine the effect of a substituent of higher steric demand on the sulfur atom, and whether this situation can be reversed by introducing a bulkier group such as *tert*-butyl on this donor centre.

Experimental Section

General: Some ¹H, ³¹P, and ¹³C NMR spectra, as well as NOESY measurements (mixing time = 500 ms) were carried out with a Varian VXR-S 300 instrument at 299.9 MHz, 121.4 MHz and 75.4 MHz, respectively. ¹H and ³¹P variable-temperature measurements at 400 MHz and 161.9 MHz, respectively, as well as ¹H-¹³C HSQC experiments were run with a Varian INOVA 400 WB spectrometer using a Highland VT unit. Chemical shifts, given in ppm,

are referred to internal TMS (¹H and ¹³C) or external 85% H₃PO₄ (³¹P); coupling constants are in Hz. The two-dimensional experiments (NOESY and ¹H-¹³C HSQC) were performed using standard pulse sequences. Solvents were dried and distilled under nitrogen before use. All the reactions were performed under argon. [Rh(NBD)Cl]₂ was purchased from Strem Chemicals and used without further purification. The ligands, (*S*)-2-(diphenylphosphanyl)-2'-(methylthio)-1,1'-binaphthalene (**1a**) and (*S*)-2-(diphenylphosphanyl)-2'-(isopropylthio)-1,1'-binaphthalene (**1b**), were prepared as previously reported.^[11] The *ees* of the samples from the catalytic runs were determined with a Hewlett Packard 5890A gas chromatograph fitted with a 25-m capillary column coated with diethyl *tert*-butylsilyl- β -cyclodextrin PS 086 (i.d. 0.25 mm), purchased from MEGA (Legnano, Italia), using He as the carrier (head pressure 60 kPa, split ratio 100).

Preparation of [(*S*)-2-(Diphenylphosphanyl)-2'-(methylthio)-1,1'-binaphthalene](2,5-norbornadiene)rhodium(i) Tetrafluoroborate (3a**):** AgBF₄ (39 mg, 0.2 mmol) was added to a solution of [Rh(NBD)Cl]₂ (48 mg, 0.1 mmol) in THF (10 mL). After stirring for 1 h, the mixture was filtered through Celite and (*S*)-2-(diphenylphosphanyl)-2'-(methylthio)-1,1'-binaphthalene (100 mg, 0.2 mmol) was added to the resulting yellow solution. A yellow solid precipitated immediately and was recovered by filtration. Yield 107 mg (70%). Crystals of **3a**·CHCl₃ suitable for X-ray structure determination were obtained by slow concentration of a chloroform solution. ¹H NMR (CDCl₃, 298 K): δ = 1.50 [br. s, 2 H, CH₂ (NBD)], 2.59 (d, *J* = 1.5 Hz, 3 H, SCH₃), 4.04 [br. s, 2 H, allylic CH (NBD)], 4.40 and 4.67 [br. s, 2 $\times$ 2 H, olefinic CH (NBD)], 6.01 (d, *J* = 8.6 Hz, 1 H, Ar), 6.76–6.8 (m, 4 H, Ar), 6.88 (d, *J* = 8.6 Hz, 1 H, Ar), 7.20–7.26 (m, 2 H), 7.30–7.44 (m, 4 H),

Table 1. Asymmetric hydrogenation of α,β -unsaturated acids and esters **4a–4c** catalysed by complexes **3a** and **3b** (substrate/catalyst = 100:1)

Substrate	R	X	Catalyst	<i>p</i> (H ₂) [bar]	<i>t</i> [h]	Conversion ^[a] [%]	<i>ee</i> ^[a] [%]	Conformation
4a	CH ₃	NHCOCH ₃	3a	2.6	16	13	60	(<i>R</i>)
4b	H	NHCOCH ₃	3a	2.3	16	31	49	(<i>R</i>)
4c	CH ₃	CH ₂ COOCH ₃	3a	1.9	16	93	8	(<i>R</i>)
4a	CH ₃	NHCOCH ₃	3b	1.9	11	11	27	(<i>R</i>)
4b	H	NHCOCH ₃	3b	4.1	16	33	11	(<i>R</i>)
4c	CH ₃	CH ₂ COOCH ₃	3b	4.6	16	94	2	(<i>R</i>)

^[a] Determined by gas chromatography.

7.51–7.59 (m, 5 H), 7.67 (d, J = 8.1 Hz, 1 H, Ar), 7.94 (d, J = 8.1 Hz, 1 H, Ar), 7.97 (d, J = 8.1 Hz, 1 H, Ar), 8.06 (d, J = 8.9 Hz, 1 H, Ar), 8.18 (d, J = 8.9 Hz, 1 H, Ar) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ = 27.1 [d, $^1J(\text{Rh},\text{P})$ = 161.7 Hz] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ = 15.27 (SCH_3), 52.99 (allylic CH, NBD), 66.50 (NBD CH_2), 71.25 (olefinic CH, NBD), 81.61 (olefinic CH, NBD), 123.30–135.09 (32 C, Ar) ppm.

Preparation of [(S)-2-(Diphenylphosphanyl)-2'-(isopropylthio)-1,1'-binaphthalene](2,5-norbornadiene)rhodium(i) Tetrafluoroborate (3b): Compound **3b** was obtained by the procedure described for **3a** except that after the addition of the ligand (S)-2-(diphenylphosphanyl)-2'-(isopropylthio)-1,1'-binaphthalene an orange solution was obtained. The solution was stirred for 1 h then concentrated. The orange precipitate formed after addition of pentane was recovered by filtration. Yield 99 mg (62%). ^1H NMR (CDCl_3 , 298 K): δ = 1.18 (d, J = 6.6 Hz, 3 H, CH_3), 1.28 (d, J = 6.6 Hz, 3 H, CH_3), 1.50 [s, 2 H, CH_2 (NBD)], 3.88 (sept, J = 6.6 Hz, 1 H, CH), 4.00 [s, 2 H, allylic CH (NBD)], 4.50 [s, 2 H, olefinic CH (NBD)], 4.6 [s, 2 H, olefinic CH (NBD)], 5.95 (d, J = 8.1 Hz, 1 H, Ar), 6.71–6.80 (m, 4 H, Ar), 6.94 (d, J = 8.4 Hz, 1 H, Ar), 7.21–7.58 (m, 11 H, Ar), 7.73 (d, J = 7.8 Hz, 1 H, Ar), 7.98 (m, 2 H, Ar), 8.14 (d, J = 8.7 Hz, 1 H, Ar), 8.27 (d, J = 8.7 Hz, 1 H, Ar) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K): δ = 26.8 [d, $^1J(\text{Rh},\text{P})$ = 161 Hz] ppm. $[\alpha]_D^{25}$ = –386 (c = 0.5, CHCl_3).

X-ray Structural Determination of 3a: X-ray diffraction data for **3a** were collected at 293 K with a Bruker diffractometer (SMART) (Mo- K_α radiation, λ = 0.71073 Å) and corrected for absorption. $\text{C}_{41}\text{H}_{32}\text{BCl}_3\text{F}_4\text{PRhS}$, M_r = 883.77, triclinic, space group $P1$, a = 9.1724(7), b = 10.7757(7), c = 10.9453(8) Å, α = 68.456(2), β = 88.282(2), γ = 72.591(2)°, V = 956.2(1) Å³, Z = 1, d_c = 1.535 g·cm^{–3}, μ = 0.802 mm^{–1}, $F(000)$ = 446, 11681 reflections measured, refinement on F^2 (8621 independent reflections) for 446 parameters, $wR2$ (on F^2 , all data) = 0.0906, $R1$ [on F , $I > 2\sigma(I)$] = 0.0358. The computer program SHELXL-97^[20] was used for structure solution and refinement. All non-H atoms were treated anisotropically. The naphthyl moieties were refined as rigid groups. Hydrogen atoms were added in calculated positions and refined riding on their respective C atoms. For all molecular representations the graphic program SCHAKAL99^[21] was used. Intermolecular interactions were calculated by means of the program PLATON.^[22] CCDC-189656 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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