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Journal of Organometallic Chemistry 680 (2003) 329–334
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Mechanistic and synthetic aspects of hydroboration with a simple atropisomeric ligand prepared from 1-(1′-(isoquinolyl)-2-naphthol

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Received 11 April 2003; received in revised form 24 June 2003; accepted 24 June 2003

Abstract

A novel triarylphosphite ligand has been prepared directly from both enantiomers of BINOL and a single enantiomer of 1′-(isoquinolyl)-2-naphthol. In one of the two cases cationic Rh complex proved to be reasonably effective in the asymmetric hydroboration of electron-poor styrenes. It was possible to identify binuclear reactive intermediates when the hydroboration pre-catalyst was examined in the presence of catecholborane at low temperatures.

Keywords: Enantiomer; Styrene; Catecholborane

1. Introduction

Some years ago we reported the synthesis of the atropisomerically chiral P, N ligand QUINAP **1** [1]. The preparation involved Suzuki coupling of the 1-positions of naphthalene and isoquinoline precursors, a phosphination sequence, and resolution via palladium complexation. It was established that the ligand is effective in Pd-catalysed asymmetric allylic alkylation [2], and in Rh-catalysed asymmetric hydroboration [3]. Only the latter reaction has been studied in depth because of the plethora of solutions for asymmetric allylic alkylation. For reasons that are not well understood, the QUINAP ligand, and structural relatives, give superior results in the Rh-catalysed asymmetric hydroboration of several vinylarenes, providing the only practical solution when the alkene bears β-substituents [4,5]. There is some relationship between catalytic efficiency and the geometry of the PN-chelate. For the QUINAP complexes, the chelate ring is a pronounced boat [6]; for other PN ligands that are efficient in the asymmetric hydrosilylation of ketones, the chelate ring is almost flat [7]. Further, the synthetic route to QUINAP permits the preparation of differently substituted phosphines [8]. The efficiency of asymmetric hydroboration varies with the electronic properties of the substituents at phosphorus in QUINAP derivatives. Given this observation and the basic problems engendered by the multistep synthesis of the ligand family, an alternative approach was developed.

2. Results and discussion

2.1. Synthesis of ligands and complexes

It has been shown before that making the phosphorus atom in QUINAP less electron-rich by changing from PPh_2 to $P(furyl)_2$ leads to higher optical yields in the Rh-catalysed hydroboration of styrenes possessing electron-withdrawing substituents. In order to obtain QUINAP-type ligands with electron-deficient phosphorus, phosphite analogs have been synthesized [9]. Starting from (*R*)-BINOL and the readily available racemic alcohol **2**, an early intermediate in the original synthesis, ligand **3** was obtained in two steps as shown in Scheme 1.

Interestingly, the two diastereomers of **3** were present not in equimolar amount, but in ~2:1 ratio. Many unsuccessful attempts were made to separate them—

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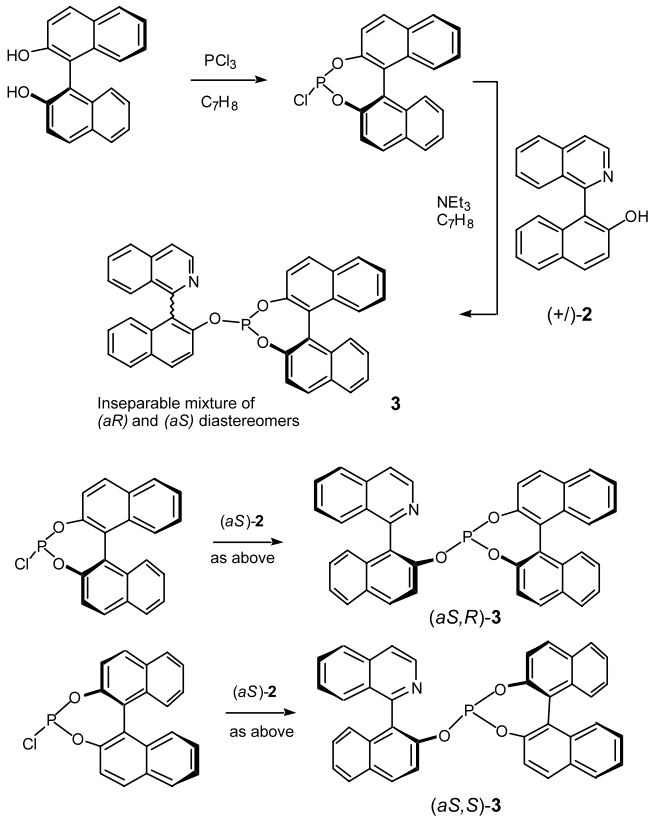
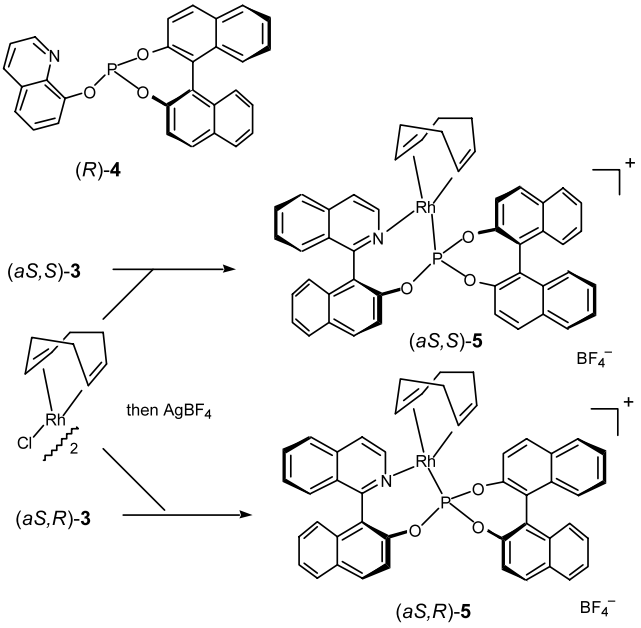
doi:10.1016/S0022-328X(03)00602-8



Scheme 1. Ligand synthesis. The configurational assignment of the quinol as (*aS*)-**2** is based on its CD spectrum in MeOH, (negative peak 220 nm, inflection 230 nm, positive peak 240 nm).

recrystallisations from various solvent mixtures, column chromatography or recrystallisation of their Pd or Rh complexes. Since alcohol **2** had previously been resolved into enantiomers through Pd complexation [10], and they have a reasonable barrier to racemisation at ambient temperature, this approach was employed here to give a single enantiomer of the amino-alcohol **4** ($\geq 95\%$ e.e.). The absolute configuration of the alcohol **2** was provisionally established as *aS*-(−) based on the characteristic change in ellipticity of the CD curve in MeOH from negative to positive with an inflection at 230 nm, in accord with both the general rule for biaryls [11]. Starting from this and (*R*)- or (*S*)-BINOL separately, two diastereoisomers of the ligand **3** were obtained, both in 93–94% d.e. As would be anticipated from the negative specific rotation observed for the binaphthol-derived phosphite (*aR*)-**4** [12], the (*aS*,*R*)-diastereoisomer[1] has a strongly negative specific rotation whereas for the (*aS*,*S*) the value is low. This implies that the specific rotation of the quinol fragment at the $[\alpha]_D$ wavelength is (*aS*)-(−) for the phosphite but (*aS*)-(+) in the parent phenol. At ambient temperature the rate of interconversion of the two diastereoisomers was very slow, and they can be stored indefinitely without interconversion.

The preparation of rhodium complexes intended as catalysts for hydroboration was carried out by previously defined methods [13]. The cationic Rh triflate product from either (*aS*,*R*)-**3** or (*aS*,*S*)-**3** was used directly as a catalyst in hydroboration reactions without further purification. The unexpectedly low regio- and enantioselectivities obtained were surprising, and inspired a closer investigation of the catalytic complexes. The NMR and MS spectra showed that the reactions of Rh(cod)(acac) with the ligands **3** in the presence of TMSOTf gave not the complexes [Rh(cod)L]OTf (as in the case of QUINAP) but $[RhL_2]$OTf [ES-MS found 1273.23; 1273.28 for the two diastereomers, calculated for the cationic component $C_{78}H_{48}N_2O_6P_2Rh$ 1273.20]. Diligated rhodium complexes were previously shown to give poor results in asymmetric hydroboration. Both diastereomers of the new ligand demonstrate strong tendency to form the $[RhL_2]^+$ cation, since their reaction with $[Rh(cod)_2]SbF_6$ (P/Rh = 1:1) also give $[RhL_2]SbF_6$ as a product, with half of the starting Rh complex remaining unreacted. Fortunately a solution to the problem was found by varying the experimental procedure such that the monoligated rhodium complex was obtained in pure form. The successful method involved reaction of the dimer $[Rh(cod)Cl]_2$ with $AgBF_4$ in THF prior to filtration and dropwise addition of a solution of the ligand in THF. The desired complexes (*aS*,*R*)-**5** and (*aS*,*S*)-**5** were, respectively, obtained as bright yellow solids (Scheme 2). Our efforts to prepare crystals suitable for X-ray analysis have not yet been successful. Overall, this procedure provided



Scheme 2. Formation of Rh complexes of the ligand **3**.

[1] To avoid ambiguity the axial chirality of the quinol, but not the binaphthol, is specified.

both diastereomers starting from a single hand of the isoquinoline entity, and either hand of the diol.

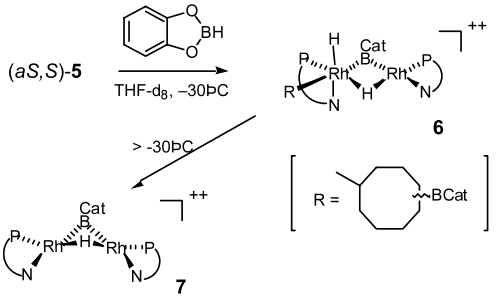
2.2. Asymmetric hydroboration with the derived Rh complexes

In practice only one of the pair proved effective in asymmetric hydroboration, and this one was applied to a variety of cases of vinylarene hydroboration in comparison with the literature results reported for the parent QUINAP complex. These results are shown in Table 1.

With electron-poor vinylarenes, where the parent QUINAP complex performs considerably less well than with electron-rich analogues, the results are adequate, but only for one of the two diastereomers of the ligand. Whilst not yet an effective or practical method, this points to the possibility of adapting the simple synthetic methods described here to provide access to related ligands of substantially higher efficiency.

2.3. NMR studies of the catalytic hydroboration pathway

Unlike asymmetric hydrogenation, where there have been extensive studies on the reaction pathway and the in situ identification of reactive intermediates by NMR [14], little progress has been made in unravelling the full pathway in asymmetric hydroboration. Both experimental [15] and theoretical studies [16] support the idea that transfer of hydride to the coordinated alkene precedes transfer of the boryl fragment. Low temperature NMR studies were carried out on the reaction mixture derived by mixing the Rh complex derived from with catecholborane, monitoring the outcome by heteronuclear NMR. Intermediate species, not previously observed in any catalytic hydroboration were obtained



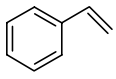
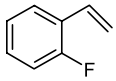
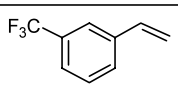
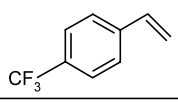
Scheme 3. The observation of reactive intermediates in the reaction of the complex (*aS*,*S*)-**5** with catecholborane in THF at low temperatures.

and provisional structural assignments are as shown in Scheme 3.

Addition of an excess of catecholborane to a solution of $[Rh(L)(cod)]BF_4$ (L = (*aS*,*S*)-**3**) at −78 °C results in the formation of a light-yellow precipitate which dissolves completely at −40 °C. The ^{1}H- and ^{31}P-NMR spectra of the reaction mixture taken in the temperature interval from −40 to −15 °C indicate the presence of a relatively high concentration of a binuclear complex **6**. Unfortunately, **6** could not be accumulated in the reaction mixture as a stable intermediate, since the rate of its decomposition (substantially to **7**, see further; and also to uncharacterisable products) is comparable to the rate of its formation.

A tentative structure for complex **6** was elucidated from its ^{1}H- and ^{31}P-NMR spectra. In the hydride region of the ^{1}H-NMR spectrum (Fig. 1a, Fig. 2) two multiplets of equal intensity at $\delta = -5.90$ and −17.96 are observed. In the phosphorus-decoupled spectrum both multiplets retain two ^{103}Rh couplings that unequivocally point to the binuclear structure **6**. The values of proton–phosphorus couplings for the low-field multiplet (161 and 124 Hz) leave no doubt that it has two

Table 1
Asymmetric hydroboration with catecholborane applied to electron-poor vinylarenes

	Alkene	Ligand	*sec*-alcohol, %	ee, %	Yield, %
1		(*aS*,*R*)-**3** (*aS*,*S*)-**3** (*S*)-QUINAP	70 77 98	2 (*S*) 68 (*S*) 92 (*R*)	55 70 75
2		(*aS*,*R*)-**3** **(*aS*,*S*)-3** (*S*)-QUINAP	80 **81** 97	1 (*S*) **51 (*S*)** 47 (*R*)	79 **78** 77
3		(*aS*,*R*)-**3** **(*aS*,*S*)-3** (*S*)-QUINAP	80 **71** 95	3 (*R*) **47 (*S*)** 37 (*R*)	76 **84** 81
4		(*aS*,*R*)-**3** (*aS*,*S*)-**3** (*S*)-QUINAP	80 74 95	2 (*R*) 31 (*S*) 45 (*R*)	81 84 81

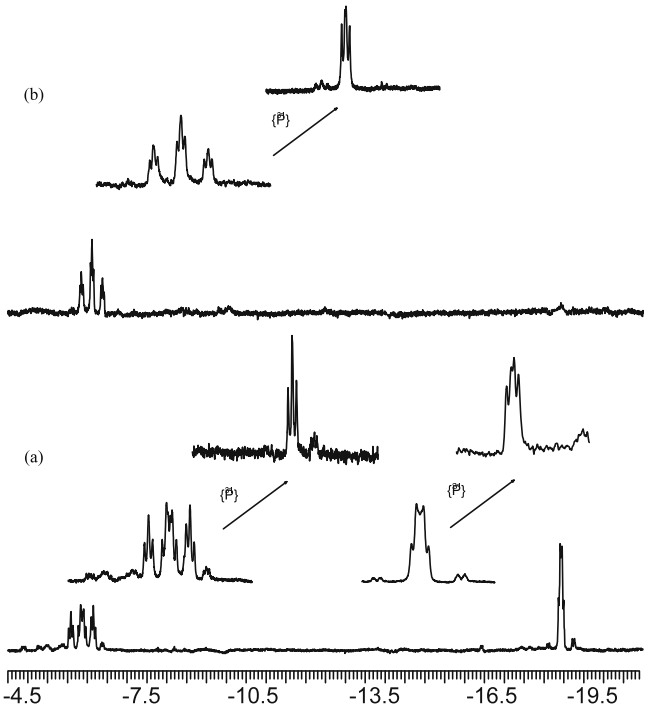


Fig. 1. The ^{1}H-NMR spectrum of the Rh hydride region as above (a) at 243 K and (b) at 263 K after the reaction has proceeded as above. Expanded and ^{31}P-decoupled spectra are inset above the traces.

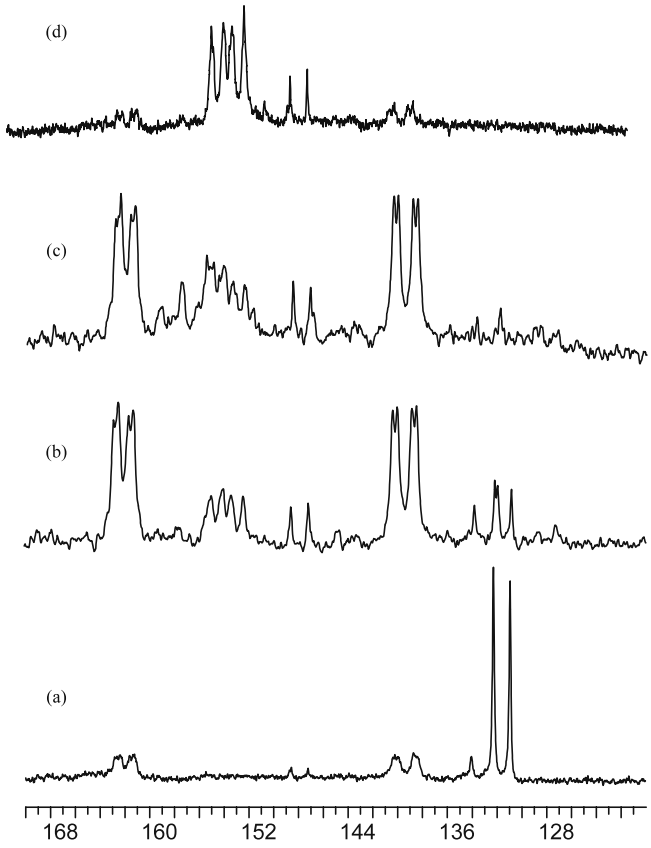


Fig. 2. Monitoring of progress in the reaction of (*aS*,*S*)-**5** with excess catecholborane, by ^{31}P-NMR in d_8-THF from −40 °C and upwards; (a) at 233 K (b) at 243 K (c) at 243 K after 1 h (d) at 263 K after the conversion of **6**–**7** had reached an optimum level. See text for detailed assignments.

inequivalent *trans*-phosphorus partners, whereas two equivalent rhodium couplings (28 Hz) place it securely in the bridging position between two rhodium atoms. The high-field proton has two inequivalent rhodium couplings (37 and 28 Hz) and probably only one phosphorus coupling At first sight the 28 Hz coupling seems to be too great for ^{4}J in the structure of **6**, however there are confirmed precedents in the literature. In the ^{31}P-NMR spectra complex **6** gives two broadened multiplets (predominantly double doublet character) at $\delta = 139$ ($^{1}J_{\mathrm{P-Rh}} = 310$ Hz) and $\delta = 162$ ($^{1}J_{\mathrm{P-Rh}} = 255$ Hz). The analysis of boron couplings is not straightforward, but at least it is quite clear that the smaller couplings are not homonuclear. The present evidence neither differentiates between the possible positional isomers (both nitrogens can exchange their positions with solvent molecules) nor indicates whether the remaining coordination sites are occupied by solvent molecules or by unreduced double bonds. When the sample was warmed to −30 °C or above, formation of another hydride species (**7**) was detected. Complex **7** has only one hydride multiplet at $\delta = -6.12$ a triplet of triplets ($^{1}J_{\mathrm{H-Rh}} = 21$ Hz, $^{2}J_{\mathrm{H-P}} = 133$ Hz) clearly indicating that it is in a bridging position and in a symmetrical environment. In the ^{31}P-NMR spectrum of **7** two slightly inequivalent phosphorus nuclei resonate at $\delta = 152$ ($^{1}J_{\mathrm{P-Rh}} = 345$ Hz) and $\delta = 153$ ($^{1}J_{\mathrm{P-Rh}} =$ 350 Hz). The assignment of the core part of the coordination sphere can be made with some confidence on this basis. The remaining ligand, designated as R, is likely to be derived from the original cyclooctadiene by partial hydroboration. The reaction that is observed is a reductive elimination of the organic product, leaving a formal binuclear adduct of the ligand and bridging catecholborane. The only precedent for these structures, realistically related to intermediates in the catalytic cycle of catalytic hydroboration, is cited in the recent review on metal–boryl chemistry [17]. The only evidence for the dicationic structures proposed here for the dimers is the cationic nature of the original complex, assumed to be sustained. Further work is necessary to reveal the detailed structure of these or related intermediates.

It was confirmed that intermediates of this structural type (or any other) were absent when similar experiments were conducted with QUINAP as ligand. The success observed in the present case may reflect an additional intrinsic stability for H-bridged dimeric species, and the known propensity for phosphite ligands to promote the formation of related intermediates [18].

3. Experimental

3.1. General

Reactions were conducted with standard vacuum line techniques under a dry argon atmosphere. Melting points were determined by means of a Reichert–Koffler block. ^{31}P-, ^{13}C-, ^{1}H-NMR spectra were recorded on a Bruker AMX500 and DPX250 instruments. Chemical shifts (ppm) are given relative to Me_4Si (^{1}H- and ^{13}C-NMR) and 85% H_3PO_4 (^{31}P-NMR). APCI mass spectra were recorded with a Micromass Platform 1 mass spectrometer through an 'Openlynx' system. Electrospray ionisation mass spectra were measured on a Micromass BioQ II-ZS mass spectrometer. High-resolution mass spectra (HRMS) were run on a V.G. Autospec spectrometer operating in positive electrospray mode. Optical rotations were measured with a Perkin–Elmer 241 spectrometer. Reactions were carried out in solvents distilled with standard drying agents. Catecholborane (Aldrich) was distilled under reduced pressure before use. (*R*)- and (*S*)-bi-1,1′-naphth-2,2′-ol (BINOL) were bought from Fluka and azeotropically dried with toluene before use. Synthesis and optical resolution of 1-(1′-(isoquinolyl)-2-naphthol was performed according to the published procedures [10].

3.2. Preparation of ligands and metal complexes

3.2.1. (*aS*) 1-(1-Isoquinolinyl)-naphth-2-yl (*R*)-1,1′-binaphthalene-2,2′-diyl phosphite (*aS,R*)-**3**

A suspension of azeotropically dried with toluene (*R*)-(+)-BINOL (0.475 g, 1.66 mmol)) and 1-methyl-2-pyrrolidinone (1 drop) in freshly distilled PCl_3 (3.5 ml) was warmed to 75 °C and stirred for 30 min. Then the excess PCl_3 was removed in vacuum followed by azeotropic distillation with toluene (3 × 4 ml) in vacuum. An obtained yellow paraffin-like solid was dissolved in toluene (20 ml) and added dropwise to a stirred suspension of 1-(1′-(isoquinolyl)-2-naphthol (0.45 g, 1.66 mmol) and dry NEt_3 (1 ml, 7.2 mmol) in toluene (10 ml) at 0 °C. The mixture was warmed to 20 °C, stirred for 14 h and filtered. Pentane (30 ml) was added to the filtrate to precipitate $NEt_3 \cdot HCl$, the mixture was filtered again and concentrated in vacuum to give a yellowish paraffin-like solid. Column chromatography (silica gel, CH_2Cl_2/ether = 5/1) yielded pure product as a white solid (0.72 g, 75% yield). M.p. 130–132 °C. $[\alpha]_D^{20} = -184.0$ ($c = 1$, CH_2Cl_2). ^{31}P-NMR (101.3 MHz, $CDCl_3$), δ: 147.4 (96.5%), 145.6 (3.5%). ^{1}H-NMR (500 MHz, $CDCl_3$), δ: 8.78 (d, $J = 5.8$ Hz, 1H), 7.98–8.04 (m, 2H), 7.87–7.95 (m, 3H), 7.82 (d, $J = 5.8$ Hz, 1H), 7.77 (d, $J = 8.2$ Hz, 1H), 7.73 (m, 1H), 7.55 (d, $J = 8.9$ Hz, 1H), 7.51 (d, $J = 8.5$ Hz, 1H), 7.31–7.46 (m, 7H), 7.17–7.28 (m, 5H), 5.93 (d, $J = 8.8$ Hz, 1H). ^{13}C-NMR (125.7 MHz, $CDCl_3$), δ: 157.2 (*C*), 147.55 (d, $J = 8.1$ Hz; *C*), 147.45 (d, $J = 4.1$ Hz; *C*), 147.1 (d, $J = 4.1$ Hz; *C*), 142.9 (*C*H), 136.5 (*C*), 133.9 (*C*), 132.9 (*C*), 132.4 (*C*), 131.7 (*C*), 131.15 (d, $J = 4.1$ Hz; *C*), 130.7 (*C*H), 130.5 (*C*H), 130.4 (*C*H), 129.4 (*C*H), 129.1 (*C*), 128.5 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 127.8 (*C*H), 127.6 (*C*H), 127.3 (*C*H), 127.1 (*C*H), 127.0 (*C*H), 126.9 (*C*H), 126.8 (d, $J = 4.0$ Hz; *C*), 126.4 (*C*H), 126.1 (*C*H), 125.8 (*C*H), 125.4 (*C*H), 125.3 (*C*H), 125.0 (*C*H), 124.4 (d, $J = 6.1$ Hz; *C*), 122.6 (*C*), 121.8 (*C*H), 121.4 (*C*H), 121.0 (d, $J = 8.1$ Hz; *C*H), 120.8 (*C*H). MS (APCI), *m*/*z*: 586 (20%) $[M+H]^+$, 272 (100%). HRMS: 586.1572. Calc. for $C_{39}H_{25}NO_3P$: 586.1583.

3.2.2. (*S*)-1-(1-Isoquinolinyl)-naphth-2-yl (*S*)-1,1′-binaphthalene-2,2′-diyl phosphite, (*aS,S*)-**3**

The same procedure as for the (*aS,R*)-diastereomer was followed. Yield: 0.615 g (64%). M.p. 135–137 °C. $[\alpha]_D^{20} = +10.0$ ($c = 1$, CH_2Cl_2). ^{31}P-NMR (101.3 MHz, $CDCl_3$), δ: 147.3 (3%), 145.6 (97%). ^{1}H-NMR (500 MHz, $CDCl_3$), δ: 8.87 (d, $J = 5.8$ Hz, 1H), 7.89–8.05 (m, 6H), 7.82 (d, $J = 5.8$ Hz, 1H), 7.58–7.74 (m, 4H), 7.24–7.53 (m, 11H), 6.82 (d, $J = 8.9$ Hz, 1H). ^{13}C-NMR (125.7 MHz, $CDCl_3$), δ: 156.9 (*C*), 147.7 (d, $J = 4.1$ Hz, *C*), 147.6 (d, $J = 6.1$ Hz, *C*), 147.1 (*C*), 142.7 (*C*H), 136.5 (*C*), 133.8 (*C*), 132.9 (*C*), 132.5 (*C*), 131.7 (*C*), 131.25 (*C*), 131.1 (*C*), 130.6 (*C*H), 130.5 (*C*H), 130.4 (*C*H), 129.7 (*C*H), 129.2 (*C*H), 129.0 (*C*), 128.48 (*C*H), 128.45 (*C*H), 128.2 (*C*H), 127.65 (*C*H), 127.5 (*C*H), 127.2 (*C*H), 127.1 (*C*H), 127.0 (*C*H), 126.7 (d, $J = 4.1$ Hz, *C*), 126.4 (*C*H), 126.1 (*C*H), 125.9 (*C*H), 125.35 (*C*H), 125.25 (*C*H), 125.0 (*C*H), 124.3 (d, $J = 4.1$ Hz, *C*), 122.7 (*C*), 121.85 (*C*H), 121.7 (*C*H), 121.2 (d, $J = 8.1$ Hz, *C*H), 120.7 (*C*H).

3.2.3. (*aS*) [1-(1-Isoquinolinyl)-naphth-2-yl (*R*)-1,1′-binaphthalene-2,2′-diyl phosphite] (cyclooctadiene)rhodium tetrafluoroborate, (*aS,R*)-**5**

Solid $AgBF_4$ (0.030 g, 7.7×10^{-5} mol) was added to a solution of $[Rh(cod)Cl]_2$ (0.014 g, 2.8×10^{-5} mol) in dry THF (2 ml), the mixture was stirred at 20 °C for 1 h and filtered through Celite. Then a solution of (*R*)-QUINAPO (0.033 g, 5.6×10^{-5} mol) in THF (1 ml) was added dropwise and the resulted red–brown mixture was stirred at 20 °C for 2 h. All the volatiles were removed in vacuum and the residue extracted with dichloromethane (3 ml). The organic extract was concentrated in vacuum to ca. 0.5 and 7 ml of ether added. The obtained yellow precipitate was filtered off and extracted one more time with CH_2Cl_2 (3 ml) to obtain 0.040 g (80% yield) of a yellow–orange solid. M.p. 193–195 °C. ^{31}P-NMR (101.3 MHz, $CDCl_3$), δ: 132.0, $^{1}J(P,Rh) = 267.3$ Hz (97%) and 130.31, $^{1}J(P,Rh) = 274.7$ Hz (3%). ^{1}H-NMR (500 MHz, $CDCl_3$), δ: 8.90 (d, $J = 6.4$ Hz, 1H), 8.39 (d, $J = 6.1$ Hz, 1H), 8.25–8.32 (m, 2H), 8.12 (d, $J = 8.2$ Hz, 1H), 7.97–8.06 (m, 3H), 7.81 (d, $J = 8.2$ Hz, 1H), 7.70–7.73 (m, 1H), 7.19–7.68

(m), 7.12 (d, $J = 8.5$ Hz, 1H), 5.83 (d, $J = 8.9$ Hz, 1H), 5.62 (brs, 1H; cod), 4.73 (brs, 1H; cod), 4.53 (brs, 1H; cod), 4.40 (brs, 1H; cod), 2.45–2.59 (m, 2H; cod), 2.23 (brs, 1H; cod), 2.19 (brs, 1H; cod), 1.99 (brs, 1H; cod), 1.70 (brs, 1H; cod), 1.40–1.60 (m, 1H; cod), 0.65–0.85 (m, 1H; cod). MS (electrospray), *m/z*: 796.21 (100%). Calc. for $C_{47}H_{36}NO_3PRh$: 796.15.

3.2.4. (*aS*)-[1-(1-Isoquinolinyl)-naphth-2-yl (*S*)-1,1′-binaphthalene-2,2′-diyl phosphite] (cyclooctadiene)rhodium tetrafluoroborate, (*aS,S*)-**5**

The same procedure as for the (*aS,R*)-diastereomer was followed. Yield: 72%. M.p. 210–212 °C. ^{31}P-NMR (101.3 MHz, $CDCl_3$), δ: 130.3, $^1J = 273.2$ Hz (97%) and 131.9, $^1J = 266.6$ Hz (3%). ^{1}H-NMR (500 MHz, $CDCl_3$), δ: 9.50 (d, $J = 6.4$ Hz, 1H), 8.50–8.56 (m, 3H), 8.23 (d, $J = 8.2$ Hz, 1H), 8.18 (d, $J = 8.9$ Hz, 1H), 8.07–8.13 (m, 3H), 7.99 (d, $J = 7.9$ Hz, 1H), 7.87 (d, $J = 9.2$ Hz, 1H), 7.78–7.82 (m, 1H), 7.75 (d, $J = 8.9$ Hz, 1H), 7.67–7.72 (m, 1H), 7.47–7.56 (m, 3H), 7.41–7.45 (m, 1H), 7.34–7.38 (m, 3H), 7.27–7.31 (m, 2H), 7.09 (d, $J = 8.6$ Hz, 1H), 5.70–5.78 (m, br, 1H; cod), 4.93 (brs, 1H; cod), 3.81–3.88 (m, br, 1H; cod), 3.61–3.67 (m, br, 1H; cod), 2.41–2.59 (m, 2H; cod), 2.14–2.22 (m, 1H; cod), 1.82–1.94 (m, 2H; cod), 1.65–1.75 (m, 1H; cod), 1.47–1.57 (m, 1H; cod), 0.85–0.96 (m, 1H; cod). MS (electrospray), *m/z*: 796.16 (100%). Calc. for $C_{47}H_{36}NO_3PRh$: 796.15.

3.3. Catalytic hydroboration of styrenes

Rh-catalysed asymmetric hydroboration reactions using preformed [Rh(cod)(QUINAPO)]BF_4 complexes as catalysts were performed on 1 mmol scale (1 mol.% of catalyst) according to the previously published technique employing a standard work-up of the reaction mixture with alkaline H_2O_2 with the only alteration that CH_2Cl_2 instead of ether was used for the extraction of the products. Conversion, regio- and enantioselectivities were determined by ^{1}H-NMR and chiral GC analyses of crude products followed previously reported procedures [4].

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