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Rhodium complexes with a new chiral amino-phosphinite ligand and their behavior as pre-catalysts in the hydroformylation of styrene

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ABSTRACT

The new amino-phosphinite chiral ligand (S_a)-4-((*S*)-1-(diphenylphosphinooxy)-3-methylbutan-2-yl)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine (**1**) has been synthesized and the corresponding more stable oxide has been characterized by X-ray analysis. The ligand behavior in styrene hydroformylation using $[Rh(acac)(CO)_2]$ and $[Rh(COD)_2]BF_4$ as precursors has been studied. With both pre-catalysts, branched aldehyde 2-phenylpropanal was obtained in mild catalysis conditions with high yield and regioselectivity but as racemic mixture, indicating the loss of the ligand (**1**) during catalytic run. To support these results, the reactions of $[Rh(acac)(CO)_2]$ and $[Rh(COD)_2]BF_4$ with the ligand 1 have been performed and the pre-catalysts behavior under CO/H_2 has been investigated.

Complexes of d^8 transition metals containing P,N-ligands have been used in homogeneous catalytic processes and the bidentate ligand coordination has been found to improve, in some cases, the catalytic activity [1]. The presence of hard nitrogen and soft phosphorus donor atoms gives to P,N-ligands peculiar features which in some cases present advantages [2]. It has been found that P,N-ligands can coordinate to metal centre *via* κ^1-P or κ^2-P,N [3]; these coordination modes can change during reaction route, with noteworthy involvements when the complex is used as pre-catalyst. For example, the behavior of amino-phosphine as hemilabile ligands, with change of coordination to metal from κ^2-P,N to κ^1-P in the catalysis conditions, allows the dangling nitrogen atom to act as "proton messenger" in the catalytic process [4]. Andrieu et al. [5] examined the coordination properties of a variety of amino-phosphine ligands in rhodium(I) complexes under variable CO pressure, and reached the conclusion that γ-P,N-ligands behave as κ^1-P-α-amino-phosphine, whereas the β-P,N amino-phosphines lead in solution to an equilibrium between κ^2-P,N and κ^1-P species; with some exception, in the examined rhodium-P,N complexes the ligand is κ^1-P coordinated, under hydroformylation conditions. To provide valuable insights into the behavior of chiral P,N-ligands in the rhodium-catalyzed hydroformylation, we synthesized a new amino-monophosphinite chiral ligand and used in the styrene hydroformylation reaction the corresponding pre-catalysts derived from the $[Rh(acac)(CO)_2]$ and $[Rh(COD)_2]BF_4$ complexes, respectively. In contrast to the significant number of articles concerning the use of amino-phosphine ligands in the rhodium-catalyzed enantio-selective hydroformylation reaction, the amino-monophosphinite ligands have been less studied [6].

The synthesis of the (S_a)-4-((*S*)-1-(diphenylphosphinooxy)-3-methylbutan-2-yl)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine (**1**) has been performed in two steps (Scheme 1) [7]: firstly azepinic ring formed, by double nucleophilic substitution of (*S*)-1-amino-3-methyl-butanol on (S_a)-2,2′-bis(bromomethyl)-1,1′-binaphthalene, refluxing for 24 h in toluene/acetonitrile mixture. The diastereomer amino-alcohol (S_a)-2-((*S*)-3H-dinaphtho[2,1-c:1′,2′-e]azepin-4(5H)-yl)-3-methylbutan-1-ol, (**2**), was obtained as white solid. In the subsequent step to a solution of compound **2** in toluene Et_3N was added and successively $ClPPh_2$ drop by drop at −10 °C. The reaction, monitored by $^{31}P\{^1H\}$ NMR, was concluded after 1.5 h. The successive work-up afforded the (S_a)-4-((*S*)-1-(diphenylphosphinooxy)-3-methylbutan-2-yl)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine, **1**, in high yields as white solid, stable under argon atmosphere, but very susceptible to air-oxidation in solution. The compound was characterized by elemental analysis and NMR spectroscopy. In the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6, compound **1** showed a singlet at 114.5 ppm and in the ^1H NMR spectrum, in the same solvent, showed a pattern very similar to that of starting amino-alcohol **2** except for a shift of the signals and the lack of the OH resonance.

With the aim of obtaining further structural information on compound **1**, we fully characterized by X-ray analysis the corresponding oxidation product (S_a)-2-((*S*)-3H-dinaphtho[2,1-c:1′,2′-e]azepin-4(5H)-yl)-3-methylbutyldiphenylphosphinate, (**3**), (Scheme 1) obtained by slow air-evaporation of CH_2Cl_2 solution of compound **1** [8].

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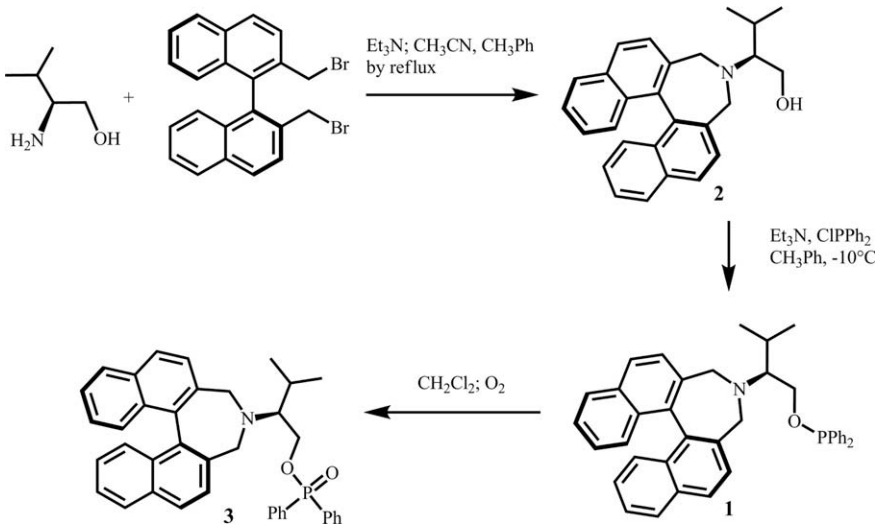


Scheme 1.

Crystallographic structure of compound **3** is shown in Fig. 1 together with atomic numbering scheme [9]. Selected bond parameters are given in the caption. The diastereomeric molecule **3** crystallizes in the non-centrosymmetric space group $P2_12_12_1$, exhibiting absolute configurations $\boldsymbol{S}_a$ and $\boldsymbol{S}$ for the anisotropic binaphthoazepine group and C(14), respectively. The lone pair of N(1) is turned away from oxygen: this conformation is stabilized by weak intramolecular H-interactions C(17)–H(17A)···N(1) and C(39)–H(39A) ···O(1). The *exo*-oriented phenyl ring of $-O_2PPh_2$ fragment is roughly perpendicular to naphthyl plane [dihedral angle 79.1(5)°]. The azepine ring adopts a twisted-boat conformation in which one N–C bond and the opposing C–C bond fused to one of the naphthyl rings form the floor of the boat. The angle between the mean planes through each of the naphthyl rings is 62.08(4)°; the naphthyl moieties are not very planar: the deviation from planarity results primarily from a small bend about the C(28)–C(21) and C(29)–C(36) axes. Indeed the dihedral angle between mean planes C(18)–C(19)–C(20)–C(21) and C(22)–C(23)–C(24)–C(25)–C(26)–C(27) is 4.7(2)° and the one between mean planes C(29)–C(36)–C(37)–C(38) and C(30)–C(31)–C(32)–C(33)–C(34)–C(35) is 6.4(1)°. The distortions of the naphthyl planes can be attributed to the effect of ring strain in the seven-membered azepine cycle

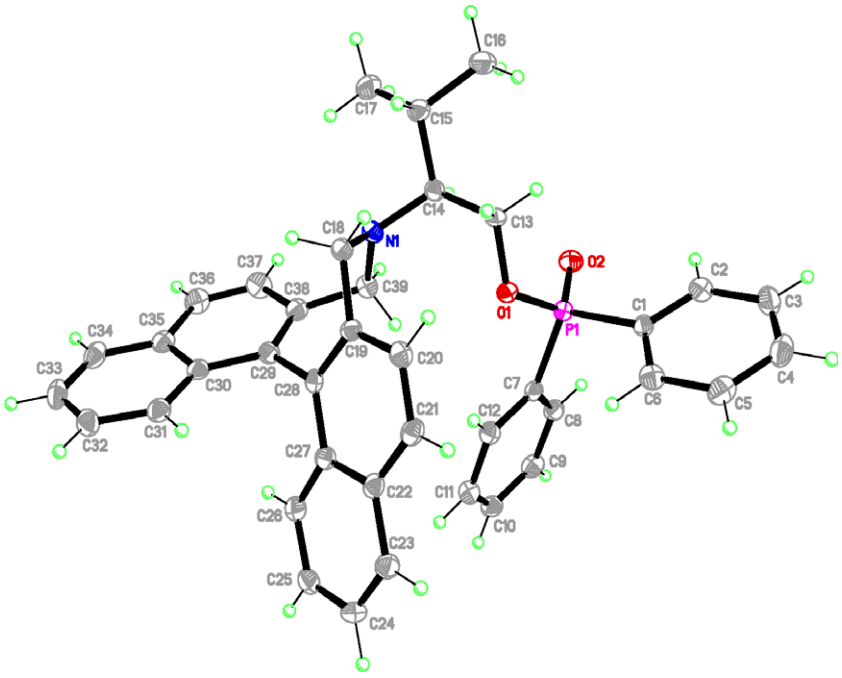


Fig. 1. Ortep view of compound **3** structure showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary size. Selected bond lengths (Å) and angles (°) are: P(1)–O(1) 1.5934(2), P(1)–O(2) 1.485(2), P(1)–C(1) 1.807(2), P(1)–C(7) 1.799(2), O(1)–C(13) 1.465(2), N(1)–C(14) 1.468(3), N(1)–C(18) 1.486(3), N(1)–C(39) 1.467(3), C(13)–C(14) 1.532(3), C(28)–C(29) 1.505(3)Å; O(2)–P(1)–O(1) 115.80(9), O(2)–P(1)–C(7) 114.6(1), O(1)–P(1)–C(7) 100.30(9), O(2)–P(1)–C(1) 111.1(1), O(1)–P(1)–C(1) 106.88(9), C(7)–P(1)–C(1) 107.3(1), O(2)–P(1)–O(1) 115.80(9), C(13)–O(1)–P(1) 120.0(1), C(39)–N(1)–C(14) 116.8(2), C(39)–N(1)–C(18) 114.2(2), C(14)–N(1)–C(18) 118.0(2)°. Selected torsion angle is: C(19)–C(28)–C(29)–C(38) 54.0(3)°. Selected hydrogen interactions are [H···A (Å), D···A (Å), D–H···A (°)]: C(17)–H(17A)···N(1) 2.56, 2.934(3), 104; C(39)–H(39A)···O(1) 2.63, 3.165(3), 115; C(21)–H(21)···O(2)i 2.47, 3.323(3), 153; C(23)–H(23)···O(2)i 2.61, 3.428(3), 148; (i) $x + 1$, y.

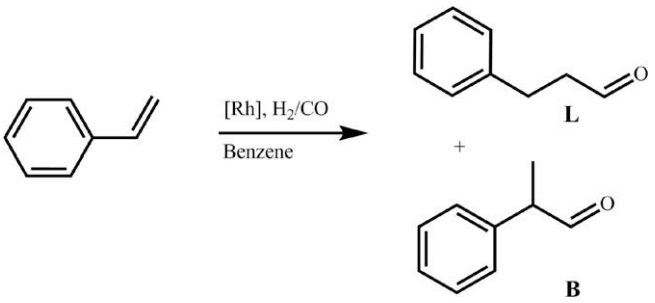
fused with both naphthyl moieties, as reported for azepinium bromide structures [10] and dinaphthazepines P,N-ligands [11]. As commonly observed in structures containing diphenylphosphinate groups [12], P(1) is a slightly distorted tetrahedron: bond angles values indicate that electrostatic repulsion between the lone pair of O(2) and bond pairs enlarges the angles involving O(2) and narrows those at the tetrahedral basis. The bond length P(1)–O(2) [1.485(2) Å] is shorter than P(1)–O(1) [1.5934(2) Å], due to its character of double bond, and is in the range for similar molecules [13]. Furthermore O(2) is involved in a weak bifurcated H-interaction with C(21) and C(23), giving rise to molecular propagation along **a** axis.

The catalytic system was generated *in situ* by mixing [Rh(acac)-$(CO)_2$] or [Rh$(COD)_2$]BF_4 and the chiral ligand **1** in a molar ratio 1:5, in benzene or dichloromethane respectively. To the catalyst solution styrene was added, then the mixture was introduced in autoclave under nitrogen stream and the gases CO and H_2 were admitted up at the desired pressure (Scheme 2) [14]. Several experiments have been carried out in the temperature range between 303 and 333 K and pressure between 40 and 60 bar for a period of 16 h. High chemo-selectivity was achieved with both the pre-catalysts, indeed the ethyl-benzene was always less than 1%. Using the [Rh(acac)$(CO)_2$] precursor, the catalytic system was not active at 318 K and 40 bar; increasing the temperature until 333 K and pressure up to 60 bar, a 100% conversion and a regioselectivity value of 94:6 B/L in favor of the branched aldehyde 2-phenylpropanal were observed, but the product was obtained as racemic mixture. A similar trend was observed when [Rh$(COD)_2$]BF_4 was used as the catalytic precursor. In this case the catalytic system was active at 318 K and 40 bar and in these conditions a yield of 34% and a value of regioselectivity of 97:3 were found, but 2-phenylpropanal was obtained as racemic mixture too.

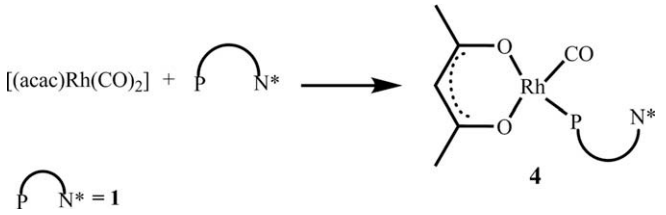
The different conversion and B/L regioselectivity values obtained at 318 K and 40 bar for [Rh(acac)$(CO)_2$] and [Rh$(COD)_2$]BF_4 pre-catalysts, indicate that the two catalytic species are different.

In order to gain informations about the catalytic systems, we have performed the reactions of [Rh(acac)$(CO)_2$] and [Rh$(COD)_2$]BF_4 precursors with ligand **1** to explore the behavior of the related products at experimental conditions of 40 bar of CO/H_2 pressure and 318 K, and in presence of CO at room temperature, respectively.

The reaction of [Rh(acac)$(CO)_2$] with compound **1**, in the molar ratio 1:1, in toluene at room temperature afforded the compound [Rh(acac)(κ^1-P-**1**)(CO)], **4**, as a yellow solid (Scheme 3) [15]. It was characterized by elemental analysis and IR and NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum, in C_6D_6 solution, showed a doublet at δ = 135.14 ppm (J_{Rh-P} = 192.4 Hz); in the ^1H NMR spectrum, in C_6D_6 solution, the signal shift of methylenic hydrogens of C*H*$_2$–O–P fragment was very diagnostic of the coordination of ligand **1** *via* P atom. In fact, after the coordination of P atom, this signal resulted shifted to higher frequency and splitted into two multiplets



Scheme 2.



Scheme 3.

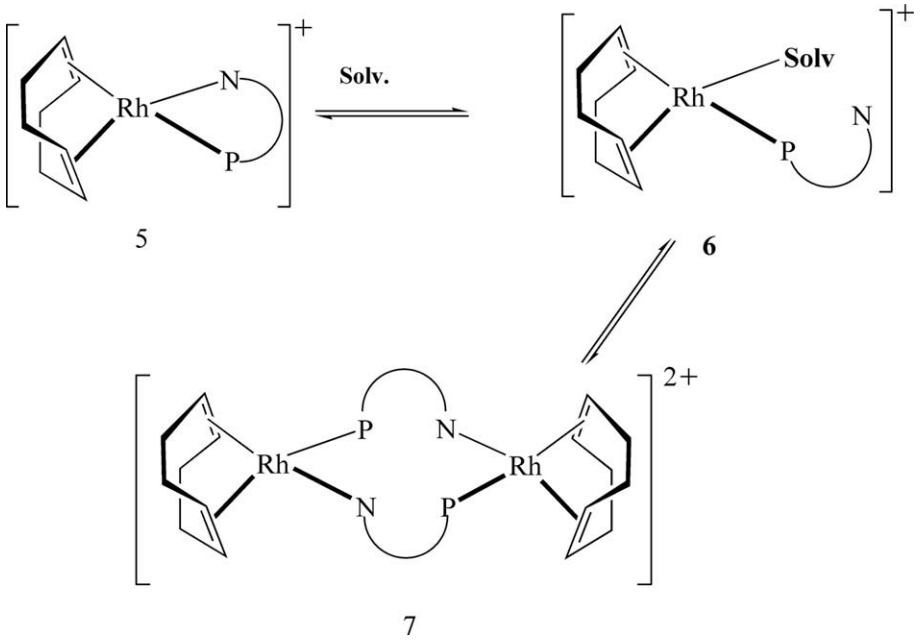
(δ = 4.34, 4.26 ppm). The presence of the acetylacetonate ion coordinated to rhodium centre was confirmed by a singlet for methine –C*H* at δ = 5.38 ppm and two singlets for methyl groups at δ = 2.05 and 1.51 ppm, respectively. The solid IR spectrum of complex **4** showed a ν(CO) band at 1974 cm^{-1}, indicating a CO ligand coordinated to rhodium(I). We tried to induce chelation of ligand **1** through N atom by refluxing a solution of compound **4** in toluene for 48 h. In this conditions the oxidized product **3** was the only isolated species.

On standing for 1 h a benzene solution containing [Rh(acac)-$(CO)_2$] and ligand **1** (in twofold excess) under 1:1 CO/H_2 pressure (40 bar) at 318 K, only the signals of compound **3** were detectable by $^{31}P\{^1H\}$ and ^1H NMR. It seems clear that under hydroformylation experimental conditions under CO/H_2 pressure compound **4** released ligand **1** or did not even form it.

The lack of enantio-selectivity in rhodium-catalyzed hydroformylation of various olefins, when chiral ligands as amino-phosphines are used, is usually found [16]; the complete displacement of the P,N-ligand from rhodium centre takes place regardless of the nature of the ligand, under hydroformylation conditions. Nevertheless rhodium-catalyzed styrene hydroformylations using pre-catalysts with chiral P,N-ligands and affording the branched aldehyde 2-phenylpropanal with discrete enantiomeric excesses were already reported in literature [6a]. The obtained results support the formation in solution of an hydride-carbonyl species [Rh(H)$(CO)_3$], under conditions in which catalytic activity is observed [17].

We also performed the reaction of the [Rh$(COD)_2$]BF_4 precursor with ligand **1**, using a molar ratio 1:1, in CH_2Cl_2 [18]. To a turbid orange solution of [Rh$(COD)_2$]BF_4 in CH_2Cl_2 an equivalent amount of ligand **1** was added. The mixture was stirred at room temperature for 2 h, concentrated and precipitated in hexane, giving a yellow solid.

We have conducted NMR studies in order to understand the nature of the species present in solution, dissolving the solid in mild polar solvents such as acetone-d_6 and THF-d_8 by Schlenk techniques. NMR spectra have clearly shown that from the reaction of [Rh$(COD)_2$]BF_4 with ligand **1** a mixture of several products formed, which chromatographic separation attempt failed owing to their instability. In particular the $^{31}P\{^1H\}$ NMR spectrum of the mixture at room temperature, showed at least three broad doublets at δ = 124.9 ppm (J_{Rh-P} = 174 Hz), 121.5 ppm (J_{Rh-P} = 194 Hz) and 125.3 ppm (J_{Rh-P} = 168 Hz) together with the free ligand peak. The assignment of these doublets was made difficult also by the instability of these complexes. Our conclusion is that, as previously observed in analogous P,N-rhodium systems [19], a dynamic equilibrium was taking place between the monomeric rhodium chelate (κ^2-P,N) complex [Rh(COD)(κ^2-**1**)]BF_4, **5**, initially formed, the solvate species [Rh(COD)(κ^1-P-**1**)]BF_4, **6**, coordinatively unsaturated transient intermediate, formed in virtue of hemilabile ligand behavior, and the dimer [Rh(COD)(**1**)]$_2$[BF_4]$_2$, **7**, having **1** as bridging ligands (Scheme 4). This reaction scheme was supported by $^{31}P\{^1H\}$ NMR spectrum assignment: the doublet at δ = 124.9 ppm (J_{Rh-P} = 174 Hz) to the monomeric species **5**, the doublet at δ = 121.5 ppm (J_{Rh-P} = 194 Hz) to the solvate species **6** and the doublet at



Scheme 4.

δ = 125.3 ppm (J_{Rh-P} = 168 Hz) to the dimer species **7**. By flushing CO into the mixture solution the species further decomposed. As for the hydroformylation reaction with the neutral [Rh(acac)$(CO)_2$] precursor, it is reasonable to suppose that an hydride-carbonyl rhodium intermediate formed also with [Rh$(COD)_2$]BF_4 precursor, by COD displacement in hydroformylation experimental conditions, leading to the branched aldehyde 2-phenylpropanal with high chemo- and regioselectivity.

To conclude, the paper describes the synthesis and the behavior in the rhodium-catalyzed styrene hydroformylation of the pre-catalysts containing the new amino-monophosphinite chiral ligand (S_a)-4-((*S*)-1-(diphenylphosphinooxy)-3-methylbutan-2-yl)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,-2′-e]azepine, **1**, and reports the crystal structure of the corresponding oxidation product, **3**. Although the conversion and the regioselectivity in favor of the branched aldehyde are very high almost in every cases, the lack of enantiomeric excess indicates that the rhodium catalysts containing the ligand **1** are not efficient in the rhodium-catalyzed styrene hydroformylation. This result is supported both by the behavior of ligand **1** in the reactions with the [Rh(acac)$(CO)_2$] and [Rh$(COD)_2$]BF_4 precursors and by the one of the related products in the hydroformylation conditions. The results support the presence of an hydride-carbonyl rhodium species as catalyst leading to the intermediates [Rh$(CO)_2(H)_3(C_6H_5CH{=}CH_2)$] and [Rh$(CO)_3$-$(H)_2(C_6H_5CH{=}CH_2)$]$BF_4$.

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Appendix A. Supplementary material

CCDC 722593 contains the supplementary crystallographic data for compound **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.11.001.

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[7] *Preparation of (S_a)-2-((S)-3H-dinaphtho[2,1-c:1′,2′-e]azepin-4(5H)-yl)-3-methylbutan-1-ol, (**2**) and (Sa)-4-((S)-1-(diphenylphosphinooxy)-3-methylbutan-2-yl)-4,5-dihydro-3H-dinaphtho[2,1-c:1′,2′-e]azepine, (**1**):* to a solution of (S_a)-2,2′-bis(bromomethyl)-1,1′-binaphthalene (1 g, 2.27 mmol), containing Et_3N (95 μl, 5.45 mmol) in toluene (25 ml), a solution of (*S*)-2-amino-3-methylbutan-1-ol (1.1 eq.) in CH_3CN (20 ml) was added drop by drop. The mixture was left to reflux at 90 °C for 24 h. Subsequently the solvent was evaporated and the residue dissolved with 40 ml of CH_2Cl_2, washed with water and brine. The organic phases were dried on $MgSO_4$ and concentrated. By adding hexane a white solid was obtained and used without further purification in the next reaction. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.98 (d, ^3J = 8.3 Hz, 2H, ArH), 7.96 (d, ^3J = 7.9 Hz, 2H, ArH), 7.57 (d, ^3J = 8.3 Hz, 2H, ArH), 7.49 (dd, ^3J = 6.7 Hz, ^4J = 1.1 Hz, 2H, ArH), 7.46 (d, ^3J = 6.5 Hz, 2H, ArH), 7.30–7.25 (m, 1H, ArH), 7.20 (d, ^3J = 7.1 Hz, 1H, ArH), 3.69 (dd, AB, ^2J = 12.2 Hz, 4H, CH_2–N–CH_2), 3.60 (m, 2H, CH_2–OH), 2.75 (m, N–CH–CH, 1H), 1.74 (sett, ^3J = 6.7 Hz, 1H, CH_3–CH–CH_3), 1.60 (b, 1H, OH), 0.88 (d, ^3J = 6.7 Hz, 3H, CH_3–CH–CH_3), 0.86 (d, ^3J = 6.7 Hz, 3H, CH_3–CH–CH_3) ppm. Anal. Calcd. for $C_{27}H_{27}NO$ (381.21): C, 85.00; H, 7.13; N, 3.67. Found: C, 84.98; H, 7.10; N, 3.65. Compound **1** was obtained by dissolving 400 mg (1.05 mmol) of **2** in a 50 ml flask under Ar with 10 ml of toluene and subsequently adding 22 μl (1.57 mmol) of triethylamine and 19 μl (1.05 mmol) of chlorodiphenylphosphine at −10 °C drop by drop. Immediately a white precipitate formed. After 1.5 h filtration of the solid was carried out under

argon atmosphere. The filtrate was concentrated and by adding hexane a white solid was obtained. ^{1}H NMR (300 MHz, C_6D_6) δ: 7.87 (d, ^3J = 6.13 Hz, 4H, ArH), 7.74 (d, ^3J = 8.5 Hz, 2H, ArH), 7.58 (d, ^3J = 8.2 Hz, 4H, ArH), 7.47 (t, ^3J = 7.4 Hz, 1H, ArH), 7.34 (t, ^3J = 7.0 Hz, 1H, ArH), 7.1 (m, 10H, ArH), 4.09 (d, ^3J = 8.0 Hz, 2H), 3.74 (s, 4H), 2.72 (m, 1H), 1.8 (sett, ^3J = 7.0 Hz, 1H), 1.08 (d, ^3J = 6.7 Hz, 3H, CH_3), 0.98 (d, ^3J = 6.7, 3H, CH_3) ppm. ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ: 114.5 ppm. Anal. Calcd. for $C_{39}H_{36}NOP$ (565.25): C, 82.81; H, 6.41; N, 2.48. Found: C, 82.78; H, 6.39; N, 2.46.

[8] *Preparation of (S$_a$)-2-((S)-3H-dinaphtho[2,1-c:1′,2′-e]azepin-4(5H)-yl)-3-methyl-butyldiphenylphosphinate, (**3**):* compound **3** was obtained by spontaneous oxidation in the air of **1** in CH_2Cl_2 solution. By slow evaporation of solvent crystals suitable for X-ray analysis were obtained. ^{1}H NMR (300 MHz, C_6D_6) δ: 7.87–7.72 (m, 12H), 7.4–7.27 (m, 10H), 4.51 (sb, 1H), 4.15 (sb, 1H), 3.44 (d AB, ^2J = 12.1 Hz, 2H), 2.91 (d, AB, ^2J = 12.1 Hz, 2H), 2.40 (m, 1H), 1.58 (sett., 1H), 0.94 (d, ^3J = 6.0 Hz, 6H) ppm. ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ: 29.93 ppm. Anal. Calcd. for $C_{39}H_{36}NO_2P$ (581.25): C, 80.53; H, 6.24; N, 2.41. Found: C, 80.50; H, 6.19; N, 2.38.

[9] Intensity data for compound **3** were collected on a Nonius/Bruker APEX II kappa CCD diffractometer with area detector at 100 K, using a grafite monochromator and monochromatic radiation Mo Kα. Cell refinement and reduction were performed with *DIRAX/LSQ* and *EVALCCD* programs. The structure was solved by Direct Methods, using *Sir 2004* program and refined with *weighted full-matrix least-square* procedure (based on F^2) (*SHELX-97*). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically calculated positions and refined using the *riding model*. Absolute configurations are in agreement with the synthetic route; inversion of configuration did not give better results during structural refinement. Crystallographic data for **3**: $C_{39}H_{36}NO_2P$ (**3**): M = 581.66 g/mol, colorless, long needle, 0.903 × 0.235 × 0.189 mm, Orthorhombic, space group $P2_12_12_1$, a = 8.492(1) Å, b = 16.847(3) Å, c = 21.744(3) Å, $\alpha = \beta = \gamma = 90°$, V = 3110.8(8) Å^3, Z = 4, Dc = 1.242 g/cm^3, mu = 0.124 mm^{-1}, F(0 0 0) = 1232, S = 1.136, R_1 = 0.0326, wR_2 = 0.0674.

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[14] *Catalytic runs:* all catalytic runs were performed in a 100 ml Berghoff stainless-steel autoclave equipped with gas and liquid inlets, a heating device, and a magnetic stirrer. The reactions were carried out in a Teflon vessel fitted to the internal wall of the autoclave, thus preventing undesirable effects due to the metal of the reactor. The autoclave was closed and degassed through three vacuum-nitrogen cycles. A solution consisting of [Rh(acac)(CO)$_2$] or [Rh(COD)$_2$]BF_4 and the ligand **1** in C_6H_6 (10 ml) and styrene (in a typical experiment 5 mmol of substrate, 0.01 mmol of complex and 0.04 mmol of ligand), were introduced under nitrogen, and gases (CO/H_2 1:1) were admitted up to the desired pressure. After 16 h the autoclave was cooled in a cold water bath and slowly vented. A sample of the homogeneous reaction mixture was then analyzed by gas chromatography.

[15] *Preparation of [Rh(acac)(CO)(κ^1-P-P,N*)], (**4**):* to a brown solution of [Rh(acac)(CO)$_2$] (50 mg, 0.194 mmol) in toluene one eq. of ligand **1** was added at room temperature. Immediately an effervescence was noted and the solution became clear yellow. After 2 h the solution was concentrated and the residue reprecipitated in hexane, giving a yellow solid in almost quantitative yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.90 (d, ^3J = 7.7 Hz, 2H, ArH), 7.86 (d, ^3J = 8.3 Hz, 2H, ArH), 7.56 (d, ^3J = 8.3 Hz, 2H, ArH), 7.46 (d, ^3J = 8.5 Hz, 4H, ArH), 7.32–7.24 (m, 4H, ArH), 7.20–7.12 (m, 4H, ArH), 7.07 (dt, ^3J = 7.4 Hz, ^4J = 2.5 Hz, 2H, ArH), 6.92 (dt, ^3J = 7.7 Hz, ^4J = 2.6 Hz, 2H, ArH), 5.46 (s, 1H, CO–C*H*–CO), 4.34 (m, 1H, CH–C*H*H–OP), 4.26 (m, 1H, CH–CH*H*–OP), 3.7 (dd, AB, ^2J = 12.3 Hz, 4H, CH_2–N–CH_2), 2.76 (m, 1H, N–C*H*–CH_2), 2.13 (s, 3H, CH_3C═O), 1.78 (sett., 1H, CH_3–C*H*–CH_3), 1.60 (s, 3H, CH_3C═O), 0.95 (d, ^3J = 6.9 Hz, 3H, CH_3–CH–CH_3), 0.92 (d, ^3J = 6.9 Hz, 3H, CH_3–CH–CH_3) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ: 135.14 (d, J_{Rh-P} = 192.4 Hz) ppm. ν IR: 1974 (C≡O), 1580 (C≡O), 1561 (C≡O) cm^{-1}.

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[18] *Reaction of [Rh(COD)$_2$]BF_4 with **1**:* to a turbid orange solution of [Rh(COD)$_2$]BF_4 (25 mg, 0.062 mmol) in 10 ml of CH_2Cl_2 one eq. of **1** was added (36 mg, 0.063 mmol) at room temperature. The reaction mixture was left to stirring for 2 h. After this time the solution was concentrated ad the residue reprecipitated in hexane, giving a yellow solid. ^{31}P{^{1}H} NMR (121 MHz, acetone-d_6) δ: 124.9 (d, J_{Rh-P} = 173.8 Hz), 125.3 (d, J_{Rh-P} = 168 Hz); 121.5 (d, J_{Rh-P} = 194 Hz) ppm.

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