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Novel phosphine–phosphites and their use in asymmetric hydrogenation

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ABSTRACT

Excellent enantioselectivities and activities have been obtained in the rhodium catalyzed asymmetric hydrogenation of dimethyl itaconate and several dehydroamino acid esters using a new class of BINOL based phosphine–phosphite ligand. The hydrogenation proceeded efficiently even at a substrate/catalyst molar ratio of 10,000 to give the product with 100% conversion and 99.1% enantioselectivity.

1. Introduction

Asymmetric hydrogenation using soluble rhodium catalysts constitutes a key synthetic step in many industrial processes.[1] The precise control of the molecular chirality plays an important role in chemistry, life science, and material science. High activity, selectivity and stability, readily accessible ligands, and enzyme-like stereocontrol are among the main features of an ideal catalyst for practical asymmetric synthesis.

The C_1-symmetric phosphine–phosphite ligands (Fig. 1) have been of great interest since Takaya and Nozaki reported on the synthesis and catalytic application of BINAPHOS.[2] Ligand (*R*,*S*)-BINAPHOS **1** provided high regio- and enantioselectivities in the rhodium-based hydroformylation of a wide range of substrates.[3] In recent years, a new series of phosphine–phosphite ligands has been developed and found to have unique catalytic properties in hydrogenations and in other asymmetric transformations.[4] Zhang et al. developed a new BINAPHOS derivative **2** that was applied

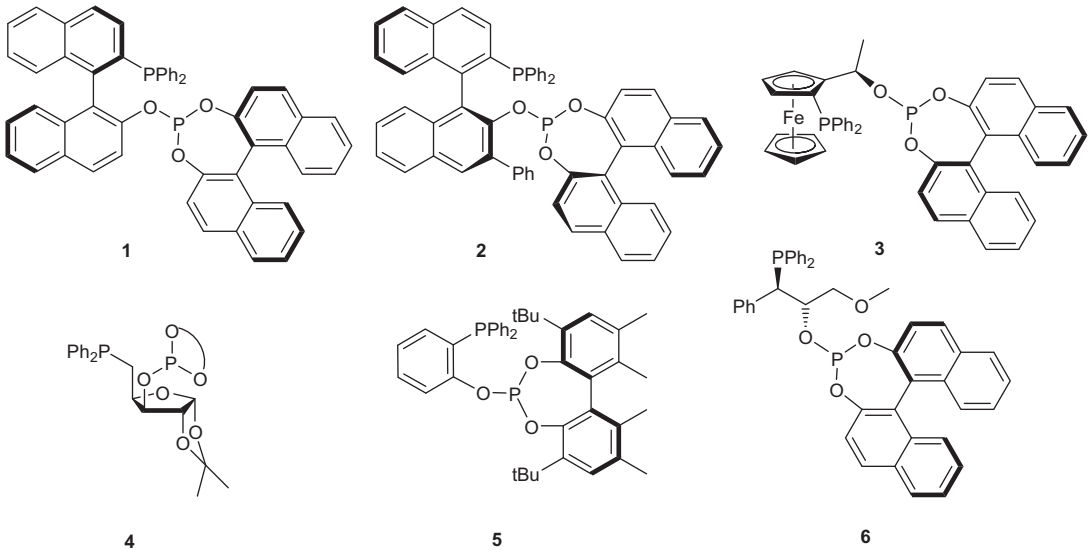

Figure 1. C_1-Symmetric phosphine–phosphite ligands.

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in the asymmetric hydrogenation of dehydroamino acid esters. They achieved 99% ee with methyl acetamidoacrylate as the substrate.[5] A series of new ferrocene based hybrid ligands of type **3** was prepared by Chan et al. and gave up to 89% ee in the hydrogenation of methyl acetamidocinnamate.[6] Monosaccharide based phosphine–phosphite ligands **4** were synthesized by Claver et al. and used in the hydrogenation of methyl acetamidoacrylate and methyl acetamidocinnamate to give the hydrogenated product with up to 99% ee.[7] Pizzano et al. applied phosphine–phosphite catalysts **5** in the hydrogenation of methyl acetamidocinnamate and several imines (up to 99% ee).[8] Vidal-Ferran et al. developed a new library of phosphine–phosphite ligands **6**, which were tested in the asymmetric hydrogenation of a wide range of substrates. According to their results (ees up to 99%) rhodium complexes modified by such ligands are undoubtedly excellent catalysts for dehydroamino acid esters.[9]

Our aim herein was the development of effective chiral ligands that could be easily prepared using inexpensive starting materials and successfully applied in asymmetric synthesis. Herein we report the preparation of new hybrid phosphine–phosphite ligands based on the axially chiral BINOL-moiety and centrally chiral pentane-2,4-diyl backbone and their use in asymmetric catalytic hydrogenations.

2. Results and discussion

2.1. Synthesis of phosphine–phosphite ligands

Chiral hydroxyalkyl phosphines can be conveniently prepared from cyclic sulfate esters, which are synthesized according to the Sharpless method.[10] The ring opening of cyclic sulfate **7** with $LiPPh_2$ takes place smoothly, with complete inversion at the stereogenic center to provide the Li-salt of the sulfated phosphine **8**. Hydrolysis gives the hydroxyalkyl phosphine **9** in a good yield and subsequent reaction with the BINOL-derived chlorophosphite gives the desired chiral phosphine–phosphite ligand **10a** (Scheme 1).

In order to explore the possibilities derived from the variation of the configurations of the stereogenic centers one new ligand **10b** was synthesized from the enantiomer of cyclic sulfate **7**. In the case of **10c**, we envisaged that the introduction of a H_8-moiety possessing a larger torsion angle could result in an improved chiral induction (Fig. 2).[11]

2.1.1. Stereoelectronic features of novel phosphine–phosphite ligands

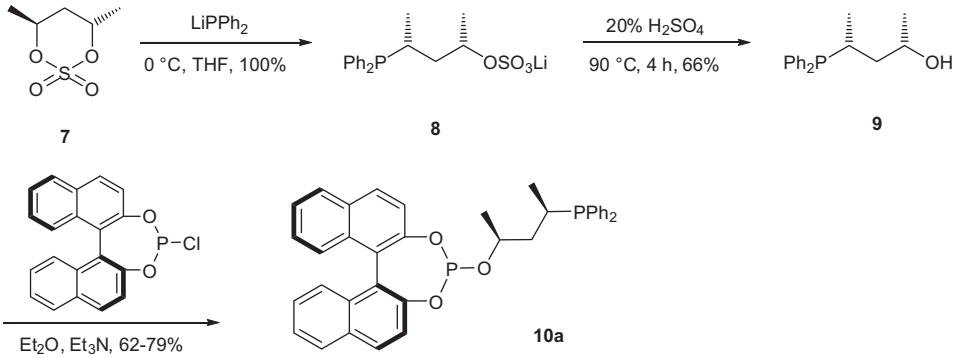
Among bifunctional compounds phosphine–phosphites are an interesting class of ligands due to their unique electronic properties. Their good σ-donor ability can be attributed to the phosphine functionality, and good π-acceptor ability to the phosphite group.

The rhodium coordination chemistry of ligands **10** was investigated because of their relevance to the asymmetric catalysis described below. The products formed upon treatment of the chiral ligands with 1 or 0.5 equiv of $[Rh(COD)_2]BF_4$ were evaluated by $^{31}P\{^1H\}$ NMR spectroscopy (Table 1 and Section 4).

At a ligand/metal ratio of 1:1, two double doublets were seen in the $^{31}P\{^1H\}$ NMR spectrum of compounds **11**. When a ratio of 2:1 was applied, two double triplets were obtained. This pattern cannot be attributed to the expected *cis*-$[Rh(\mathbf{10})_2]BF_4$ complexes. The observed NMR characteristics instead correspond to the structure of **12**, where the phosphorus atoms of a similar chemical environment are in a *trans*-position (Scheme 2). The unique electronic features of our ligands were also supported by the coordination chemical shifts of the phosphorus atoms; the phosphite site is shifted to high frequency, while the phosphine site is shifted in the opposite direction.

A simple way of evaluating the σ-donor ability of the phosphorous functionalities is by measuring the magnitude of the ^1J(Se–P) coupling constant in the ^{77}Se isotopomer of the corresponding seleno-phosphate and phosphine–selenide.

The synthesis of the diselenides was performed by reacting the corresponding ligand with elemental selenium. According to the preparation method developed by Pizzano et al., the reaction proceeds in a stepwise manner and needs a prolonged reaction time



Scheme 1. Synthesis of new chiral phosphine–phosphite ligands.

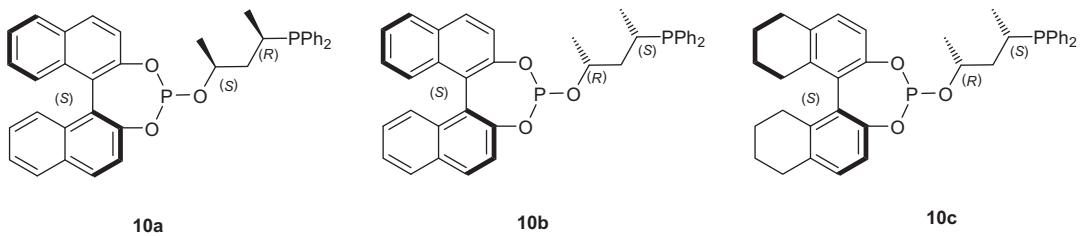
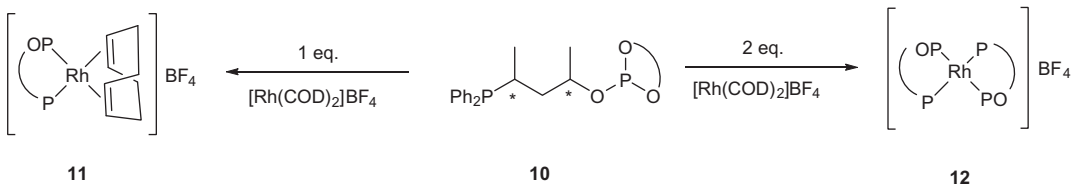


Figure 2. Novel phosphine–phosphite ligands.

Table 1
$^{31}P\{^{1}H\}$ NMR data of compounds **10** and **11**

Ligand	$\delta(P_A)$ (ppm)	$^{1}J(MP_A)$ (Hz)	$\delta(P_B)$ (ppm)	$^{1}J(MP_B)$ (Hz)	$^{1}J(P_AP_B)$ (Hz)	$\delta_{lig}(P_A)$ (ppm)	$\delta_{lig}(P_B)$ (ppm)	$\Delta\delta(P_A)$ (ppm)	$\Delta\delta(P_B)$ (ppm)
10a	140.73	259.5	24.35	139.2	47.9	153.50	0.00	−12.77	24.35
10b	132.83	264.0	35.94	142.6	51.2	149.33	−0.07	−16.50	36.01
10c	126.53	259.5	35.88	143.7	51.2	142.05	−0.01	−15.52	35.88

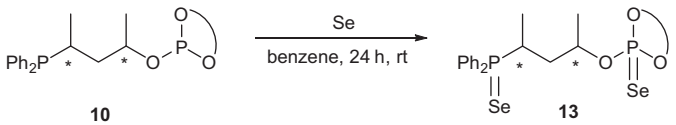
All spectra measured in $CDCl_3$, at 20 °C at 121.495 or 161.976 MHz with chemical shifts to high frequency of 85% H_3PO_4. P_A is in the phosphite group and P_B is in the phosphino group. The coordination chemical shift, $\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$.



11 **10** **12**

Scheme 2. Coordination abilities of ligands **10**.

Table 2
$^{31}P–^{77}Se$ coupling constants in compounds **13**



10 **13**

Entry	Compound	$^{1}J(P–Se)_A$ (Hz)	$^{1}J(P–Se)_B$ (Hz)
1	**13a**	1033.6	754.0
2	**13b**	1029.2	755.2
3	**13c**	1020.2	754.0

All spectra measured in benzene at 20 °C at 121.495 MHz with chemical shifts to high frequency of 85% H_3PO_4. $^{1}J(P–Se)_A$ is the coupling constant in the phosphite group and $^{1}J(P–Se)_B$ in the phosphino group.

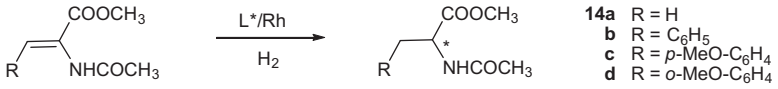
(2–8 days) to reach completion at 100 °C in toluene.[12] In contrast to this, phosphine–phosphite ligands **10** react readily with selenium powder to produce the desired diselenides in benzene in 24 h at room temperature.

From the data shown in Table 2, it is possible to conclude that there is no remarkable difference in the coupling constants of the phosphine fragment. It matches our expectations since the substituents on the phosphorous atoms are structurally identical. On the other hand, in compound **10c**, the phosphite moiety shows a much lower coupling constant, which indicates its higher basicity due to the partially saturated binaphthyl unit.

2.2. Asymmetric catalytic hydrogenation

Ligands **10a** and **10b** were evaluated in the Rh-catalyzed asymmetric hydrogenation of several dehydroamino acid esters (Table 3). The cationic Rh(I)-complexes were prepared in situ by mixing the corresponding Rh(I)-precursor with 1.1 M equiv of the ligand under argon in CH_2Cl_2. Hydrogenation reactions were carried out at 1 bar hydrogen pressure at 0 and 20 °C. As shown in Table 3, there were no significant differences between the catalytic performances of ligand **10a** and **10b** under identical conditions. It can also be seen that the structure of the substrates does have a slight influence on the enantioselectivity of the reaction. However, the activities of our catalytic systems are excellent since the conversions are almost complete in each case (Table 3, entries 2–11) after 1 h reaction time. Generally, ligand **10a** provides the best ees, up to 97.1% in the hydrogenation of **14d**. These slight differences in the catalytic properties of the ligands tested prompted us to term compound **10a** as *matched* and **10b** as a *mismatched* li-

Table 3
Hydrogenation of dehydroamino acid esters using ligands **10a** and **10b**



14a-d

Entry	Ligand	Substrate	T (°C)	Conv. (%)	ee (%)
1	**10a**	**14a**	20	90.8	96.8 (*R*)
2	**10b**	**14a**	20	100	93.8 (*R*)
3	**10b**	**14a**	0	95.3	96.8 (*R*)
4	**10a**	**14b**	20	99.7	95.1 (*R*)
5	**10b**	**14b**	20	100	95.1 (*R*)
6	**10b**	**14b**	0	96.6	94.1 (*R*)
7	**10a**	**14c**	20	100	96.5 (*R*)
8	**10b**	**14c**	20	100	96.8 (*R*)
9	**10b**	**14c**	0	100	95.9 (*R*)
10	**10a**	**14d**	20	100	97.1 (*R*)
11	**10b**	**14d**	20	100	92.5 (*R*)
12	**10b**	**14d**	0	81.6	94.6 (*R*)

Reaction conditions: 2.5 mmol substrate in 5 mL of CH_2Cl_2; catalyst: 0.0055 mmol of **10a** or **10b,** and 0.0050 mmol of $[Rh(COD)_2]BF_4$; hydrogen pressure:1 bar; reaction time: 60 min.

gand.[13] Since the favored enantiomer was the (*R*)-product in each case, it is evident that the BINOL-moiety governs the stereochemical outcome of the reaction.

In order to improve the catalytic performance of our system, [Rh(**10**)(COD)]BF_4 complexes were prepared and examined in the hydrogenation of **14b** at 5 bar hydrogen pressure (Table 4). The Rh-complex of ligand **10a** provided the best ee (95.8%). The effect of H_8-binaphthyl moiety on the enantioselectivity was not remarkable since changing ligand **10b** for **10c** only slightly increased the ee from 94.0% to 94.6%.

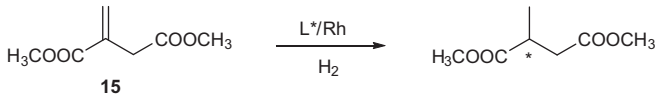
Table 4
Hydrogenation of substrate **14b** using [Rh(**10**)(COD)]BF_4 complexes

Entry	Catalyst	Conv. (%)	ee (%)
1	[Rh(COD)(**10a**)]BF_4	100	95.8 (*R*)
2	[Rh(COD)(**10b**)]BF_4	100	94.0 (*R*)
3	[Rh(COD)(**10c**)]BF_4	100	94.6 (*R*)

Reaction conditions: 2.5 mmol of substrate in 5 mL of CH_2Cl_2; catalyst: 0.005 mmol [Rh(COD)(**10a–c**)]BF_4; H_2 pressure: 5 bar; temperature: 20 °C; reaction time: 60 min.

The novel ligands were then tested in the asymmetric catalytic hydrogenation of dimethyl itaconate (Table 5). The hydrogenation reactions were performed under different conditions (0 or 20 °C and 1 or 5 bar) using *in situ* prepared catalysts. The *matched–mismatched* features observed previously in the hydrogenation of dehydroamino acid esters seemed to change switch, compound **10b** gave much higher ees than **10a** in each case (Table 5, entries 1–3). According to our observations, it can be assumed that substrates with certain structural and electronic features can strongly influence the enantioselectivity of the reaction and even switch the *matched–mismatched* properties of the ligands. Furthermore, the hydrogenation of **15** afforded the desired product with excellent enantioselectivity (up to 99.2%). As Table 5 shows, modification of the catalyst structure by introducing the H_8-binaphthyl moiety instead of H_0 resulted in an expected improvement. Although differences between the corresponding ees (entries 4 and 7, 5, and 8) are quite small, it is clearly visible that ligand **10c**, which possesses a larger torsion angle, provided higher values than **10b**. It is also notable that in the case of **10c** only a slight decrease was observed in the ee (from 99.3% to 99.2%), when the pressure increased from 1 to 5 bar. The temperature dependence, considering the results obtained at 1 bar, was insignificant.

Table 5
Hydrogenation of **15** using novel phosphine–phosphite ligands



15

Entry	Ligand	*T* (°C)	*p* (bar)	Time (min)	Conv. (%)	ee (%)
1	**10a**	0	1	120	5.0	93.5
2	**10a**	20	1	300	93.6	93.8
3	**10a**	20	5	60	100	87.6
4	**10b**	0	1	300	61.0	99.2
5	**10b**	20	1	180	100	99.1
6	**10b**	20	5	60	100	92.6
7	**10c**	0	1	120	100	99.4
8	**10c**	20	1	120	100	99.3
9	**10c**	20	5	60	100	99.2

Reaction conditions: 2.5 mmol of substrate in 5 mL of CH_2Cl_2; Catalyst: 0.0055 mmol of **10** or **11,** and 0.0050 mmol of [Rh(COD)$_2$]BF_4.

It is interesting to note that the activity of our catalytic systems changes depending upon the structure of the substrates. In general, Rh-catalysts modified by **10** seem to be more active when **14a–d** were used as substrates instead of **15**.

Inspired by the results shown in Table 5 and in order to discover the limits of our catalytic system, we decided to increase the substrate/rhodium molar ratio (Table 6). At a ratio of 500, the reaction was completed after 30 min, even under atmospheric pressure, to provide the product with higher than 99% ee. Furthermore, at a molar ratio of 5000 and 10,000, the ee still remained very high. To the best of our knowledge, the catalytic activity of our system is exceptional among phosphine–phosphites. Additionally, increasing the molar ratio from 500 to 10,000 only caused the ee to decrease slightly from 99.4% to 99.1%, that is, 1 g of our ligand could be used to produce 2.7 kg of 2-methylsuccinic acid dimethyl ester with high enantiomeric purity in 2 h.

Table 6
Hydrogenation of **15** using ligand **10c**

Entry	Time (min)	*p* (bar)	S/Rh	Conv. (%)	ee (%)
1	30	1	500	100	99.4 (*R*)
2	30	5	500	100	99.3 (*R*)
3	60	5	5000	76.9	99.0 (*R*)
4	120	5	10000	99.3	99.1 (*R*)

Reaction conditions: 5 mmol of substrate in 10 mL of CH_2Cl_2; catalyst: added from a stock solution using P/Rh = 2.2; temperature: 20 °C.

3. Conclusion

In conclusion, novel chiral phosphine–phosphite ligands have been synthesized and applied to the asymmetric catalytic hydrogenation of dehydroamino acid esters and dimethyl itaconate. According to the results a strong influence of the substrates on the selectivity and on the reaction rate was observed. The results also demonstrated that the phosphine–phosphites **10** are efficient catalysts in asymmetric hydrogenation reactions. Ligands **10b** and **10c** provided excellent enantioselectivities of up to 99.4% in the hydrogenation of dimethyl-itaconate. Furthermore, ligand **10c** resulted in 99.1% ee and a remarkable activity even at a substrate/rhodium molar ratio of 10,000. Finally, it is worth noting the attractive features of our system: (i) the starting materials are inexpensive and easily available; (ii) the ligands have a highly modular structure; (iii) very high activity and selectivity are maintained when the S/C ratio is increased; (iv) the reaction is environmentally benign and energy saving because of the high S/C ratio. We anticipate that this catalytic system will find use in an extensive array of applications.

4. Experimental

4.1. General experimental details

All manipulations were carried out under argon using Schlenk techniques. Solvents were purified, dried and deoxygenated by standard methods. H_0- and H_8-chlorophosphite,[14] and the hydroxyalkyl phosphines[15] were prepared according to the literature. All other starting materials were purchased from Aldrich. $^{31}P\{^1H\}$-, ^1H NMR and $^{13}C\{1H\}$-spectra were recorded on either a VARIAN UNITY 300 spectrometer operating at 121.42, 300.15, and 75.43 MHz, on a Bruker Avance 400 spectrometer operating at 161.976, 400.130, 100.613 MHz, or on a Bruker DRX-500 spectrometer operating at 202.45, 500.13, and 125.76 MHz, respectively.

4.2. Hydrogenation process

The substrate (2.5 mmol) was placed under argon in a stainless steel autoclave equipped with a gas inlet. A mixture of [Rh(COD)$_2$]BF_4 (0.005 mmol) and **10** (0.0055 mmol) or [Rh(**10**)(COD)]BF_4

(0.005 mmol) was stirred in 5 mL of solvent for 20 min. The catalyst solution was then transferred into the autoclave via syringe. The autoclave was pressurized with hydrogen (5 bar). After stirring the reaction mixture for 1 h, the hydrogen pressure was released carefully. The reaction mixture was filtered over a pad of silica and analyzed by chiral GC. Hydrogenation reactions at 1 bar were carried out in glass vessels using the procedure described above. The conversions of the hydrogenation reactions of dimethyl itaconate, acetamidoacrylic acid methyl ester and the enantiomeric excesses of the products were determined by chiral GC using a Hewlett Packard HP 4890 D, equipped with β-Dex 255 column (30 m × 0.25 mm, d*f* = 0.25 μm), N_2 as carrier gas, a split/splitless injector at 250 °C, and a FID at 250 °C. In the case of the hydrogenation of dimethyl itaconate retention times at 85 °C isotherm were 18.8 min for (*R*), 20.0 min for (*S*) and 27.6 min for the substrate. In the case of hydrogenation of acetamidoacrylic acid methyl ester retention times at 140 °C isotherm were 6.7 min for (*R*), 7.4 min for (*S*) and 5.9 min for the substrate. The conversions of the hydrogenation reactions of (*Z*)-α-acetamidocinnamic acid methyl ester, 4-methoxy-(*Z*)-α-acetamidocinnamic acid methyl ester, 2-methoxy-(*Z*)-α-acetamidocinnamic acid methyl ester, and the enantiomeric excesses of the products were determined by chiral GC using a Hewlett Packard HP 4890 D, equipped with Chiralsil-L-Val column (25 m × 0.25 mm, d*f* = 0.12 μm), N_2 as carrier gas, a split/splitless injector at 250 °C, and a FID at 250 °C. Temperature program: 2 min at 140 °C; 2 °C/min from 140 °C to 180 °C; 40 min at 180 °C. Retention times were 12.3 min for (*R*), 13.2 min for (*S*), and 22.1 min for (*Z*)-α-acetamidocinnamic acid methyl ester; 25.7 min for (*R*), 26.3 min for (*S*) enantiomers, and 53.6 min for 4-methoxy-(*Z*)-α-acetamidocinnamic acid methyl ester; 21.9 min for (*R*), 22.6 min for (*S*), and 34.9 min for 2-methoxy-(*Z*)-α-acetamidocinnamic acid methyl ester, respectively.

4.3. (2*R*,4*S*)-2-Diphenylphosphino-4-{(*S*)-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yloxy}-pentane 10a

At first, (2*R*,4*S*)-4-(diphenylphosphino)-pentane-2-ol **9** (1.9 g, 6.976 mmol) and triethylamine (0.81 g, 8.00 mmol) were dissolved in 30 mL of ether at room temperature. Next, H_0-chlorophosphite (2.8 g, 8.00 mmol) was dissolved in 30 mL of ether at −10 °C. The solution of the phosphine was added to the solution of the chlorophosphite at −10 °C and stirred for 30 min. The mixture was filtered through a pad of activated Al_2O_3 and washed with 4 × 5 mL of ether. The solvent of the filtrate was removed under reduced pressure to obtain 2.55 g (yield: 62.2%) of **10a** as a white foam. $[\alpha]_D^{20} = +336.6$ (*c* 1.135, CH_2Cl_2), mp: 60–63 °C. Anal. Calcd for $C_{37}H_{32}O_3P_2$: C, 75.76; H, 5.50. Found: C, 75.34; H, 5.45. ^{1}H NMR (500.130 MHz, $CDCl_3$): δ = 0.94 (dd, ^3J(P,H) = 15.7 Hz, ^3J(H,H) = 6.9 Hz, 3H, CH_3), 1.23 (m, diast. 1H, CH_2), 1.30 (d, ^3J(H,H) = 6.3 Hz, 3H, CH_3), 1.71 (m, diast. 1H, CH_2), 2.54 (m, 1H, C*H*–P), 4.55 (m, 1H, C*H*–O), 6.93–7.91 ppm (aromatic 22H). ^{13}C{^{1}H} NMR (75.468 MHz, $CDCl_3$): δ = 15.95 (dd, 1C, CH_3), 23.85 (d, 1C, CH_3), 25.39 (d, 1C, CH_2), 41.73 (dd, 1C, CH), 70.50 (dd, 1C, CH), 122–148 ppm (aromatic 32C). ^{31}P{^{1}H} NMR (121.495 MHz, $CDCl_3$): δ = 0.00 (s), 153.51 ppm (s).

4.4. [Rh(COD)(10a)]BF_4 11a

Ligand **10a** (129.9 mg, 0.2216 mmol) dissolved in CH_2Cl_2 (5 mL) was added dropwise to a solution of [Rh(COD)$_2$]BF_4 (90 mg, 0.2216 mmol) in CH_2Cl_2 (5 mL). The resulting orange solution was stirred for 20 min, concentrated, filtered, and finally treated with Et_2O (3 × 5 mL) to give 180 mg of [Rh(COD)(**10a**)]BF_4 as an orange powder. Yield: 92%, mp 178–179 °C. ^{31}P{^{1}H} NMR (121.495 MHz, $CDCl_3$): δ = 24.35 (dd, ^1J(Rh,P) = 139.2 Hz, ^2J(P,P) = 49.0 Hz), 140.73 ppm (dd, ^1J(Rh,P) = 259.5 Hz, ^2J(P,P) = 49.0 Hz).

4.5. [Rh(10)$_2$]BF_4 12a

A mixture of **10a** (30 mg, 0.0512 mmol) and [Rh(COD)$_2$]BF_4 (10.4 mg, 0.0256 mmol) in an NMR tube was dissolved in $CDCl_3$. ^{31}P{^{1}H} NMR (121.495 MHz, $CDCl_3$): δ = 27.27 (dt, ^1J(Rh,P) = 121.4 Hz, ^2J(P,P) = 52.3 Hz), 158.48 ppm (dt, ^1J(Rh,P) = 215.0 Hz, ^2J(P,P) = 52.3 Hz).

4.6. (2*S*,4*R*)-2-Diphenylphosphino-4-{(*S*)-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yloxy}-pentane 10b

The title compound was obtained by the procedure described for **10a**; white foam. Yield: 75.7%. $[\alpha]_D^{20} = +344.8$ (*c* 1.05, CH_2Cl_2), mp: 61–66 °C. Anal. Calcd for $C_{37}H_{32}O_3P_2$: C 75.76, H 5.50. Found: C, 75.66; H, 5.95. ^{1}H NMR (400.130 MHz, $CDCl_3$): δ = 0.98 (ddd, ^3J(P,H) = 15.13 Hz, ^3J(H,H) = 6.83 Hz, ^6J(P,H) = 2.29 Hz, 3H, CH_3), 1.21 (dd, ^3J(H,H) = 6.14 Hz, ^4J(P,H) = 1.83, 3H, CH_3), 1.25 (m, diast. 1H, CH_2), 1.75 (m, diast. 1H, CH_2), 2.63 (m, 1H, CH), 4.53 (m, 1H, CH-*O*), 7.10–8.00 (aromatic, 22H). ^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$): δ = 16.52 (d, 1C, CH_3), 24.28 (d, 1C, CH_3), 26.35 (d, 1C, CH_2), 42.29 (dd, 1C, CH), 71.31 (dd, 1C, CH), 122–149 ppm (aromatic, 32C). ^{31}P{^{1}H} NMR (161.976 MHz, $CDCl_3$): δ = 1.61 (s), 149.33 ppm (s).

4.7. [Rh(COD)(10b)]BF_4 11b

[Rh(COD)(**10b**)]BF_4 was obtained by the procedure described for [Rh(COD)(**10a**)]BF_4; yellow powder. Yield: 90%, mp 155–160 °C. ^{31}P{^{1}H} NMR (121.495 MHz, $CDCl_3$): δ = 33.82 (dd, ^1J(Rh,P) = 143.7 Hz, ^2J(P,P) = 51.2 Hz), 130.83 ppm (dd, ^1J(Rh,P) = 264.0 Hz, ^2J(P,P) = 51.2 Hz).

4.8. [Rh(10b)$_2$]BF_4 12b

[Rh(**10b**)$_2$]BF_4 was obtained by the procedure described for [Rh(**10a**)$_2$]BF_4. ^{31}P{^{1}H} NMR (121.495 MHz, $CDCl_3$): δ = 36.69 (dt, ^1J(Rh,P) = 127.0 Hz, ^2J(P,P) = 53.5 Hz), 146.21 ppm (dt, ^1J(Rh,P) = 212.7 Hz, ^2J(P,P) = 53.5 Hz).

4.9. (2*S*,4*R*)-2-Diphenylphosphino-4-{(*S*)-5,5′,6,6′,7,7′,8,8′-octahydro-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-2-yloxy}-pentane 10c

The title compound was obtained by the procedure described for **10a** starting from the corresponding phosphine and H_8-chlorophosphite; white foam. Yield: 78.9%. $[\alpha]_D^{20} = +185.9$ (*c* 1.135, CH_2Cl_2), mp: 64 °C. Anal. Calcd for $C_{37}H_{40}O_3P_2$: C, 74.73; H, 6.78. Found: C, 75.02; H, 6.95. ^{1}H NMR (300.130 MHz, $CDCl_3$): δ = 0.97 (dd, ^3J(P,C) = 15.1 Hz, ^3J(H,H) = 6.5 Hz, 3H, CH_3), 1.20 (d, ^3J(H,H) = 6.03 Hz, 3H, CH_3), 1.20 (m, diast. 1H, CH_2, overlapped) 1.58 (m, 2H, CH_2), 1.80 (m, 6H, 3CH_2), 1.80 (m, diast. 1H, CH_2, overlapped), 2.31 (m, 2H, CH_2), 2.72 (m, 1H, *CH*–P, overlapped), 2.72 (m, 2H, CH_2), 2.84 (m, 4H, 2CH_2), 4.53 (m, 1H, *CH*–O), 6.84–7.81 ppm (aromatic 14H). ^{13}C{^{1}H} NMR (75.468 MHz, $CDCl_3$): δ = 15.73 (d, 1C, CH_3), 22.53 (s, 1C, CH_2), 22.58 (s, 1C, CH_2), 22.70 (s, 1C, CH_2), 22.74 (s, 1C, CH_2), 23.72 (d, 1C, CH_3), 25.53 (d, 1C, CH_2), 27.84 (d, 1C, CH_2), 29.41 (s, 2C, CH_2), 41.66 (dd, 1C, CH_2), 70.29 (dd, 1C, CH_2), 119–147 ppm (aromatic 32C). ^{31}P{^{1}H} NMR (161.976 MHz, $CDCl_3$): δ = −0.01 (s), 142.05 ppm (s).

4.10. [Rh(COD)(10c)]BF_4 11c

[Rh(COD)(**10c**)]BF_4 was obtained by the procedure described for [Rh(COD)(**10a**)]BF_4; yellow powder. Yield: 90%, mp 199–200 °C. ^{31}P{1H} NMR (121.495 MHz, $CDCl_3$): δ = 35.88 (dd,

^1J(Rh,P) = 143.7 Hz, ^2J(P,P) = 51.2 Hz), 126.53 (dd, ^1J(Rh,P) = 259.5 Hz, ^2J(P,P) = 51.2 Hz).

4.11. [Rh(10c)$_2$]BF$_4$ 12c

[Rh(**10c**)$_2$]BF$_4$ was obtained by the procedure described for [Rh(**10a**)$_2$]BF$_4$. ^{31}P{^{1}H} NMR (121.495 MHz, $CDCl_3$): δ = 38.62 (dt, ^1J(Rh,P) = 129.1 Hz, ^2J(P,P) = 53.3 Hz), 142.02 ppm (dt, ^1J(Rh,P) = 211.5 Hz, ^2J(P,P) = 53.3 Hz).

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