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Rhodium complexes with a new chiral nitrogen-containing BINOL-based diphosphite or phosphonite ligand: synthesis and application to hydroformylation of styrene and/or hydrogenation of prochiral olefins

Ioannis D. Kostas[1]*, Kalliopi A. Vallianatou[1], Jens Holz[2] and Armin Börner[2,3]

[1]National Hellenic Research Foundation, Institute of Organic and Pharmaceutical Chemistry, Vas. Constantinou 48, 116 35 Athens, Greece
[2]Leibniz Institut für Organische Katalyse an der Universität Rostock e.V. (IfOK), A.-Einstein-Str. 29a, 18059 Rostock, Germany
[3]Fachbereich Chemie der Universität Rostock, A.-Einstein-Str. 3a, 18059 Rostock, Germany

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Two new cationic rhodium(I) complexes with a chiral nitrogen-containing BINOL-based diphosphite or phosphonite ligand have been synthesized. Chiral diphosphite was prepared by the reaction of *N*-phenyldiethanolamine with two equivalents of [(*R*)-(1,1′-binaphthalene-2,2′-diyl)]chlorophosphite. In its rhodium complex the ligand is bound to the metal via both phosphorus atoms, and a Rh–N interaction is also possible. Synthesis of the chiral phosphonite was achieved by the reaction of 2-(*N*,*N*-dimethylaminophenyl)-bis(diethylamino)phosphine with one equivalent of *R*-BINOL. In its rhodium complex, the ligand is *P*,*N*-bonded, forming a five-membered chelate ring. The first complex was applied to hydroformylation of styrene and displayed high activity and chemo- and regioselectivity, but unfortunately no asymmetric induction was found. Both complexes were evaluated in the hydrogenation of prochiral olefins with moderate activities and low enantioselectivities. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: chiral ligand; *P*,*N*-ligand; diphosphite; phosphonite; BINOL; rhodium complex; enantioselective catalysis; hydroformylation; hydrogenation; homogeneous catalysis

INTRODUCTION

Asymmetric catalysis is of substantial academic and industrial interest, and the development of novel chiral ligands remains the most attractive area in the field of transition-metal asymmetric reactions.[1–4] Hydroformylation represents one of the most important homogeneously catalysed reactions worldwide,[5,6] and in particular asymmetric hydroformylation provides a potentially powerful synthetic tool for the transformation of cheap olefins into valuable chiral aldehydes.[1–2,4–7] Although hydroformylation is highly utilized industrially, the production of chiral aldehydes by asymmetric hydroformylation has no industrial application up to now, and thus the development of new catalysts that provide high activity and chemo-, regio- and enantioselectivity remains a challenge of high importance. Asymmetric hydrogenation, on the other hand, has also received much attention during the last 35 years,[1–4,8–9] and to date is probably the most important enantioselective homogeneously catalysed industrial process.[10] Among several chiral ligands, mono- or diphosphites[11–16] as well as mono- or diphosphonites[17–19] have been largely overlooked in asymmetric catalysis to date.

Ligands with mixed donors of different coordination abilities, so-called hemi-labile ligands, have been of great interest due to the improved catalytic activity of

*Correspondence to: Ioannis D. Kostas, National Hellenic Research Foundation, Institute of Organic and Pharmaceutical Chemistry, Vas. Constantinou 48, 116 35 Athens, Greece.
E-mail: ikostas@eie.gr
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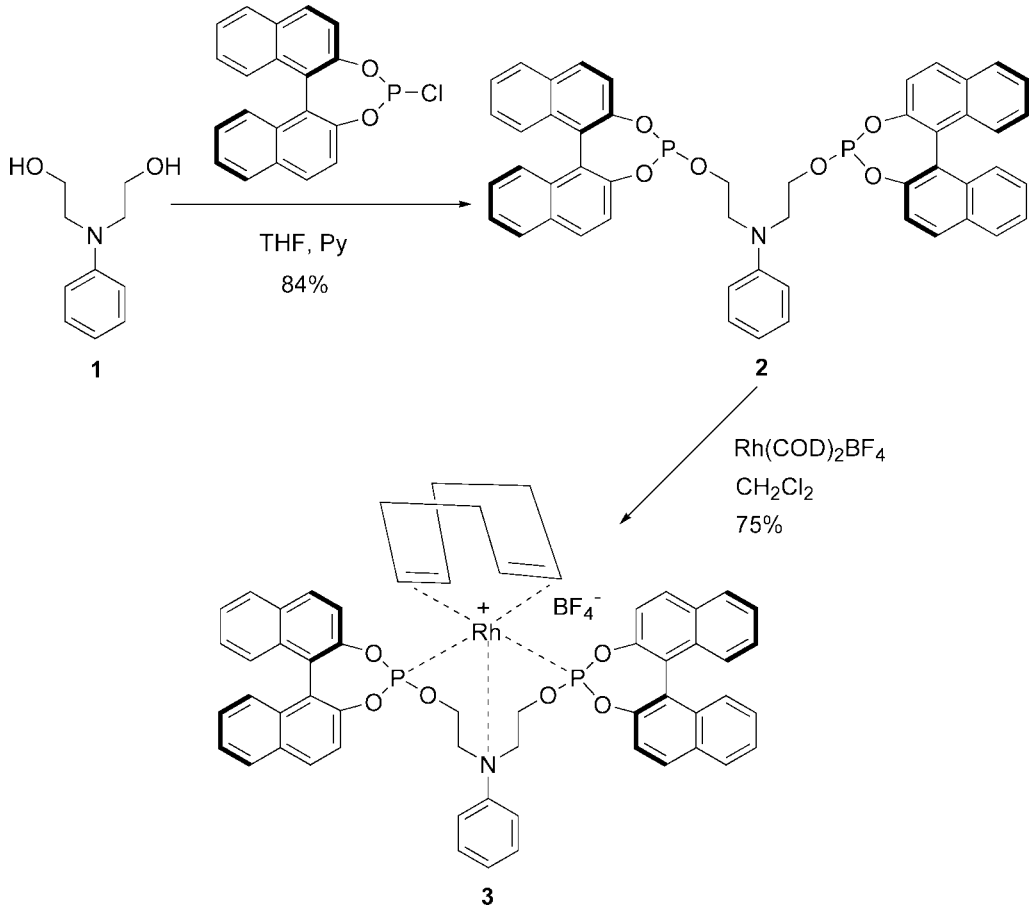
their transition-metal complexes in certain homogeneously catalysed reactions.[20–22] Our groups previously have published several achiral functionalized hemi-labile nitrogen- and/or sulfur-containing phosphorus ligands and their applications to non-enantioselective homogeneous catalysis,[23–27] as well as chiral phosphorus ligands for asymmetric induction.[28–32] Taking into account that bidentate ligands have been found to give excellent control in asymmetric catalysis, and in particular chiral *P*,*N*-ligands represent some of the most important asymmetric inducers,[33–34] in the present work we wish to publish the synthesis of new rhodium complexes with a chiral nitrogen-containing diphosphite or phosphonite ligand and their applications to hydroformylation and hydrogenation.

RESULTS AND DISCUSSION

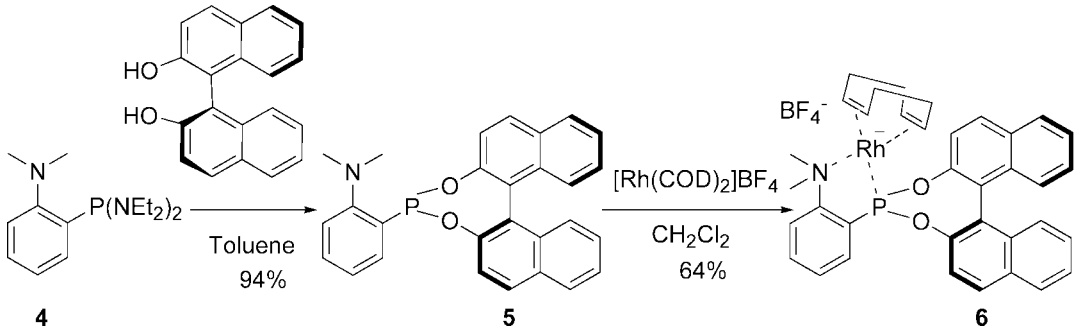
Synthesis of the chiral ligands and the rhodium complexes

Chiral diphosphite **2** was prepared by the reaction of *N*-phenyldiethanolamine **(1)** with two equivalents of [(*R*)-(1,1′-binaphthalene-2,2′-diyl)]chlorophosphite in tetrahydrofuran (THF) in the presence of pyridine (Scheme 1). The presence of only one singlet at δ 140.00 in the ^{31}P NMR spectrum of the ligand clearly indicates the equivalence of the two phosphorus atoms. Treatment of $[Rh(COD)_2]BF_4$ in dichloromethane solution with one equivalent of ligand **2** yielded the cationic rhodium complex **3**. Because we failed to grow crystals of the complex suitable for X-ray analysis, the coordination mode in the complex was determined by NMR. The ^{31}P NMR spectrum of **3** shows a doublet at δ 123.17 ($J_{Rh,P} = 259.4$ Hz). This observation, together with the lack of coupling between the two phosphorus atoms, indicates that both phosphorus atoms are equivalent and bonded to the metal. Additionally, the observation in the ^{13}C NMR spectrum of **3**, in which the NCH_2 resonance is shifted to low field compared with the corresponding resonance in the free ligand, is evidence for a probable Rh–N interaction.[23,25,35]

Synthesis of the chiral phosphonite **5** was achieved by the reaction of 2-(*N*,*N*-dimethylaminophenyl)-bis(diethylamino) phosphine (**4**, prepared by a known procedure)[36] with one equivalent of *R*-BINOL (Scheme 2). Treatment of $[Rh(COD)_2]BF_4$ with one equivalent of ligand **5** yielded the cationic rhodium complex **6**. The chemical shift (δ 168.87) and the Rh–P coupling constant (248.0 Hz) in the ^{31}P NMR



Scheme 1. Synthesis of rhodium complex with a chiral nitrogen-containing diphosphite.

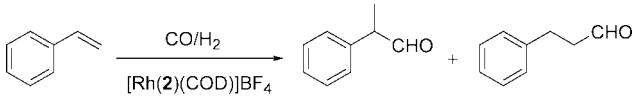


Scheme 2. Synthesis of rhodium complex with a chiral nitrogen-containing phosphonite.

spectrum of **6** are in accordance with the corresponding values of five-membered chelate rhodium complexes with *P,N*-phosphonites,[37] indicating a Rh–N interaction. The shifting of the NCH_3 resonance in the ^1H and ^{13}C NMR spectra of **6** at low field compared to the corresponding resonances in the ligand **5** are also evidence for this interaction.[23,25,35]

Hydroformylation

The catalytic activity of the rhodium complex **3** was tested on the hydroformylation of styrene under variable conditions of pressure and temperature (Scheme 3 and Table 1). Catalysis was performed by mixing styrene, $[Rh(COD)_2]BF_4$ and ligand **2** in the ratio 1000 : 1 : 1.1. The catalyst displays a high to quantitative chemoselectivity to aldehydes (>99.5%), a high activity and a high regioselectivity (up to 96%) towards the branched aldehyde. The variation observed in this work in



Scheme 3. Hydroformylation of styrene.

Table 1. Hydroformylation of styrene catalysed by [Rh(**2**)(COD)]BF_4[a]

Entry	*P* (bar)	*T* (°C)	Time (h)	Conv. (%)[b]	B/L[b]
1	100	25	20	44	96/4
2	100	40	4	66	95/5
3	100	60	1	95	91/9
4	100	60	4	100	91/9
5	100	80	0.5	100	75/25
6	50	40	4	37	95/5
7	20	40	62	95	85/15
8	10	40	62	52	81/19

[a] Reactions were carried out in dichloromethane, with styrene, $[Rh(COD)_2]BF_4$ and **2** in the ratio 1000 : 1 : 1.1.
[b] Conversions and regioselectivities (branched/linear aldehyde) were determined by GC. In all experiments, the enantiomeric excess concerning the branched aldehyde was determined by chiral GC and found to be negligible.

the conversions of styrene and the regioselectivities in the resulting aldehydes, under variable conditions of pressure and temperature, was as expected for hydroformylation of styrene using rhodium systems.

Although this system has high activity, unfortunately the branched 2-phenylpropanal was always obtained as a racemic mixture and the enantioselectivity was not increased by using a ligand/Rh ratio of 2 : 1. The negligible enantioselectivity observed by complex **3** is not very surprising because, in the literature, examples of rhodium systems with *N*-containing phosphites or phosphonites affording high conversion, chemo- and regioselectivity but no enantioselectivity for the hydroformylation of styrene have been reported.[37] These results are explained by displacement of the ligand from the rhodium centre during the catalytic cycle and the formation of unmodified achiral hydrido-carbonyl-rhodium species.[37] Additionally, a possible reason for the zero values of enantioselectivity observed by complex **3** is the conformationally flexible large metal chelate ring in **3**, in accordance with the explanation given for the low enantioselectivities observed for asymmetric hydrogenation by DIOP-type 1,4-diphosphanes, in which the seven-membered chelate ring is conformationally flexible.[38]

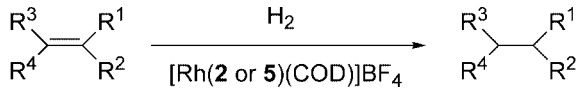
Hydrogenation

Complexes **3** and **6** were tested in the enantioselective hydrogenation of the standard substrates (*Z*)-*N*-acetamido cinnamate (*Z*-ApMe) and dimethyl itaconate ($ItMe_2$), as well as the industrially important (*E*)- and (*Z*)-methyl 3-acetamidobutenoate (*E*- and *Z*-AbMe) (Scheme 4 and Table 2). Catalysis was performed by *in situ* mixing of the substrate, $[Rh(COD)_2]BF_4$ and ligand **2** or **5** in the ratio 100 : 1 : 1 under normal pressure at 25 °C. For ligand **2**, hydrogenations were also performed under 50 bar of H_2 pressure. In most cases the enantioselectivities were higher in solvents of low polarity (THF, dichloromethane) than in methanol. With the exception of dimethyl itaconate, other prochiral substrates were reduced with very low rates. Probably, in these hydrogenations, strong hemi-labile interactions of the nitrogen functionalities with the rhodium centre take place.[21] Usually such interactions give rise to 18-electron complexes of rhodium that cannot undergo oxidative addition of hydrogen, therefore inhibition

Table 2. Hydrogenation of prochiral substrates catalysed by [Rh(**2** or **5**)COD]BF_4[a]

Entry	Ligand	Substrate	Solvent	*P* (bar)	Time (min)	Conv. (%)[b]	% ee (Conf.)[c]
1	**2**	*Z*-ApMe	THF	1	1150	100	8.8 (*S*)
2	**2**	*Z*-ApMe	Methanol	1	1250	100	2.0 (*S*)
3	**5**	*Z*-ApMe	THF	1	180	5	8.8 (*R*)
4	**5**	*Z*-ApMe	Methanol	1	120	6	32.4 (*R*)
5	**2**	*E*-AbMe	THF	1	1250	13	23.3 (*S*)
6	**2**	*E*-AbMe	Methanol	1	1250	52	0.9 (*S*)
7	**5**	*E*-AbMe	Methanol	1	1020	83	0
8	**2**	*Z*-AbMe	THF	1	1140	10	6.1 (*S*)
9	**2**	*Z*-AbMe	Methanol	1	1350	90	0.6 (*S*)
10	**5**	*Z*-AbMe	Methanol	1	160	22	1.8 (*R*)
11	**2**	$ItMe_2$	THF	1	1250	100	4.7 (*R*)
12	**2**	$ItMe_2$	Methanol	1	140	100	0.3 (*R*)
13	**5**	$ItMe_2$	THF	1	210	100	0
14	**5**	$ItMe_2$	Methanol	1	31	100	0
15	**5**	$ItMe_2$	Dichloromethane	1	130	4	11.6 (*R*)
16	**2**	*Z*-ApMe	THF	50	300	100	28.7 (*S*)
17	**2**	*E*-AbMe	THF	50	1440	35	5.7 (*S*)
18	**2**	*Z*-AbMe	THF	50	1080	15	11.4 (*S*)
19	**2**	$ItMe_2$	THF	50	960	100	10.3 (*R*)

[a] The experiments were performed in 15 ml of solvent at 25 °C, with substrate, $[Rh(COD)_2]BF_4$ and ligand in the ratio 100 : 1 : 1.
[b] Conversions were determined by ^1H NMR.
[c] Enantiomeric excess was determined as described in Ref. 29.



***Z*-ApMe:** R^1 = COOMe, R^2 = NHAc, R^3 = H, R^4 = Ph
***E*-AbMe:** R^1 = COOMe, R^2 = H, R^3 = Me, R^4 = NHAc
***Z*-AbMe:** R^1 = H, R^2 = COOMe, R^3 = Me, R^4 = NHAc
$ItMe_2$: R^1 = CH_2COOMe, R^2 = COOMe, R^3 = H, R^4 = H

Scheme 4. Hydrogenation of prochiral substrates.

of the hydrogenation is observed macroscopically. Only after dissociation of the hemi-labile group is an unsaturated catalytically active rhodium species formed. In the case of ligand **2** after the dissociation, a ten-membered chelate ring is formed. This ring is conformationally flexible so that no stereodifferentiation occurs. The reason for the poor stereoselectivity achieved with ligand **5**, which forms a five-membered chelate ring, is unclear.

EXPERIMENTAL

General

[(*R*)-(1,1′-Binaphthalen-2,2′-diyl)]chlorophosphite was prepared by the reaction of (*R*)-1,1′-bi(2-naphthol) with an excess of PCl_3.[28] The synthesis of 2-(*N*,*N*-dimethylaminophenyl)-bis(diethylamino)phosphine **(4)** was achieved by a known procedure[36] via lithiation of 2-bromo-*N*,*N*-dimethylaniline, which in turn was prepared by methylation of 2-bromo-aniline.[39] Complex $[Rh(COD)_2]BF_4$ was prepared from rhodium trichloride according to a literature procedure.[40–42] Both (*E*)- and (*Z*)-methyl 3-acetamidobutenoate (*E*- and *Z*-AbMe) were synthesized following a known protocol.[29] All other chemicals were commercially available. All preparations and catalysis were carried out under argon by using dry and degassed reagents and solvents.

Hydroformylation using syngas (CO_2–H_2, 1:1) was performed in a stainless-steel autoclave (300 ml) with magnetic stirring. Hydrogenation experiments were carried out under normal pressure and isobaric conditions with an automatic gas-measuring device (1.0 atm overall pressure over the solution). Some hydrogenations were performed under 50 bar of H_2 pressure in an autoclave. The NMR measurements were made using a Bruker AC 300 (300.13 MHz, 75.47 MHz and 121.50 MHz for ^1H, ^{13}C and ^{31}P, respectively); ^1H and ^{13}C NMR shifts were referenced to the solvent and the ^{31}P NMR shifts were referenced to external 85% H_3PO_4 in D_2O. Distinction of the CH, CH_2 and CH_3 carbons in the ^{13}C-NMR spectra was performed by DEPT-NMR experiments. Chemical ionization mass spectrometry measurements were made using a Finnigan MAT TSQ 7000 and electron impact gas chromatography–mass spectrometry was carried out using a Varian Saturn 2000 with a

30 m × 0.25 mm DB5-MS column. Gas chromatography was undertaken using a Varian Star 3400 CX with a 30 m × 0.53 mm DB5 column. Optical rotations were measured on a Perkin-Elmer 141 or Gyromat-HP polarimeter. The enantiomeric excess of the aldehyde (hydroformylation product) was determined by gas chromatography of the distilled product (Varian Star 3400 CX with a β-DEX 225, fused silica capillary column 30 m × 0.25 mm × 0.25 μm). The enantiomeric excesses of the hydrogenation products were determined as described elsewhere.[29]

Syntheses

N,N-Bis{[(R)-1,1′-binaphthalene-2,2′-diyl-phosphite]ethyl}benzenamine **(2)**

A solution of *N*-phenyldiethanolamine (0.22 g, 1.22 mmol) in THF (20 ml) was added dropwise to a solution of [(*R*)-(1,1′-binaphthalene-2,2′-diyl)]chlorophosphite (0.86 g, 2.44 mmol) and pyridine (0.53 ml) in THF (20 ml), using an ice–water cooling bath, and then stirred at room temperature overnight. The reaction mixture was filtered to remove the salts, the volatile materials of the resulting solution were evaporated under reduced pressure and the remaining solid was washed with ether (2 × 20 ml) and dried at 75 °C under vacuum to yield **2** (0.83 g, 1.03 mmol, 84%) as a white solid; m.p.: 177–180 °C. $[\alpha]_D^{25} = -430$ (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 7.98–7.73 (m, 8H, Ar); 7.49–7.21 (m, 16H, Ar); 7.07 (t, $J = 7.9$ Hz, 2H, Ar); 6.69 (t, $J = 7.3$ Hz, 1H, Ar); 6.49 (d, $J = 8.6$ Hz, 2H, Ar); 4.04–3.95 (m, 2H, CH_2O); 3.88–3.77 (m, 2H, CH_2O); 3.60–3.42 (m, 4H, CH_2N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.73–112.07 (Ar); 62.05 (CH_2O); 51.90 (CH_2N). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 140.00 (s).

Rhodium(1+)-[(1,2,5,6)-1,5-cyclooctadiene]-⟨N,N-Bis{[(R)-1,1′-binaphthalene-2,2′-diyl-phosphite]ethyl}benzenamine⟩-tetrafluoroborate(1−) **(3)**

A solution of the ligand **2** (0.07 g, 0.08 mmol) in dichloromethane (5 ml) was added dropwise to the dark-red solution of $[Rh(COD)_2]BF_4$ (0.03 g, 0.08 mmol) in dichloromethane (2 ml) using a dry ice–acetone cooling bath. The reaction mixture was warmed slowly to room temperature within 1 h and stirred at this temperature for an additional 2 h. The resulting orange solution was evaporated under reduced pressure and the remaining solid was washed with ether (2 × 5 ml) and dried, yielding **3** (0.07 g, 0.06 mmol, 75%) as an orange solid; m.p.: 280 °C. ^{1}H NMR (CD_2Cl_2): δ 8.21–7.89 and 7.68–7.35 (2 × m, 24H, Ar); 6.95–6.89 (m, 2H, Ar); 6.53 (t, $J = 7.3$ Hz, 1H, Ar); 6.23 (d, $J = 8.5$ Hz, 2H, Ar); 6.10 (br s, 2H, COD-CH); 4.17 (br m, 4H); 3.84 (br m, 2H); 3.55 (br m, 4H); 2.34 (br m, 4H); 1.81 (br m, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 153.11–111.12 (Ar); 107.44 and 107.34 (COD-CH); 68.65 (CH_2O); 54.80 (CH_2N); 31.96 and 27.89 (COD-CH_2). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 123.17 (d, $J_{Rh,P} = 259.4$ Hz). ESI MS *m/z*: 951 ([M−COD−BF_4 + CH_3CN]$^+$).

P-(N,N-Dimethylaminophenyl)-[(R)-1,1′-binaphthalene-2,2′-diyl]phosphonite **(5)**

A solution of (*R*)-1,1′-bi(2-naphthol) (0.28 g, 0.98 mmol) in toluene (50 ml) was added to 2-(*N,N*-dimethylaminophenyl)-bis(diethylamino)phosphine **(4)** (0.29 g, 0.98 mmol) and the mixture was refluxed for 63 h. The solvent was evaporated under reduced pressure and the remaining solid was washed with pentane (2 × 15 ml) and dried, yielding **5** (0.40 g, 0.92 mmol, 94%) as a white solid; m.p.: 180–190 °C. $[\alpha]_D^{25} = -89.6$ (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): 8.04–6.72 (5 × m, 16H, Ar); 2.95 (s, 6H, NCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.97–111.90 (Ar); 46.49 (NCH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 178.81 (s). GC–MS (EI) *m/z* (relative intensity): 435 (17) [M]$^+$; 286 (100); 149 (40).

Rhodium(1+)-[(1,2,5,6)-1,5-cyclooctadiene]-{P-(N,N-dimethylaminophenyl)-[(R)-1,1′-binaphthalene-2,2′-diyl]phosphonite}-tetrafluoroborate(1−) **(6)**

A solution of the ligand **5** (0.06 g, 0.14 mmol) in dichloromethane (10 ml) was added dropwise to the dark-red solution of $[Rh(COD)_2]BF_4$ (0.06 g, 0.14 mmol) in dichloromethane (5 ml) using a dry ice–acetone cooling bath. The reaction mixture was warmed slowly to room temperature within 1 h and stirred at this temperature for an additional 2 h. The resulting dark-orange solution was evaporated under reduced pressure to ~0.5 ml, and slow diffusion of ether caused the precipitation of an orange solid. The supernatant solution was decanted and the solid was washed with ether (15 ml) and dried, yielding rhodium complex **6** (0.07 g, 0.09 mmol, 64%). ^{1}H NMR ($CDCl_3$): δ 8.15–6.73 (m, 16H, Ar); 5.94 (br s, 1H, COD-CH); 5.68 (br s, 1H, COD-CH); 5.30 (br s, 1H, COD-CH); 4.26 (br s, 1H, COD-CH); 3.32 (s, 6H, NCH_3); 2.73–2.40 (m, 8H, COD-CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.29–117.92 (Ar); 107.42 (d, $J_{Rh,C} = 7.3$ Hz, COD-CH); 79.44 (d, $J_{Rh,C} = 12.2$ Hz, COD-CH); 71.74 (d, $J_{Rh,C} = 12.2$ Hz, COD-CH); 53.42 (br m, NCH_3); 32.56–26.73 (COD-CH_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 168,87 (d, $J_{Rh,P} = 248.0$ Hz). FAB MS: *m/z* 646 ([M−BF_4]$^+$).

Hydroformylation

In a typical experiment, a solution of ligand **2** in dichloromethane (4 mM, 3.3 ml, 0.013 mmol) and a solution of $[Rh(COD)_2]BF_4$ in dichloromethane (4 mM, 3 ml, 0.012 mmol) were placed under argon in a flame-dried Schlenck flask and stirred at room temperature for 15 min, after which styrene (1.37 ml, 11.957 mmol) was added. The resulting solution was transferred under argon via a syringe to an oven-dried autoclave, which was then closed and pressurized with syngas ($CO-H_2$, 1 : 1) to the appropriate initial pressure and brought to the corresponding temperature. After the required reaction time, the autoclave was cooled to room temperature and the pressure was carefully released. A sample of the solution was passed through celite and analysed by GC and GC–MS. Conversions were determined by GC. The

remaining reaction mixture was distilled by vacuum and the distilled products were analysed by GC using a chiral column in order to determine the enantiomeric excess of the aldehyde.

Hydrogenation

Complex $[Rh(COD)_2]BF_4$ (0.0041 g, 0.01 mmol), solvent (7.5 ml), a solution of ligand **2** or **5** in the same solvent (1.3 mM, 7.5 ml, 0.01 mmol) and the prochiral olefin (1 mmol) were mixed and the reaction mixture was stirred vigorously under hydrogen (1 bar) at 25 °C until the calculated amount of hydrogen had been consumed. Some experiments were performed in an autoclave using 50 bar of hydrogen pressure. Conversions were determined by ^1H NMR and enantioselectivities by chiral GC.

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