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Communication

Synthesis of novel rhodium phosphite catalysts for efficient and selective isomerization–hydroformylation reactions

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ABSTRACT

New modular H_8-BINOL-based phosphite ligands have been synthesized. High activity and regioselectivity has been achieved in the rhodium-catalyzed isomerization–hydroformylation of internal olefins. The active catalysts have been characterized by *in situ* NMR studies.

1. Introduction

Hydroformylation of olefins constitutes one of the most important homogeneously catalyzed processes in industry, which covers an annual production of almost ten million tons of aliphatic aldehydes [1]. Although hydroformylation reactions are widely applied in natural product synthesis [2] and organic synthesis [3], there still exists a significant academic and industrial interest to develop more active and selective catalysts for such transformations [4]. From an economical point of view one of the most important goals in current hydroformylation research is the selective conversion of internal olefins to linear aldehydes (Scheme 1) [5].

This domino reaction sequence offers the opportunity to use cheaper mixtures of internal and terminal olefins as feedstock for bulk chemicals and to save time and energy, which is needed for the additional purification steps [6]. In order to obtain the industrially desired linear aldehydes from internal olefins, the catalyst system needs to actively isomerize internal olefins (Scheme 1, step a). Notably, the thermodynamic mixture, even of low molecular weight olefins e.g. butenes, contains less than 5% of the terminal olefin. Hence, hydroformylation of the terminal olefin must occur at much faster rate, typically a factor 10–100, compared to the hydroformylation of the different internal olefins (Scheme 1, step b *versus* step c). Moreover, hydroformylation of the terminal olefin needs to be highly selective towards the linear aldehyde (Scheme 1, step c).

Major advancements have been made toward this goal in the last decade. Particularly, efforts have been spent on the design and synthesis of new ligands. Notable examples constitute the bisphosphite ligands of UCC [7] and Dupont/DSM [8], Xantphos ligands by van Leuween and co-workers [9], acylphosphite and phosphonite ligands by Börner and co-workers [10] or substituted Naphos ligands, that were introduced by us [11]. Recently, also efficient pyrrole-based tetraphosphorous ligands were developed by Zhang and co-workers [12]. In addition, regioselective isomerization–hydroformylation sequences of internal olefins have been reported in a biphasic system with water-soluble sulfonated Naphos derivatives [13]. Among the various ligand types for isomerization–hydroformylation reactions, bulky bisphosphites are probably the most versatile class of ligands [7,14]. In general, phosphite ligands are attractive because they are easily prepared from inexpensive PCl_3 and alcohols. Moreover, they are less sensitive to air and other oxidizing agents than phosphines.

2. Results and discussion

Herein, we report the synthesis of new modular H_8-BINOL-based phosphite ligands that display excellent activity in the hydroformylation of internal and terminal olefins with high selectivities for the linear aldehydes.

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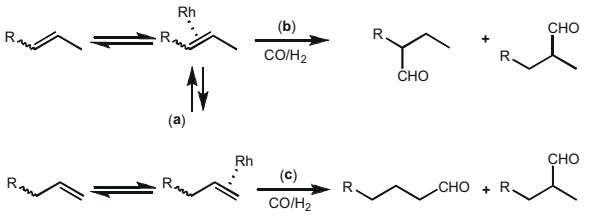


Scheme 1. Isomerization–hydroformylation reactions: From internal olefins to linear aldehydes.

Recently, we developed an improved route for the synthesis of octahydrogenated 3,3′-dibromo-substituted binaphthols [15]. Applying this three step sequence a variety of novel binaphthol derivatives is accessible on multi-g scale. Based on their availability we had the idea to apply these building blocks for novel bisphosphite ligands depicted in Fig. 1.

While monodentate ligands based on the dibromo-substituted H_8-BINOL skeleton are well known [16], no bisphosphites bearing at least two substituted H_8-BINOL skeletons have been described so far. Nevertheless, the synthesis of selected ligands [17] proceeds straightforward in four steps from commercially available 2,2′-binaphthol **1a** [18]. After hydrogenation with Pd/C and regioselective bromination of octahydrobinaphthol the resulting 3,3′-dibromooctahydro-2,2′-binaphthol was treated with phosphortri chloride to give the corresponding chlorophosphite **2**. Subsequent treatment of partially hydrogenated and non-hydrogenated binaphthol derivatives **1a–c** with two equivalents of **2** in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine (DMAP) gave ligands **3**–**5** (Scheme 2).

Surprisingly, when using 2,2′-dihydroxybiphenyl as bridging part ring interconversion occurred and different compounds were detected by ^{31}P NMR. Nevertheless, from this mixture the asymmetric diphosphite ligand **6** could be successfully isolated and its structure is unambiguously proven by means of different NMR spectroscopic data such as NOESY, COSY, HMQC, HMQC-TOCSY, and HMBC (Scheme 3).

In order to understand the nature of catalytically active rhodium complexes of these ligands high pressure NMR studies were performed in the presence of ligand **3** (Fig. 2). It is well known that bidentate phosphite ligands form stable rhodium-hydride species, denoted as [HRh(PP)(CO)$_2$], which are characterized by a trigonal-bipyramidal structure under typical hydroformylation condition [19]. Hence, complex **8** was prepared *in situ* under 20 bar of CO/H_2 by adding 1.1 equivalent of **3** to the catalyst precursor [Rh(acac)(CO)$_2$]. From the lineshape (Fig. 2a, a doublet of triplet-like patterns, splitting 252 Hz), which is not first order, a dinuclear structure with chemically equivalent, but magnetically inequivalent phosphorus atoms can be deduced. No clear statement is possible whether this intermediate has terminal or bridging carbonyl groups, but such a complex has been described with the BIPHEPHOS ligand (**10**) [20]. Complex formation occurred within 1 h at room temperature as evidenced by the presence of one broad doublet in the ^{31}P NMR spectra and one triplet of doublets for the hydride signal in the ^{1}H NMR spectra (Fig. 2b and c). The ^{1}H-decoupled ^{31}P NMR spectra displays a typical Rh–P coupling constant (^1J (Rh,P) = 240 Hz) of a rhodium-hydride complex with trigonal-bipyramidal structure. The hydridorhodium complex shows a small P–H coupling constant (^2J (P,H) = 8.4 Hz) indicative of a bisequatorial (ee) coordination mode [18]. Further evidence for the bisequatorial complex is provided by IR measurements owing to two absorption bands for carbonyl vibrations around 1993 and 2017 cm^{-1}, which are characteristic for ee isomers [21].

Next, we investigated the catalytic potential of the novel bisphosphite ligands in comparison with known highly active ligands **9** [10] and BIPHEPHOS **10** (Fig. 3) [7,22], and the unsubstituted H_8-Binaphthol-based ligand **11** [23]. Ligand **11** has been prepared starting from racemic binaphthol.

Therefore, ligands **3**–**6** were tested in the rhodium-catalyzed hydroformylation of different internal and terminal olefins. The active catalysts were prepared *in situ* by adding an appropriate amount of bisphosphite ligand to [Rh(acac)(CO)$_2$]. All reactions were carried out in THF with isooctane as internal standard. Initially, the effects of ligand/metal ratio, temperature, and pressure on the regioselectivity were studied using 2-pentene as substrate. We applied 2-pentene as a benchmark for internal olefins, especially for the commercially important 2-butene. As expected without any ligand only low activity (TOF = 179) and low regioselectivity (*n*/iso = 41:59) are observed (Table 1, entry 1). On the other hand adding **3** high yield (85%) and excellent regioselectivity (*n*/iso = 90:10) are obtained under similar conditions (Table 1, entry 6). As shown in Table 1 a ligand/metal ratio of 2 is sufficient to achieve high regioselectivity. Applying a higher ligand/metal ratio the reaction rate decreased but the regioselectivity did not improve (Table 1, entry 2). This is an important advantage compared to most known hydroformylation catalysts based on bisphosphites, for which a larger excess of ligand is required. In agreement with other known catalysts the CO/H_2 pressure influences both the regioselectivity as well as the reaction rate (Table 1, entry 4–6)). At high pressure (50 bar) the reaction rate and linear selectivity were lower compared to 10–20 bar synthesis gas pressure. Among the different biphosphites, ligands **3** and **5** gave remarkably high linear to branched aldehyde ratios with the highest reaction rate (Table 1, entries 6 and 9). With respect to *n*-selectivity and activity, they outperform known ligands **9** and **10**. Ligand **11** shows a linear/branched ratio of 41:59 (Table 1, entry 13). It seems that the *ortho*-substitutions in the H_8-Binol unit are crucial to achieve high *n*-selectivity.

In order to compare the ligands more appropriately, hydroformylations of 1-pentene, 1-octene and 2-octene were performed as typical benchmark reactions (Table 2). Again, without any added ligand typical non-selective hydroformylations are observed (Table 2, entries 1, 8, 13). In case of 1-pentene as substrate the 3,3'-dibromo-bis-substituted bisphosphite-rhodium catalyst (Rh/**3**) showed best activity combined with high *n*-selectivity (Table 2, entry 2). Here, a turnover frequency up to 2310 h^{-1} and excellent linear/branched ratio up to 95/5 were observed. Similarly, the hydroformylation of 1-octene in the presence of **3** occurred with a high reaction rate (average rate = 1686 mol aldehyde per mol of Rh

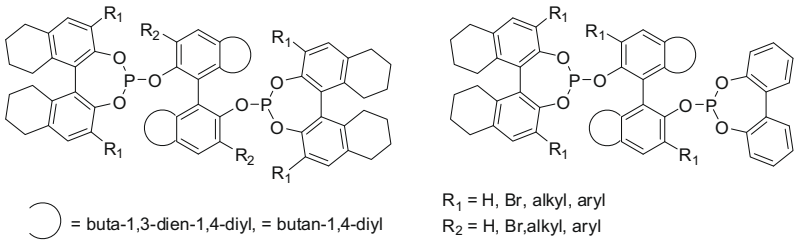
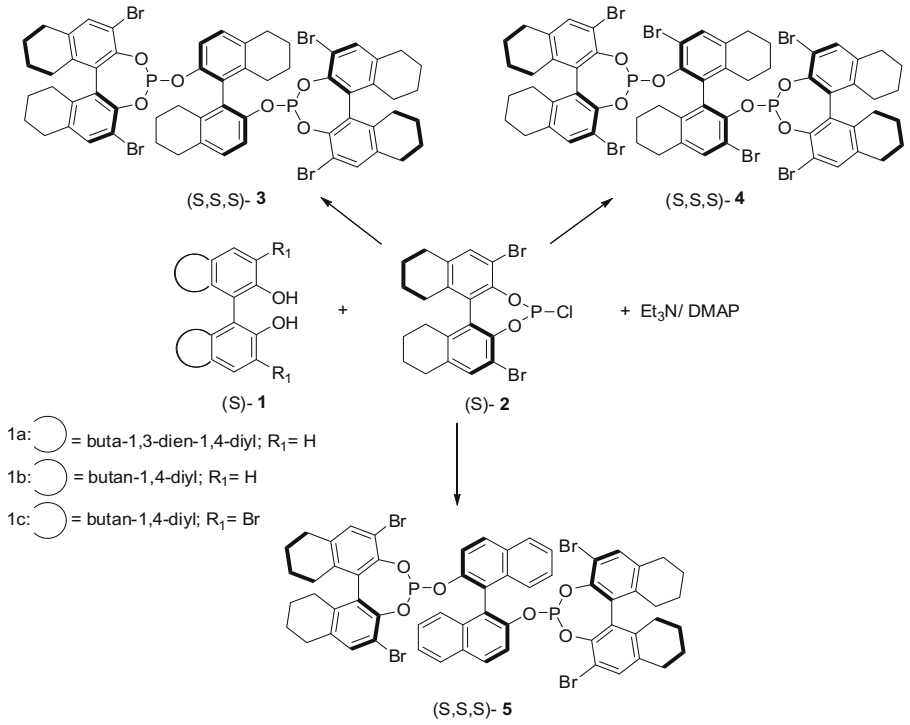
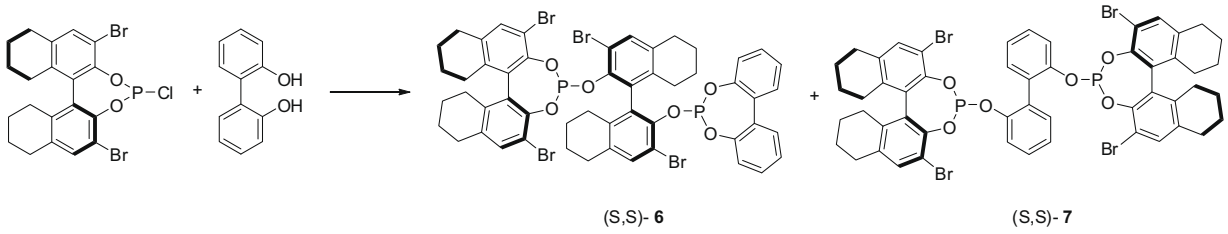


Fig. 1. Novel bisphosphite ligands.



Scheme 2. Modular synthesis of ligands **3**–**5**.



Scheme 3. Synthesis of ligand **6**.

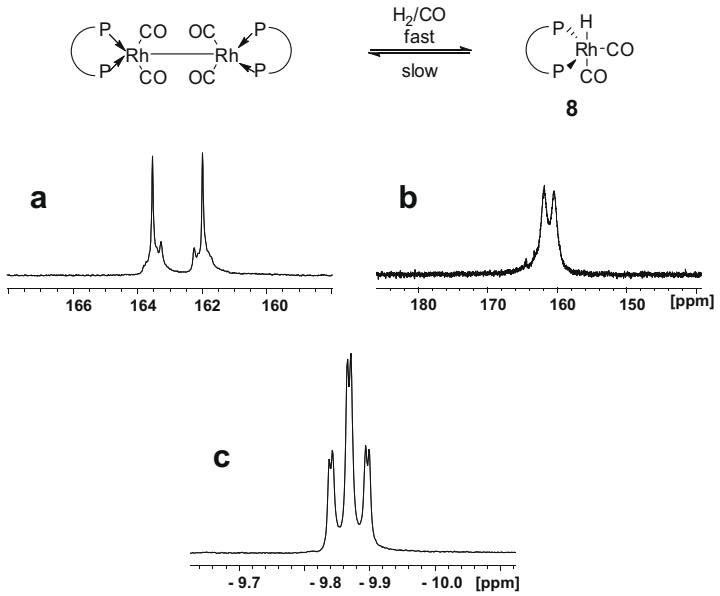


Fig. 2. Formation of complex **8**: (a) ^{31}P NMR after 35 min under pressure at rt; (b) ^{31}P NMR after 60 min under pressure at rt; (c) ^{1}H NMR of the hydride complex at rt.

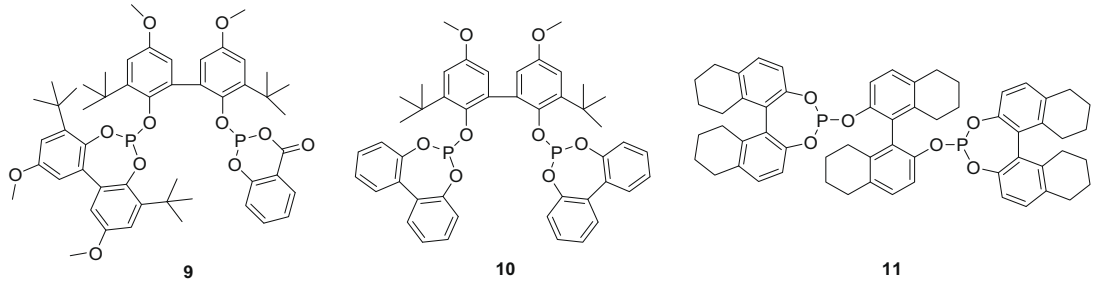
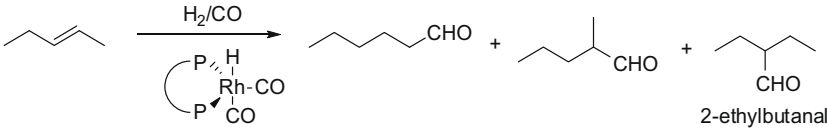


Fig. 3. Known ligands **9, 10** and **11**.

Table 1
Isomerization–hydroformylation of 2-pentene.



Entry[a]	L	Rh/L	P (bar)	Yield%[d]	*n*/iso[e]	TOF (h^{-1})
1			20	17	41/59	179
2	**3**	1/3	20	77	90/10	824
3[b]	**3**	1/2	20	46	88/12	495
4	**3**	1/2	50	63	81/19	677
5	**3**	1/2	10	85	90/10	914
6	**3**	1/2	20	85	90/10	916
7[c]	**3**	1/2	20	26	90/10	1712
8	**4**	1/2	20	40	85/15	432
9	**5**	1/2	20	84	89/11	900
10	**6**	1/2	20	45	88/12	481
11	**9**	1/2	20	85	69/31	913
12	**10**	1/2	20	39	96/4	420
13	**11**	1/2	20	82	41/59	877

[a] 30 mmol of 2-pentene, 1.39×10^{-5} mol Rh(acac)$(CO)_2$ (50 ppm Rh), Rh/L/substrate = 1/2/2146, 30 ml THF, isooctane as internal standard, CO/H_2 = 1/1 constant, 2 h, 120 °C.
[b] T = 100 °C.
[c] Yield determined after 20 min.
[d] Yield determined by GC analysis.
[e] 2-Ethylbutanal was not detected except in entry 1.

per h) and a high selectivity for the linear aldehyde (linear/branched ratio of 96:4). Also in the reaction of less reactive 2-octene significant amounts of *n*-nonanal were found (*n*/iso ratio up to 87:13; Table 2, entry 14), indicative of the high tendency of these catalysts for alkene isomerization.

No significant differences are observed between ligands **3** and **5**, which only differ in the bridging part (H_8-BINOL *versus* BINOL). However, the less bulky ligand **6** gave lower reaction rate in the case of 1- and 2-pentene in comparison with ligands **3**, **4**, and **5** demonstrating the importance of steric bulkiness on both sides of the bisphosphite.

Finally, several other olefins were hydroformylated in the presence of Rh(acac)$(CO)_2$/**3**. The results of the catalytic reactions are listed in Table 3. 2,3-Dimethyl-1-butene represents the class of 1,1-disubstituted alkenes. Here, the aldehyde selectivity and regioselectivity is higher than 99%. Also in the case of 3,3-dimethyl-1-butene the corresponding linear aldehyde is the exclusive reaction product (Table 3, entry 2). The hydroformylation of styrene proceeded preferentially to give the linear aldehyde, too (Table 3, entry 5). However, due to the increased thermodynamic stability of the intermediate benzylrhodium complex, the selectivity is lower. Interestingly, applying *N*-vinylphthalimide the major product is the branched aldehyde due to the increased stability of the branched metal complex (Table 3, entry 4). In addition to pure starting materials also mixtures of olefins are selectively converted [24]]. Hence, domino isomerization–hydroformylation of a *n*-octene mixture containing only 3.3% of 1-octene led preferentially to *n*-nonanal (n/iso selectivity = 84:16) (Table 3, entry 6).

3. Conclusions

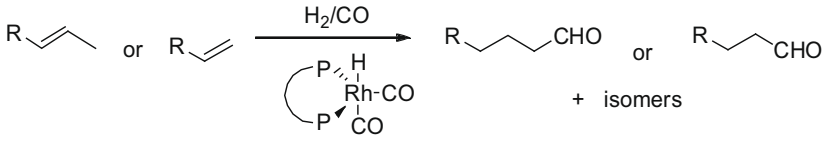
In summary, new modular bisphosphite ligands have been conveniently synthesized. The corresponding rhodium complexes are highly active catalysts for isomerization–hydroformylation reactions of internal olefins. The active catalysts have been characterized by *in situ* NMR studies. Under model conditions some of the new ligands display higher activity compared to highly active acylphosphite **9** and BIPHEPHOS **10**.

4. Experimental

4.1. General methods

All reactions were performed under argon atmosphere using standard Schlenk techniques. The solvents were dried by standard procedures, distilled and stored under argon.

Table 2
Hydroformylation of benchmark olefins.

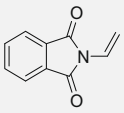


Entry[a]	Olefin	Ligand	Yield (%)[d]	*n*/iso[e]	TOF (h^{-1})
1	1-pentene		95	48/52	2538
2	**1-pentene**	**3**	**86**	**95/5**	**2310**
3	1-pentene	**4**	94	74/26	2528
4	1-pentene	**5**	83	95/5	2226
5	1-pentene	**6**	78	94/6	2097
6	1-pentene	**9**	90	87/13	2410
7	1-pentene	**10**	75	99/1	2009
8[b]	1-octene		11	48/52	234
9[b]	**1-octene**	**3**	**82**	**96/4**	**1686**
10[b]	1-octene	**4**	76	96/4	1564
11[b]	1-octene	**5**	78	92/8	1605
12[b]	1-octene	**6**	76	95/5	1571
13[c]	2-octene		21	32/68	110
14[c]	2-octene	**3**	73	87/13	377
15[c]	2-octene	**4**	54	86/14	280
16[c]	**2-octene**	**5**	**77**	**85/15**	**396**
17[c]	2-octene	**6**	59	85/15	305

[a] 30 mmol of olefin, 5.59×10^{-6} mol Rh(acac)$(CO)_2$ (20 ppm Rh), Rh/L/substrate = 1/3/5364, T = 100 °C, P = 50 bar (CO/H_2 = 1/1) constant, 30 ml THF, isooctane as internal standard, 2 h.
[b] Rh(acac)$(CO)_2$ (7.29×10^{-6} mol) (25 ppm Rh), Rh/L/substrate = 1/3/4111, T = 120 °C, P = 20 bar (CO/H_2 = 1/1) constant.
[c] Rh(acac)$(CO)_2$ (1.46×10^{-5} mol) (50 ppm Rh), Rh/L/substrate = 1/3/2059, T = 120 °C, P = 20 bar (CO/H_2 = 1/1) constant.
[d] Yield of aldehyde determined by GC analysis.
[e] 2-Ethylbutanal was not detected except in entry 1; in the hydroformylation of 1-octene and 2-octene the branched aldehydes consist mainly of 2-methyloctanal. No significant amounts (<2%) of other products were detected apart from isomerized olefin except in cases without any ligand added.

^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker Spectrometer AV 300 and AV 400. The calibration of ^1H and ^{13}C spectra was carried out on solvent signals ($\delta CDCl_3$ = 7.27 and 77.0; δC_6D_6 = 7.16 and 128.06 and δCD_2Cl_2 = 5.32 and 53.8). The ^{31}P NMR chemical shifts are referenced to 85% H_3PO_4. The ^1H and ^{13}C NMR signals were assigned by DEPT spectra. EI mass spectra were recorded on an MAT 95XP spectrometer (Thermo ELECTRON CORPORATION). Chemical shifts are given in ppm and coupling constants are reported in Hz. IR spectra were recorded as toluene-d_8 on a Nicolet 6700 FT-IR. Hydroformylation reactions were performed in100 ml autoclaves connected to burettes as gas reservoir that kept the CO/H_2 gas pressure constant throughout the reaction. The following compounds were prepared according to the literature procedures: Octahydrobinaphthol **1b** [25], (*S*)-3,3'–dibromo–5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'–diol **1c** [26] and phosphorochloridite [27].

Table 3
Substrate screening with Rh/**3** catalyst.

Entry	Substrate	*t* (h)	Yield%[g]	*n*/iso	TOF (h^{-1})
1[a,b]		2	41	>99	875
2[a,c]		1	97	>99	2051
3[a,c]		24	55		49
4[a,d]		2	80[h]	35/65[i]	1592
5[e]		1	>99	70/30	1998
6[f]	Octene mixture	4	84	84/16	461

[a] 30 mmol of substrate, T = 120 °C, P = 20 bar (CO/H_2 = 1/1) constant, 30 ml THF.
[b] Rh(acac)$(CO)_2$ (7.09×10^{-6} mol) (25 ppm Rh), Rh/L/substrate = 1/3/4230.
[c] Rh(acac)$(CO)_2$ (1.41×10^{-6} mol), Rh/L = 1/2/2115.
[d] Rh Rh(acac)$(CO)_2$ (50 ppm), Rh/L = 1/2.
[e] 30 mmol of substrate, 1.50×10^{-5} mol Rh(acac)$(CO)_2$, Rh/L/substrate = 1/3/2000, T = 100 °C, P = 20 bar (CO/H_2 = 1/1), 15 ml toluene.
[f] 95 mmol of substrate (3.3% 1-octene, 48.4% Z/E-2-octene, 29.2% Z/E-3-octene, 16.4% Z/E-4-octene, 2.1% isomers, 0.6% octane), 4.32×10^{-5} mol Rh(acac)$(CO)_2$ 100 ppm Rh, Rh/L/substrate = 1/2/2203, 40.5 ml toluene, performed by Dr. D. Selent/LIKAT Rostock.
[g] Yield of aldehyde determined by GC analysis.
[h] Isolated yield.
[i] Regioselectivity determined by NMR.

4.1.1. (11bS)-2,6-Dibromo-4-chloro-8,9,10,11,12,13,14,15-octahydro dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine ***2***

A three necked round-bottomed flask was charged with (*S*)-3,3'-dibromo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diol **1c** (20 mmol) in toluene (200 ml). The solution was cooled at 0 °C. Then a mixture containing PCl_3 (21 mmol), toluene (30 ml) and Et_3N (46 mmol) was added slowly via cannula and the medium was allowed to stir overnight at room temperature. The solvent and slight excess of PCl_3 were evaporated in vacuum. The compound was crystallized from pentane. White crystals, 90% yield: ^{31}P NMR (121.5 MHz, $CDCl_3$): δ (ppm) = 171.9; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.38 (s, 2H, arom.), 2.86–2.74 (m, 4H, $2CH_2$), 2.62–2.46 (m, 2H, CH_2), 2.31–2.12 (m, 2H, CH_2), 1.85–1.46 (m, 8H, $4CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 143.6 (d, J(P,C) = 3.2, C), 143.1 (d, J(P,C) = 3.9, C), 138.3 (d, J(P,C) = 1.9, C), 137.6 (d, J(P,C) = 1.9, C), 137.4 (d, J(P,C) = 1.3, C), 136.6(d, J(P,C) = 1.3, C), 133.4 (2C), 130.8 (C), 130.7 (C), 129.0 (d, J(P,C) = 1.9, C), 112.9 (d, J(P,C) = 3.2, C), 112.5 (d, J(P,C) = 2.6, C), 29.1 (CH_2), 29.1 (CH_2), 27.8 (CH_2), 27.6 (CH_2), 22.5 (CH_2), 22.4 (CH_2), 22.3 (CH_2), 22.2 (CH_2); MS (70 eV, EI): m/z (%) = 516(7.31),

452([M$^+$],100), 399(2.69), 371(7.45), 329(2.65), 292(73.87), 274(14.81), 205(6.47), 165(6.87), 91(9.77), 69(13.63), 43(14.00); HR-MS: (calc.) 513.90942, (found) 513.910640 for $C_{20}H_{18}O_2Br_2Cl_1P_1$.

4.1.2. (1S)-2,2'-bis((11bS)-2,6-Dibromo-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl ***3***

A solution of (S)-H_8-binaphthol 1b (1.3 mmol), Et_3N (3 mmol) and DMAP (0.3 mmol) in toluene (20 ml) was added slowly to a solution of the corresponding phosphoruschloridite **2** (2.63 mmol) at 0 °C and this temperature was kept for 1 h. The reaction mixture was stirred overnight and then filtered through a sintered glass funnel. Evaporation of the solvent gave white foam.

Yield = >99%; (purity = >97%). ^{31}P NMR (162 MHz, C_6D_6): δ (ppm) = 138.3; ^{1}H NMR (400 MHz, C_6D_6): δ (ppm) = 7.79 (d, J = 8.3, 2H, H_8-BINOL), 7.20 (s, 2H, Br_2–H_8-BINOL), 7.09(s, 2H, Br_2–H_8-BINOL), 6.98 (d, J = 8.3, 2H, H_8-BINOL), 2.72–2.55 (m, 6H, 3CH_2), 2.44–2.24 (m, 12H, 6CH_2), 2.22–2.10 (m, 2H, CH_2), 2.02–1.86 (m, 4H, 2CH_2), 1.62–1.49 (m, 6H, 3CH_2), 1.49–1.30 (m, 14H, 7CH_2), 1.29–1.05 (m, 4H, 2CH_2); ^{13}C NMR (100.6 MHz, C_6D_6): δ (ppm) = 147.9 (t, J(P,C) = 4.8, 2C), 144.5 (t, J(P,C) = 2.1, 2C), 143.9 (t, J(P,C) < 1, 2C), 137.9 (2C), 137.4 (2C), 136.6, (2C), 136.0 (2C), 135.1 (2C), 134.1 (2C), 133.3 (J(C,H) = 162 Hz, 2CH), 133.1 (J(C,H) = 163 Hz, 2CH), 131.4 (t, J(P,C) = 2.4, 2C), 129.8 (2CH), 129.3 (t, J(P,C) < 1, 2C), 129.0 (t, J(P,C) = 1.4, 2C), 119.1 (t, J(P,C) = 5.2, 2CH), 114.1 (d, 2C, J(P,C) = 1.3), 113.7 (2C), 29.9 (2CH_2), 28.9 (2CH_2), 28.9 (2CH_2), 28.1 (t, J(P,C) = 2.0, 2CH_2), 27.8 (2CH_2), 27.6 (2CH_2), 23.3 (2CH_2), 23.2 (2CH_2), 22.6 (2CH_2), 22.5 (4CH_2), 22.4 (2CH_2); MS (70 eV, EI): m/z (%) = 1254 ([M$^+$], 0.56), 1175 (4.02), 1095 (1.24), 760 (17.39), 759 (48.46), 757 (100.00), 755 (44.88), 677 (7.34), 482 (7.34), 401 (8.62), 323 (17.65); HR-MS: [M+Na]$^+$ (calc.) 1273.01778, (found) 1273.01636; [M+K]$^+$ (calculated) 1288.99172, (found) 1288.99114 for $C_{60}H_{56}Br_4O_6P_2$.

4.1.3. (11bS,11b'S)-4,4'-((S)-3,3'-Dibromo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2,2'-diyl)bis(oxy)bis(2,6-dibromo-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine) ***4***

Treatment of chlorophosphite **2** and **1c**, as described for compound **3**, afforded the bisphosphite **4** as a white powder. Yield = >99% (purity = >94%). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ (ppm) = 137.0; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.27 (s, 2H, arom.), 7.24 (s, 2H, arom.), 7.15 (s, 2H, arom.), 2.85–2.67 (m, 8H, 4CH_2), 2.65–2.39 (m, 8H, 4CH_2), 2.35–2.07 (m, 6H, 3CH_2), 2.03–1.89 (m, 2H, CH_2), 1.86–1.65 (m, 12H, 6CH_2), 1.86–1.24 (m, 12H, 6CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 144.7 (m, 2C), 144.1 (m, 2C), 143.2 (2C), 137.2 (2C), 137.2 (2C), 136.4 (2C), 135.9 (2C), 134.9 (2C), 134.8 (2C), 132.9 (2CH), 132.9 (2CH), 132.8 (2CH), 130.7 (m, 2C), 130.6 (2C), 129.3 (2C), 113.8 (2C), 113.2 (2C), 112.2 (2C), 29.3 (2C), 29.1 (2C), 29.0 (2C), 27.9 (2C), 27.6 (4C), 22.7 (2C), 22.6 (4C), 22.6 (2C), 22.6 (2C), 22.4 (2C); MS (70 eV, EI): m/z (%) = 1412 ([M$^+$], 0.78), 1334 (3.70), 1254 (1.55), 1174 (2.82), 917 (69.86), 915 (100.00), 911 (18.84), 481 (18.45); HR-MS: [M+Na]$^+$ (calc.) 1434.83267, (found) 1434.83466 for $C_{60}H_{54}(79Br)_3(81Br)_3NaO_6P_2$.

4.1.4. (1S)-2,2'-Bis((11bS)-2,6-dibromo-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy)-1,1'-binaphthyl ***5***

A solution of (S)-BINOL **1a** (0.8 mmol), Et_3N (1.85 mmol) and DMAP (0.3 mmol) in Et_2O/THF (7/1, 20 ml) was added slowly to a solution of the corresponding chlorophosphite **2** (1.65 mmol) in Et_2O at 0 °C and this temperature was kept for 1 h. The reaction mixture was stirred overnight and then filtered through a sintered glass funnel. Evaporation of the solvent gave white foam mixture. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ(ppm) = 136.6 (major pick 80%); ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.03 (s, 1H, arom.), 8.00 (s, 1H, arom.), 7.94–7.89 (m, arom.), 7.88 (s, 1H, arom.), 7.85 (s, 1H, arom.), 7.45–7.43 (m, arom.), 7.43–7.41 (m, 1H, arom.), 7.39 (s, 1H, arom.), 7.38–7.34 (m, arom.), 7.32–7.25 (m, arom.), 7.20–7.14 (m, arom.), 2.93–2.64 (m, CH_2), 2.56–2.37 (m, CH_2), 2.14–1.98 (m, CH_2), 177–1.60 (m, CH_2), 1.53–1.37 (m, CH_2); ^{13}C NMR (75 MHz, CD_2Cl_2): δ (ppm) = 148.4, 143.5, 143.0, 138.1, 137.1, 136.9, 135.9, 134.1, 133.1, 132.9, 131.7, 131.5, 131.0, 130.3, 128.9, 128.7, 128.4, 127.6, 127.2, 125.8, 125.4, 124.5, 124.2, 123.1, 121.8, 118.2, 113.3, 112.7, 29.2 (2C), 29.1 (2C), 27.9 (2C), 27.7 (2C), 22.7 (4C), 22.5 (2C), 22.5 (2C); MS (70 eV, EI): m/z (%) = 1247 ([M$^+$], 0.35),1169 (3.41), 1082 (0.36), 916 (4.00), 852 (1.34), 750 (100.00), 584 (9.42), 401 (3.62), 315 (11.14), 268 (28.20), 119 (5.66); HR-MS (ESI$^+$-TOF/MS): [M+Na]$^+$ (calc.) 1264.95518, (found) 1264.95262 for $C_{60}H_{48}Br_4NaO_6P_2$.

4.1.5. (11bS)-2,6-Dibromo-4-((S)-3,3'-dibromo-2'-(dibenzo[d,f][1,3,2]dioxaphosphepin-6-yloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-yloxy)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine ***6***

Treatment of chlorophosphite 2 and 2,2′-dihydroxybiphenyl as described for compound **3**, afforded a mixture of bisphosphites as a white powder. The compound **6** was isolated by precipitation in Et_2O. Isolated yield = 70%; ^{31}P NMR (162 MHz, CD_2Cl_2): δ (ppm) = 142.7 (d, J(P, P) = 50, 1P), 137.0 (d, J(P, P) = 50, 1P); ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 7.58 (s, 1H, Br_2–H_8-BINOL), 7.47 −7.45 (m, 1H, Ph), 7.45–7.42 (m, 1H, Ph), 7.39–7.32 (m, 2H, Ph), 7.30 (s, 2H, Br_2–H_8-BINOL and Ph), 7.28–7.27 (m, 1H, Ph), 7.26 (s, 1H, Br_2–H_8-BINOL), 7.22 (s, 1H, Br_2–H_8-BINOL), 7.14 (dt, J = 8.0, J = 1.04, 1H, Ph), 6.86 (dt, J = 8.0, J = 1.0, 1H, Ph), 2.85–2.33 (m, 12H, 6CH_2), 2.23–2.89 (m, 4H, 2CH_2), 1.84–1.34 (m, 16H, 8CH_2); ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ (ppm) = 150.0 (d, C, J(P, C) = 7.3, Ph), 149.0 (d, J(P, C) = 3.2, C, Ph), 146.4 (C), 144.9 (d, J(P, C) = 6.8, C), 144.0 (d, J(P, C) = 5.0, C), 143.3 (d, J(P, C) = 2.8, C), 138.5 (C), 137.9 (d, J(P, C) = 1.6, C), 137.3 (C), 137.0 (C), 136.7 (d, J(P, C) = 1.2, C), 136.2 (C), 135.7 (d, J(P, C) < 1, C), 135.3 (d, J(P, C) < 1, C), 134.2 (CH), 133.4 (CH), 133.1 (CH), 133.0 (CH), 131.9 (d, J_{PC} = 3.6, C, Ph), 130.9 (d, J(P, C) = 5.3, C), 130.8 (d, J(P, C) = 2.5, C, Ph), 130.2 (C), 130.0 (CH, Ph), 129.9 (CH, Ph), 129.7 (d, J(P, C) = 4.3, C),129.54 (CH, Ph),129.5 (d, J(P, C) < 2, C), 129.3 (CH, Ph), 128.5 (C), 125.8 (CH, Ph), 125.4 (CH, Ph), 123.1 (CH, Ph), 122.6 (d, J(P, C) = 1.6, CH, Ph), 113.4 (d, J(P, C) = 2.6, C), 113.1 (C), 112.,7 (d, J(P, C) = 5.0, C), 111.7 (d, C, J(P, C) = 2.5), 29.8 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.0 (CH_2), 27.8 (CH_2), 27.8 (CH_2), 27.5 (CH_2), 23.0 (CH_2), 22.9 (CH_2), 22.8 (2CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.7 (CH_2), 22.6 (CH_2). MS (70 eV, EI): m/z (%) = 1146 ([M$^+$], 1.69), 1067 (10.70), 915 (36.47), 649 (100.00), 481 (13.16), 355 (15.71), 281 (16.79), 215 (29.13), 168 (30.25), 131 (18.00), 69 (62.55); HR-MS (ESI$^+$-TOF/MS): [M+Na]$^+$ (calc.) 1164.92388, (found) 1164.92199; [M+K]$^+$ (calc.) 1180.89782, (found) 1180.89876 for $C_{52}H_{44}Br_4O_6P_2$.

4.1.6. 2,2'-Bis(8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl ***11***

4.1.6.1. Mixture of diastereomers. ^{31}P NMR (162 MHz, CD_2Cl_2): δ (ppm) = 140.6, 138.8 (d, J(P, P) = 28, 1P), 137.5 (d, J(P, P) = 28, 1P), 138.6, 138.3. MS (70 eV, EI): m/z (%) = 938 ([M$^+$], 2.37), 599 (100.00), 469 (4.44), 323 (19.38), 276 (6.35), 141 (0.81).

4.2. In situ HP-NMR hydroformylation experiment

In a typical experiment, a sapphire tube was filled under Argon with a solution of Rh(acac)(CO)$_2$ (0.045 mmol) and ligand (molar ratio PP/Rh = 1.1) in d_8-toluene. The HP-NMR tube was pressurized to 20 bar CO/H_2 and afterwards heated to 80 °C.

4.3. [HRh(CO)2(3)] 8 at room temperature

^{31}P NMR (121.5 MHz, d_8-toluene): δ (ppm) = 161.2 (broad d, ^1J(Rh,P) = 240 Hz); ^{1}H NMR (300 MHz, d_8-toluene): δ (ppm) = 16.00 (s, OH, enol), 7.99 (d, 2H, J = 8.22), 7.17 (s, 2H), 7.11 (s, 2H), 7.08 (d, 2H, J = 8.53), 4.88 (1H, acac), 2.82–2.66 (m, CH_2), 1.54 (s, 6H, CH_3 acac (enol)), 1.52–0.76 (m, CH_2), −9.87 (dt, Rh–H, ^2J(P,H) = 8.4 Hz, ^1J(Rh,H) = 1.5 Hz); ^{103}Rh NMR: δ (ppm) = −1116; IR: ν_{CO} = 2017.5, 1993.7 cm^{-1}.

4.4. General procedure for hydroformylation experiments

The olefin is added under argon to a solution of Rh(acac)$(CO)_2$ and the corresponding ligand in THF (30 ml). Then, the reaction mixture is transferred into the autoclave (100 ml). The autoclave is charged with syngas and heated at the indicated reaction temperature. Then, the pressure is adjusted to the desired value (20 bar or 50 bar for 1-pentene). After the reaction time the autoclave is cooled to 0 °C and the pressure is released. Isooctane was used as internal standard. The resulting reaction mixture was immediately analyzed by gas chromatography.

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[17] In addition to the shown 3,3′-dibromo-H8-binaphthol-based ligands and the un-substituted ligand **11**, 3,3′-diaryl- and 3,3′-dialkyl-substituted-H8-binaphthol-based bisphosphites have been prepared by a similar procedure starting from different 2,6-dialkyl- or 2,6-diaryl-4-chloro-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepines and 3,3′-diaryl or 3,3′-dialkyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol. The latter compounds are easily obtained by standard procedures starting from octahydrogenated 3,3′-dibromo-substituted binaphthol. Their application as ligands in the hydroformylation of industrially relevant olefins (e.g. butenes and octenes) is currently under investigation.

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