Chiral Cooperativity in Diastereomeric Diphosphite Ligands: Effects on the Rhodium-Catalyzed Enantioselective Hydroformylation of Styrene

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Diastereomeric diphosphites (L∩L = **3**−**8**) have been synthesized from enantiomerically pure pentane-2,4-diol and axially chiral 3,3′-bis(trialkylsilyl)-2,2′-bisphenol phosphorochloridites and 3,3′-bis(trialkylsilyl)-2,2′-bisnaphthol phosphorochloridites. These diphosphites have been used to test the influence of chiral cooperativity in the rhodium-catalyzed asymmetric hydroformylation of styrene. Systematic variation in chirality at both the chiral ligand bridge and the axially chiral biphenyl and binaphthyl substituents revealed a remarkable effect on the selectivity of the hydroformylation catalysts. For the atropisomeric bisnaphthol-based diphosphites, cooperative effects were observed in the asymmetric hydroformylation of styrene. High enantioselectivities (87%) and regioselectivities up to 95% for 2-phenylpropanal were found under mild reaction conditions (15−50 °C, 20 bar of syn gas $CO-H_2$ [1:1]) for the ligand derived from (2*R*,4*R*)-pentane-2,4-diol and (*S*)-bisnaphthol. The same high enantiomeric excess was observed for the free-rotating bisphenol-substituted ligands. The highest selectivity was obtained with trimethylsilyl substituents at the *ortho* position. The solution structures of the active catalysts [HRhL∩L-$(CO)_2$ complexes (L∩L = **3**−**8**)], have been studied by ^{31}P and ^{1}H NMR spectroscopy at variable temperature (313−213 K). Spectroscopic data, in combination with the obtained results in catalysis, suggest that diphosphite ligands (L∩L) containing the conformationally flexible axially chiral biphenyl moieties predominantly exist as single atropisomers in the HRhL∩L-$(CO)_2$ complexes. Comparison of the bisphenol and bisnaphthol substituents suggests that the high enantiomeric excesses obtained with the former are caused by the preferential formation of the most selective diastereomer.

Introduction

In the last 3 decades a considerable amount of research has been devoted to phosphine[1]- and phosphite[2]-modified homogeneous hydroformylation catalysts. While phosphine-modified platinum hydroformylation catalysts require rather severe reaction conditions and generally are not very chemo- and regioselective, phosphite-modified rhodium catalysts operate under mild reaction conditions, producing a high proportion of aldehydes. As a result, the application of chiral phosphites in hydroformylation catalysts has been recently exploited as an efficient route to enantiomerically pure aldehydes.[3] The products can be used as precursors for the synthesis of high-value-added compounds such as pharmaceuticals, agrochemicals, flavors, and fragrances.[4] Wink and co-workers were the first to report on the rhodium-catalyzed hydroformylation of styrene with chiral diphosphites as ligands. Achiral propanediol bridges, substituted with chiral (bis)dioxaphospholanes as chiral auxiliaries, were used, but the reaction lacked enantioselectivity.[5] In contrast, Takaya *et al.* reported on the asymmetric hydroformylation of vinyl acetate with enantioselectivities up to 49% with chiral bis(triarylphosphite)−rhodium(I) complexes.[6]

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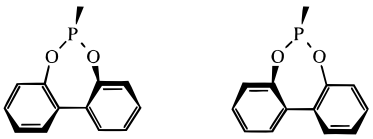


S *R*

Figure 1. Atropisomerism in dibenzo[*d*,*f*][1,3,2]dioxaphosphepins.

Recent contributions have shown that diphosphites containing both a chiral ligand bridge and additional axially chiral biphenyl or binaphthyl substituents are efficient ligands in the rhodium-catalyzed asymmetric hydroformylation of various olefinic substrates.[6−11] An important breakthrough was reported by Union Carbide. They used bulky diphosphites derived from homochiral 2,4-pentanediol and obtained high enantioselectivities in the asymmetric hydroformylation of styrene of around 90%.[8] From NMR and IR spectroscopy it was concluded that particularly diphosphites containing a chiral 1,3-diol ligand bridge form stable and enantioselective rhodium hydroformylation catalysts.[7,10,11] Since the biaryl moieties of the diphosphites used in this study contain bulky substituents, hindered rotation around the biaryl axis can be expected. The additional chirality originating from the atropisomeric biaryl substituents results in several possible diastereomers. Since low rotational barriers have been reported in compounds containing dibenzo[*d*,*f*][1,3,2]dioxaphosphepins (Figure 1),[12,13] it is reasonable to assume that the actual rhodium diphosphite catalyst can consist of several diastereomers. Complex formation from chiral ligands and chiral substrates can give matched and mismatched diastereomers, resulting in double stereodifferentiation.[14] A study of Burgess *et al.* on asymmetric hydrogenation with DIOP−DIPAMP hybrid ligands showed moderate differences between matched and mismatched diastereomeric ligands.[15] Chiral cooperativity between two modes of chirality was reported by Togni and Pastor for the gold-catalyzed aldol reaction using chiral ferrocenylamine ligands.[16]

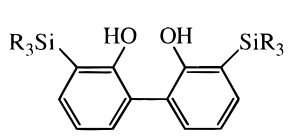
We now report on the asymmetric hydroformylation of styrene using enantiopure *ortho*-substituted bisnaphthol containing diphosphites. All combinations of the atropisomerically pure binaphthyl moieties and enantiomerically pure bridge could be synthesized. This enabled us to study the origin of the high enantioselectivities obtained with chiral diphosphite ligands.[8,10b]

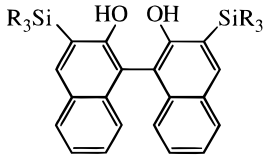
Results

Synthesis of Diastereomeric Diphosphite Ligands. To study the effect of chiral cooperativity, we synthesized a series of diphosphites based on homochiral pentane-2,4-diol ligand backbones substituted with bulky 2,2′-bisphenols and bulky 2,2′-bisnaphthols. Since interconversion around the binaphthyl bond is energetically highly unfavorable, stable diastereomeric diphosphites could be obtained in an optically pure form. The absolute configuration of the synthesized diastereomers is given in a shorthand notation as (*S*,2*R*,4*R*,*S*), (*S*,2*S*,4*S*,*S*), (*R*,2*R*,4*R*,*R*), and (*S*,2*R*,4*R*,*R*). The indicators *S* and *R* refer to the absolute configurations around the chiral axis, while the indicators 2*R*,4*R* and 2*S*,4*S* refer to the absolute configurations of carbon atoms C_2 and C_4 in the pentane-2,4-diol backbone. The structures having the configuration (*S*,2*R*,4*R*,*R*) and (*R*,2*R*,4*R*,*S*) are equivalent as a consequence of the C_2 symmetry.

Recently the presence of bulky substituents on aromatic biphenyl and binaphthyl positions was shown to have a significant effect on the catalyst performance.[7,8,10,11] In this study ligands were used with *ortho* substituents having increasing steric bulk (trimethyl-, triethyl-, and *tert*-butyldimethylsilyl).

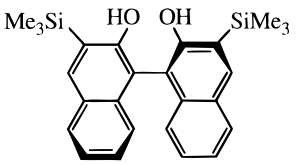
Preparation of 3,3′-Bis(trialkylsilyl)- and 3,3′-Bis(triaryl)silyl-Substituted 2,2′-Bisphenols and 2,2′-Bisnaphthols. For the introduction of *ortho* trialkyl and triaryl substituents at aromatic positions, we first applied the route recently described by Yamamoto *et al.* for the synthesis of *ortho*-substituted 2,2′-bisnaphthols.[17ab]

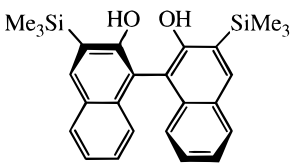




1a (R = Me)
1b (R = Et)
1c (R_3 = *tert*-BuMe_2)
1d (R = Ph)

(R/S)- **2a** (R = Me)
(R/S)- **2b** (R = Et)
(R/S)- **2c** (R_3 = *tert*-BuMe_2)
(R/S)- **2d** (R = Ph)





(S) - **2a** *(R)* - **2a**

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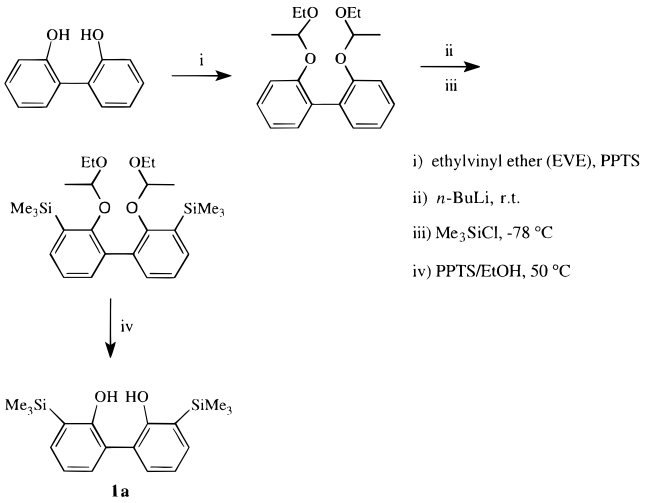
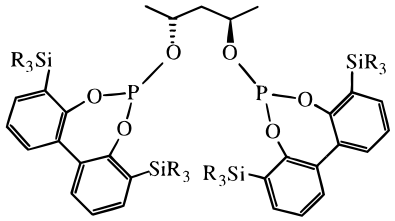
Scheme 1. Straightforward Reaction Route to 3,3′-Bis(trimethylsilyl)-2,2′-bisphenol (1a)



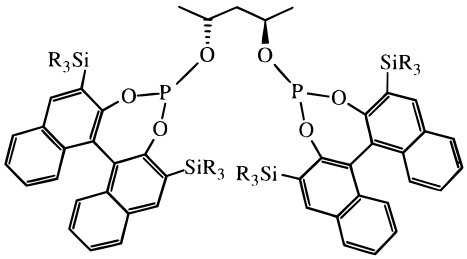
The *ortho* lithiation of 2,2′-dimethoxy-1,1′-biphenyl followed by reaction with bromine was accompanied by the formation of about 25% of a regioisomer of 3,3′-dibromo-2,2′-dimethoxy 1,1′-biphenyl. In contrast with results reported by Yamamoto,[17] the final products, 2,2′-bis(trimethylsilyl) ethers of 2,2′-bisphenol and 2,2′-bisnaphthol, were not stable during short path column purification on silica gel. The overall yield was very low and therefore a more straightforward reaction route was applied for the preparation of *o*-bis(trimethylsilyl)-substituted diaryl dialcohols **1** and **2**. Ethyl vinyl ether (EVE) was used in combination with pyridinium *p*-toluenesulfonate (PPTS) for protection of the hydroxy groups in quantitative yields (Scheme 1, step i).[18,19]

A one-pot synthesis comprising bis *ortho* lithiation followed by reaction with trimethylsilyl chloride (Scheme 1, ii and iii) resulted in the formation of 3,3′-bis-(trimethylsilyl)-2,2′-bis(1-ethoxyethoxy)-1,1′-biphenyl. Deprotection with pyridinium *p*-toluenesulfonate[19] in ethanol under mild reaction conditions (Scheme 1, iv) gave **1a** in only four reaction steps (overall yield 32%). The same procedures were applied to obtain racemic (*R*/*S*)-(±)-**2a** and enantiomerically pure (*S*)-(−)-**2a** and (*R*)-(+)-**2a** in an overall yield up to 85%. *β*-Methoxyethoxymethyl ethers[20] (MEM) have also been used as protecting groups, but this resulted in low selectivity in the lithiation step.[21]

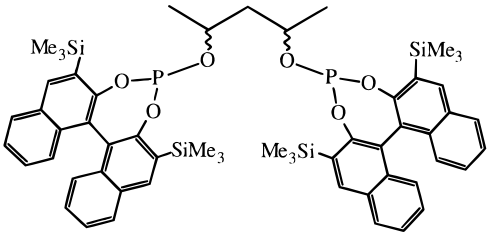
Preparation of Diastereomeric Diphosphites (L∩L = 3−8). Optically pure (2*R*,4*R*)- and (2*S*,4*S*)-pentane-2,4-diol have been used as C_2 symmetrical backbones for the synthesis of the diphosphites **3**−**8**. The bis *o*-trialkylsilyl-substituted diols **1** and **2** reacted quantitatively with 1 equiv of phosphorus trichloride to yield the corresponding phosphorochloridites in the presence of a base. Diphosphites **3a**−**c**, **4a**−**c**, and **5**−**7** were synthesized in good yields (47−96% isolated) by adding 2 equiv of the phosphorochloridite to enantiomerically pure pentane-2,4-diol in the presence of triethylamine. Via the same route, the preparation of the bulky diphosphite **3d** and **4d** (R = Ph) resulted in the formation of mono-substituted diol accompanied by a considerable amount of hydrolyzed phosphorochloridite. Attempts to synthesize **3d** by adding 2 equiv of phosphorochloridite to the more reactive (2*R*,4*R*)-pentane-2,4-diolate were not successful either.[22] Diphosphite **8**, having the configuration (*R*,2*R*,4*R*,*S*), was synthesized *via* a two-step procedure. One equivalent of the phosphorochloridite derived from (*R*)-(+)-**2a** was added to (2*R*,4*R*)-pentane-2,4-diol. The mono-substituted product was isolated from the reaction mixture and transformed to **8** in a subsequent reaction with the phosphorochloridite derived from (*S*)-(−)-**2a**.



3a (R = Me)
3b (R = Et)
3c (R_3 = *tert*-BuMe_2)
3d (R = Ph)



4a (R = Me)
4b (R = Et)
4c (R_3 = *tert*-BuMe_2)
4d (R = Ph)



5 : (*S*,2*R*,4*R*,*S*)
6 : (*S*,2*S*,4*S*,*S*)
7 : (*R*,2*R*,4*R*,*R*)
8 : (*R*,2*R*,4*R*,*S*)

Diphosphites **3**−**8** were purified by column chromatography on silica gel and characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy. At room temperature, no diastereomers could be observed for **3** with NMR, which suggests that a fast interconversion around the biphenyl bonds results in a time-averaged configuration on the NMR time scale. These observations are consistent with results recently reported in a variable temperature

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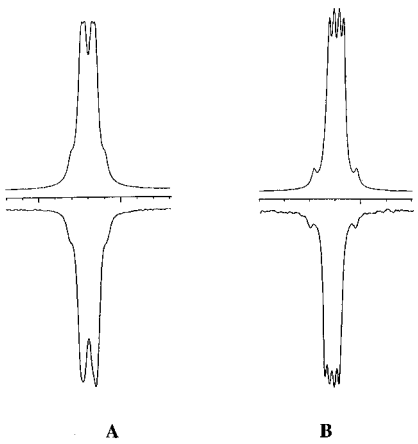

Figure 2. (A) Calculated and recorded (lower trace) $^{31}P-^{1}H$ NMR spectrum of **3a** (δ = 145.1 ppm, $^{3}J_{PHbackbone}$ = 5.5 Hz, $^{6}J_{PP}$ = 5.2 Hz). (B) Calculated and recorded (lower trace) $^{31}P-^{1}H$ NMR spectrum of **3b** (δ = 147.1 ppm, $^{3}J_{PHbackbone}$ = 7.0 Hz, $^{6}J_{PP}$ = 9.0 Hz).

NMR study by Whiteker *et al.*[12a] High-resolution (0.1 Hz) proton-coupled phosphorus NMR showed second-order multiplets for **3a** and **3b** (Figure 2, parts a and b, respectively). The calculated spin-simulated $^{31}P-^{1}H$ NMR spectra revealed phosphorus−phosphorus coupling constants ($^{6}J_{PP}$) of 5.2 and 9.0 Hz for **3a** and **3b**, respectively. It is noted that the observed coupling constants may be due to average values of the fast interchanging diastereomers. A recent study by Pastor and co-workers showed different phosphorus−phosphorus coupling constants for diastereomers in the slow exchange limit.[13] Six-bond phosphorus−phosphorus coupling constants ($^{6}J_{PP}$) in the range of 4.5 and 12 Hz have been reported by Szalontai[23] *et al.* in similar diphosphites. Generally, long-range phosphorus−phosphorus coupling is explained by through space interaction.[24] Further evidence for through space phosphorus−phosphorus coupling was obtained from the ^{13}C NMR spectra. Virtual triplets were found for the aromatic carbon atoms $C_{1,1'}$ and $C_{3,3'}$ of **3a** and **3b** with an observed J_{PC} coupling constant up to 6.8 Hz (benzene-d_6, 293 K). The observed coupling constant is an average of the $^{3}J_{P^1C}$ of about 14 Hz and the $^{9}J_{P^2C}$ of 0 Hz. Diphosphite **3c** did not show any phosphorus−phosphorus coupling in either ^{31}P or ^{13}C NMR spectra. We therefore conclude that in **3c** the phosphorus atoms have no interaction with one another in solution.[23]

For **4a**−**c** the diastereomers with absolute configurations (*S*,2*R*,4*R*,*S*), (*S*,2*R*,4*R*,*R*), and (*R*,2*R*,4*R*,*R*) were formed in the statistical 1:2:1 molecular ratio, as was concluded from ^{31}P NMR. The (*S*,2*R*,4*R*,*R*) diastereomer with two inequivalent phosphorus atoms shows ^{31}P NMR signals at different chemical shifts. In contrast, C_2 symmetrical diastereomers having the configuration (*S*,2*R*,4*R*,*S*) and (*R*,2*R*,4*R*,*R*) give rise to single ^{31}P absorptions. The four expected signals were observed with equal intensities. Diastereomeric mixtures of **4a**−**c** were purified from residual side products by column chromatography on silica gel. No detailed characterization by ^{13}C and ^{1}H NMR has been carried out since the mixtures of diastereomers gave partially overlapping spectra.

Table 1. ^{31}P and ^{1}H NMR Data of HRhL∩L(CO)$_2$ Complexes, L∩L = 3−8[a,b]

		δ				
L∩L	T (K)	^{31}P[c]	^{1}H[c]	$^{1}J_{Rh-P}$[d]	$^{1}J_{Rh-H}$[d]	$^{2}J_{P-H}$[d]
3a	333	163.5	−10.57	232.1	5.0	3.0
3b	293	162.4	−10.48	227.2	6.0	9.0
3c	293	166.0	−10.37	236.9	3.0	<2.0
5	293	166.3	−10.28	232.1	3.0	<2.0
6	293	158.4[e]	−10.44	232.1[e]	<2.0	<2.0
7	293	*e,f*	−10.42	e,f	<2.0	<2.0
8	293	167.6, 166.5	−10.24	235.1, 234.2	<2.0	<2.0

[a] Prepared in toluene-d_8. [b] $^{31}P\{^{1}H\}$, ^{31}P, and ^{1}H spectra recorded under atmospheric conditions at room temperature. [c] Chemical shifts (δ) in ppm. [d] Coupling constants (J) in hertz. [e] Other undefined rhodium species are present. [f] The ^{31}P NMR chemical shifts could not be determined.

The ^{31}P and ^{13}C NMR spectra of **5**, synthesized from (2*R*,4*R*)-pentane-2,4-diol and enantiomerically pure (*S*)-(−)-**2a**,[25] display long-range phosphorus−phosphorus coupling. A phosphorus−phosphorus coupling constant ($^{6}J_{PP}$) of 13 Hz was derived from the simulated ^{31}P NMR spectrum. Virtual triplets were observed for the aromatic carbon atoms $C_{1,1'}$ and $C_{3,3'}$ with average J_{PC} coupling constants between 3 and 6 Hz. In contrast with the ^{31}P and ^{13}C NMR spectra of **5**, no long-range phosphorus−phosphorus interactions could be observed for diphosphites **6**−**8**. The inversed absolute configurations at carbon atoms C_2 and C_4 of the pentane-2,4-diol backbone and the axial chirality, as well, probably gave rise to solution structures without appreciable time-averaged phosphorus−phosphorus interaction.[23]

Solution Structures of Hydroformylation Catalysts. Hydridorhodium diphosphite dicarbonyl complexes [HRhL∩L(CO)$_2$, L∩L = **3a**−**c** and **5**−**8**] have been prepared and analyzed *in situ* under standard hydroformylation reaction conditions (Table 1).[10,11] At 293 K the ^{31}P NMR spectra for HRhL∩L(CO)$_2$ complexes (L∩L = **3a**−**c**) showed broadened doublets (spectral bandwidths: $\Delta\varpi_{1/2}$ between 100 and 200 Hz), which suggest fluxional processes on the NMR time scale. Further proof for fluxional processes was provided by ^{31}P NMR measurements at variable temperature. At 333 K, the ^{31}P resonance for the complex HRh(**3a**)(CO)$_2$ appeared as a sharp doublet ($\Delta\varpi_{1/2}$ = 11 Hz). The ^{31}P NMR signals of HRh(**5**)(CO)$_2$ (absolute configuration *S*,2*R*,4*R*,*S*), appeared already as a sharp doublet ($^{1}J_{RhP}$ = 232.1 Hz, $\Delta\varpi_{1/2}$ < 20 Hz) at room temperature. The enantiomers **6** and **7**, with absolute configurations (*S*,2*S*,4*S*,*S*) and (*R*,2*R*,4*R*,*R*), respectively, showed a rather different behavior upon coordination to rhodium. Attempts to make HRhL∩L(CO)$_2$ complexes for these ligands resulted in the formation of a complex mixture of rhodium−diphosphite species. HRhL∩L(CO)$_3$ complexes in which the diphosphites act as monodentates are probably formed as side products (^{31}P NMR; *e.g.* L∩L = **6**, δ 157.4 ppm (d) $^{1}J_{RhP}$ = 236.9 Hz, 142.4 ppm (s)). Furthermore, the occurrence of considerable ligand decomposition in complexes with **6** and **7** was evidenced by resonances between 0 and 15 ppm in the ^{31}P NMR

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Table 2. NMR Data of HRhL∩L(CO)$_2$ Complexes, L∩L = 3−8 at 213K[a,b]

	δ								
L∩L	$^{31}P_1$[c]	$^{31}P_2$[c]	^1H[c]	$^1J_{RhP1}$[d]	$^1J_{RhP2}$[d]	$^2J_{P1P2}$[d]	$^1J_{RhH}$[d]	$^2J_{P1H}$[d]	$^2J_{P2H}$[d]
3a	167.6	161.5	−10.24	236.9	227.2	256.4	3.0	<2.0	<2.0
3b	166.8	153.2	−10.25	236.9	232.1	261.2	15.0	<2.0	<2.0
3c	168.1	165.5	−10.11	244.2	225.4	247.0	<2.0	<2.0	<2.0
5	167.3	167.3	−10.15	239.9	228.1	260.3	3.0	<2.0	<2.0
6	[e]								
7	[e]								
8	169.2	169.0	−10.24	234.5	235.7	277.6	<2.0	<2.0	<2.0

[a] HRhL∩L(CO)$_2$ complexes prepared in toluene-d_8. [b] $^{31}P\{^1H\}$, ^{31}P, and ^1H spectra recorded in toluene-d_8 under atmospheric conditions. [c] Chemical shifts (δ) in ppm. [d] Coupling constants (J) in hertz. [e] The HRhL∩L(CO)$_2$ complexes of **6** and **7** could not be synthesized in pure form.

Table 3. Hydroformylation of Styrene with HRhL∩L(CO)$_2$, L∩L = 3a−c[a]

						%					
entry	ligand	T (°C)	pCO	pH$_2$	TOF[b]	conv[c]	iso[d]	n[e]	PhEt[f]	ee[g]	abs conf[h]
1	**3a**	50	10	10	130	52	84	13	3	60	(*S*)
2	**3a**	40	10	10	45	21	89	8	3	67	(*S*)
3	**3a**	25	10	10	9	26[i]	93	5	2	87	(*S*)
4	**3a**	25	10	20	8	69[j]	95	4	1	53	(*S*)
5	**3b**	50	10	10	20	14	85	12	3	25	(*S*)
6	**3b**	40	10	10	13	7	93	3	4	34	(*S*)
7	**3b**	25	10	10	2	7[k]	89	8	3	29	(*S*)
8	**3c**	50	10	10	27	30	67	29	4	11	(*S*)
9	**3c**	50	10	20	33	53	81	17	2	14	(*S*)
10	**3c**	50	5	10	43	72	71	23	6	20	(*S*)
11	**3c**	25	10	10	3	8[l]	78	20	2	4	(*S*)

[a] Styrene catalyst molar ratio is 1000, P:Rh molar ratio of 2.2. [b] TOF in mol styrene (mol Rh)$^{-1}$ h^{-1} determined after 1 h reaction time by GC. [c] Percent conversion of styrene. [d] Selectivity to branched aldehyde. [e] Selectivity to linear aldehyde. [f] Selectivity to ethyl benzene. [g] Enantiomeric excess. [h] Absolute configuration. [i] After 23 h. [j] After 110 h. [k] After 24 h. [l] After 72 h.

Table 4. Hydroformylation of Styrene with Diastereomeric HRhL∩L(CO)$_2$, L∩L = 4a−c[a]

				%					abs
entry	ligand	T (°C)	TOF[b]	conv[c]	iso[d]	n[e]	PhEt[f]	ee[g]	conf[h]
12	**4a**	50	104	38	86	13	1	21	(*S*)
13	**4a**	25	14	20[i]	91	7	2	47	(*S*)
14	**4b**	50	256	94	90	9	1	20	(*S*)
15	**4b**	25	17	51[j]	94	6	0	28	(*S*)
16	**4c**	50	163	47	85	14	1	7	(*S*)
17	**4c**	25	16	36[j]	93	6	1	15	(*S*)
18	**4a**[k]	25	11	26	94	6	0	57	(*S*)

[a] Styrene catalyst molar ratio is 1000, P:Rh molar ratio of 2.2, p(CO) = p(H$_2$) = 10 bar. [b] TOF in mol styrene (mol Rh)$^{-1}$ h^{-1} determined after 1 h by GC. [c] Percent conversion of styrene. [d] Selectivity to branched aldehyde. [e] Selectivity to linear aldehyde. [f] Selectivity to ethyl benzene. [g] Enantiomeric excess. [h] Absolute configuration. [i] After 23 h. [j] After 24 h. [k] P:Rh molar ratio of 8.8.

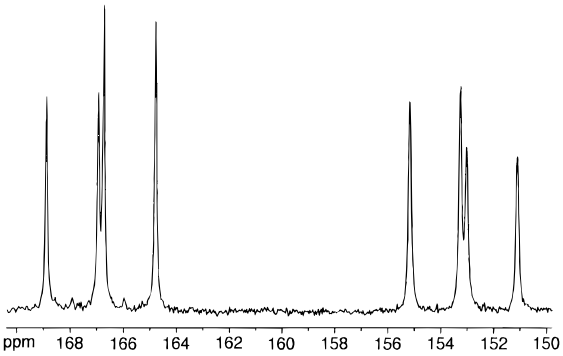

Figure 3. ^{31}P NMR spectrum of HRhL∩L(CO)$_2$, L∩L = **3b** (T = 213 K).

spectra.[26] As is the case for **5**, HRh(**8**)(CO)$_2$ is formed quantitatively under standard reaction conditions. The ^{31}P NMR spectrum of HRh(**8**)(CO)$_2$ appeared as a double AB signal caused by the intrinsically inequivalent phosphorus P_1 and P_2 ($^2J_{P1P2}$ = 278 Hz, $^1J_{RhP1}$ = 234.2 Hz, and $^1J_{RhP2}$ = 235.1 Hz). For diphosphite L∩L = **4a** (**4a** ≡ **5**:**7**:**8** = 1:1:2) the HRhL∩L(CO)$_2$ complex was prepared using a ligand to rhodium ratio of 4. The HRhL∩L(CO)$_2$ complex appeared as a diastereomeric mixture derived from **5** and **8** in a ratio of 2.65:1. No complexes derived from **7** were observed.

At low temperature (213 K), the ^{31}P NMR spectra of HRhL∩L(CO)$_2$ complexes of **3a**−**c** and **5** appeared as sharp double AB systems with spectral bandwidths ($\Delta\varpi_{1/2}$) between 10 and 15 Hz. The phosphorus atoms (P_1 and P_2) showed different coupling constants with rhodium (see Table 2, $^1J_{RhP1}$ and $^1J_{RhP2}$; see Figure 3 for the ^{31}P NMR spectrum of HRh(**3b**)(CO)$_2$). The low-temperature ^{31}P NMR spectrum of HRh(**8**)(CO)$_2$ closely resembled that observed at room temperature. The intrinsically different phosphorus atoms P_1 and P_2 give rise to double AB resonances. All complexes showed phosphorus−phosphorus coupling constants ($^2J_{P1P2}$) between 247 and 261 Hz. The hydride signal appeared as a broadened doublet because of the coupling with rhodium ($^1J_{RhH}$ between 3 and 15 Hz). The phosphorus−hydride couplings ($^2J_{P1H}$ and $^2J_{P2H}$) were very small (<2 Hz). The coupling constants are indicative of trigonal bipyramidal hydridorhodium species with bis-equatorially coordinating diphosphites.[10]

Hydroformylation Experiments. Diphosphites **3**−**8**, with sterically demanding bis *o*-trialkylsilyl substituents, were used in the rhodium-catalyzed asymmetric hydroformylation. After standard catalyst preparation conditions, styrene was hydroformylated at various reaction conditions. The results are given in Tables 3−5. For ligand **3a** (Table 3, entries 1−4), the reaction rate decreases with temperature. A temperature decrease from 50 to 25 °C reduces the initial turnover

(26) Traces of H_2O can cause hydrolysis of the diphosphite ligand to H-phosphonates (δ between 0 and 15 ppm) under the reaction conditions.

Table 5. Hydroformylation with HRhL∩L(CO)$_2$, L∩L = 5−8[a]

entry	ligand	T (°C)	TOF[b]	% conv[c]	% iso[d]	% n[e]	% PhEt[f]	% ee[g]	abs conf[h]
19	**5**	50	133	43	83	13	4	58	(*S*)
20	**5**	25	17	38[i]	88	8	4	69	(*S*)
21	**5**	15	11	12[i]	92	6	2	86	(*S*)
22	**6**	50	281	98	89	10	1	8	(*R*)
23	**6**	40	259	89	91	8	1	18	(*R*)
24	**6**	25	45	21	94	5	1	40	(*R*)
25	**7**	50	387	99	87	10	3	12	(*S*)
26	**7**	40	186	99	92	6	2	30	(*S*)
27	**7**	25	28	18	95	4	1	38	(*S*)
28	**8**	50	12	36	87	11	2	16	(*S*)
29	**8**	40	6	25	88	11	1	18	(*S*)
30	**8**	25	4	2	91	8	1	23	(*S*)

[a] Styrene catalyst molar ratio is 1000, $p(CO) = p(H_2) = 10$ bar, P:Rh ratio 2.2. [b] TOF in mol styrene (mol Rh)$^{-1}$ h^{-1} determined after 1 h by GC. [c] Percent conversion of styrene after 5 h. [d] Selectivity to branched aldehyde. [e] Selectivity to linear aldehyde. [f] Selectivity to ethyl benzene. [g] Enantiomeric excess. [h] Absolute configuration. [i] After 24 h.

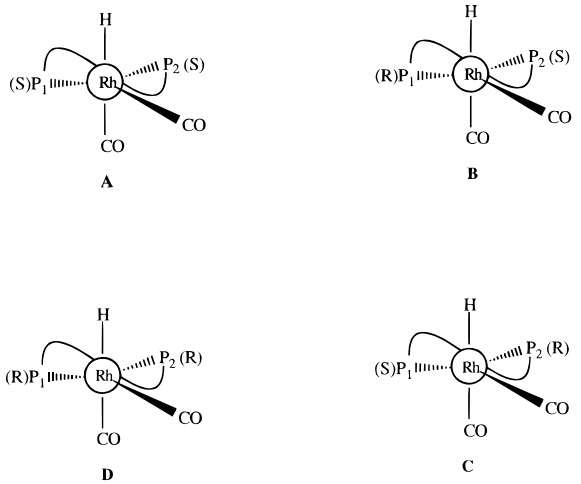

Figure 4. Diastereomeric HRhL∩L(CO)$_2$ complexes (**A**−**D**). The indicators (*R*) and (*S*) refer to axial chirality in the biaryl substituents.

frequencies from 130 to 9 mol mol^{-1} h^{-1}. Enantiomeric excesses of 60−87% were found using ligand **3a**.

The effects of the steric bulk of ligands **3** on reaction rates and the asymmetric induction were examined. The rhodium catalyst derived from ligand **3b**, with bulky triethylsilyl substituents at the *ortho* positions, resulted in a very low reaction rate (entries 5−7).

Comparably low reaction rates were found at 50 °C with the *tert*-butyldimethyl analogue **3c** (entry 8). The reaction was accelerated by an increased partial pressure of hydrogen (entry 9) and decreased partial pressure of CO (entry 10). At relatively long reaction time the enantiomeric excess dropped to 4% (entry 11).

The results of the asymmetric hydroformylation of styrene with ligands **4a**−**c** are given in Table 4. These ligands exist as mixtures of diastereomers and therefore mixtures of hydridorhodium catalysts are formed.

At 25 °C high proportions of branched aldehyde were found (91−93%). At 50 °C high turnover frequencies were observed for HRhL∩L(CO)$_2$ complexes of **4b** (entry 14) and **4c** (entry 16). The highest enantioselectivity (47%, entry 13) is again obtained using ligands with trimethylsilyl substituents at the *ortho* positions of the bisnaphthol groups. This enantiomeric excess could be improved to 57% using a larger excess of ligand **4a** (P:Rh ratio of 8.8, entry 18).

Diastereomerically pure ligands **5**−**8** having fixed absolute configurations have also been used in the asymmetric hydroformylation of styrene. The results are given in Table 5.

The results obtained using **5** (entries 19−21) resemble strongly those reported for the bisphenol analogue **3a** (Table 3, entries 1−3). In the temperature range of 50−15 °C the catalytic system shows almost identical reaction rates and regio- and enantioselectivities.

Hydridorhodium complexes of the enantiomeric ligands **6** and **7** show high catalytic activities, albeit with low asymmetric induction (entries 22−27). Hydroformylation using ligand **8** results in both low catalytic activity and low enantioselectivity (entries 28−30).

Discussion

For the synthesis of 3,3′-bis(trimethylsilyl)-substituted 2,2′-bisphenols and racemic (*R*/*S*)-(±)-, enantiomerically pure (*S*)-(−)-, and (*R*)-(+)-2,2′-bisnaphthols, ethyl vinyl ether (EVE) was successfully applied as protecting group. Thus, the reaction route was considerably shortened compared with the method reported by Yamamoto *et al.*[17a]

The different behavior of ligands **3** and **5**−**8** in the formation of the HRhL∩L(CO)$_2$ complexes clearly demonstrates that both the absolute configuration of the 2,4-pentanediol ligand backbone and the chiral bisnaphthol substituents determine the stability and catalytic performance of the rhodium complexes. Well-defined stable complexes could be prepared with ligands **3**, **5**, and **8**, whereas ligands **6** and **7** lead to undefined mixtures of complexes and ligand decomposition. Using an excess of the statistical mixture of diastereomers **4a** resulted in the formation of complexes derived from **5** and **8** only. Despite the 2-fold higher concentration of **8**, the complex derived from ligand **5** proved to be the most stable one, as was concluded from its preferential formation (73%) observed by ^{31}P and ^{1}H NMR.

Since the phosphorus atoms have different orientations toward the axial hydride and carbon monoxide ligands, they are inequivalent in the C_1 symmetrical HRhL∩L(CO)$_2$ complexes derived from **3a**−**c** and **5**. This means that four diastereomeric hydridorhodium diphosphite dicarbonyl complexes (Figure 4, **A**−**D**) can be formed. However, simple doublets are observed in the ^{31}P NMR spectra (T = 293 K) of trigonal bipyramidal HRhL∩L(CO)$_2$ complexes of **3a**−**c** and **5**, which suggests a fast fluxional processes on the NMR time scale exchanging the phosphorus atoms in the complexes. Evidence for such an exchange process in HRhL∩L(CO)$_2$ complexes of **3a**−**c** and **5** was obtained from the low-temperature ^{31}P NMR spectra. At 213 K sharp double AB systems were observed, which indicates that the slow-exchange region was reached. Since the phosphorus atoms P$_1$ and P$_2$ of HRh(**8**)(CO)$_2$ are intrinsically different, the low-temperature ^{31}P NMR spectrum closely resembled that observed at room temperature. The observed coupling constants for all complexes are indicative of trigonal bipyramidal hydridorhodium species with bis-equatorially coordinating diphosphites.[10]

The possibility that the phosphorus chemical shifts of the four diastereomeric HRhL∩L(CO)$_2$ complexes (**A**−**D**) derived from ligands **3a**−**c** accidentally coincide was excluded on the basis of the ^{31}P and ^{1}H NMR spectra of the diastereomeric complexes HRh(**5**)(CO)$_2$ and HRh-

(**8**)$(CO)_2$. Complexes of **5** and **8**, schematically represented as structures **A** and **C**, respectively, cannot undergo inversion around the binaphthyl bonds and they exhibit different ^{31}P NMR spectra (see Tables 1 and 2). The low-temperature ^{31}P NMR spectra of HRhL∩L$(CO)_2$, L∩L = **3a**−**c**, show a large resemblance with the low-temperature ^{31}P NMR spectra of HRh(**5**)-$(CO)_2$. These results make it plausible that HRhL∩L-$(CO)_2$ complexes containing ligands **3a**−**c**, which can freely interchange around the biphenyl linkage, exist as one particular diastereomer in the HRhL∩L$(CO)_2$ complex. However, it should be kept in mind that the dihedral angles of the bisphenol moieties can differ from the more rigid bisnaphthols which can also have its impact on the characteristics of the phosphorus.

Rhodium-catalyzed hydroformylation of styrene with **3** as ligand results in high enantiomeric excesses up to 87%. For comparison, bulky *tert*-butyl groups at the *ortho* positions gave rise to lower enantiomeric excesses (up to 68%) under the same reaction conditions.[10b] At longer reaction times (110 h) the enantiomeric excess dropped to 53%, probably caused by catalyst decomposition. The increased branched (iso) to normal aldehyde ratios observed at lower reaction temperatures and higher CO and H_2 pressures (entries 3 *vs* 4 and 8 *vs* 9) are generally explained by a decreased β-H elimination of the branched rhodium alkyl intermediate.[27,28]

The introduction of larger substituents at the *ortho* position showed the expected trend of steric bulkiness on the reaction rate. The reaction rates decreased with an increase in steric bulk of the *ortho* substituents; *i.e.*, $C(CH_3)_3$[29] < $Si(CH_3)_3$ < Si(*t*-Bu)$(CH_3)_2$ < $Si(CH_2CH_3)_3$ (see turnover frequencies at 50 °C, entries 1, 5, and 8, Table 3). However, the bulky Si(*t*-Bu)$(CH_3)_2$- and $Si(CH_2CH_3)_3$-containing ligands **3b**,**c** did not result in an improvement of the enantiomeric excess. The optimal steric bulk in the *ortho* position seems to be obtained with trimethylsilyl substituents. Therefore, the trimethylsilyl group was also used for the optically pure bisnaphthol substituents in ligands **5**−**8**.

From the results in Table 5 it can be concluded that the absolute configuration around the binaphthyl axis has a dramatic effect on the catalyst performance. When both the pentane backbone and the binaphthyl substituents have all *S* (**6**) or all *R* (**7**) configuration, a low enantiomeric excess is observed. *In situ* NMR studies showed that the HRhL∩L$(CO)_2$ complexes of **6** and **7** could not selectively be synthesized. The coexistence of highly active rhodium species, in which the ligands coordinate as monodentates,[30] is held responsible for the low enantioselectivity and relatively high reaction rates observed.

Ligands **5** and **8** both form stable rhodium complexes, but only diastereomer **5** shows chiral cooperativity and consequently gives a high ee. The results obtained for **5** resemble those observed for **3a**.

These results strongly support the conclusion that fast interchanging atropisomers of **3a** adopt predominantly the (*S*,2*R*,4*R*,*S*) conformation in the HRh(**3a**)$(CO)_2$ complex, which is in agreement with the observed low-temperature NMR spectrum; *i.e.*, resonances belonging to competitive diastereomeric hydridorhodium complexes could not be detected in any appreciable amounts. Further evidence for the existence of single diastereomeric HRhL∩L$(CO)_2$ complexes containing ligands **3a**−**c** can be derived from the results found for **4a** and **5** (Tables 4 and 5). Hydroformylation using **4a**, which consists of three diastereomers, resulted in lower asymmetric inductions (entries 12 and 13) compared with the results obtained with the single isomer **5** (entries 19 and 20). The turnover frequency of the hydroformylation reaction using ligand **4a** equals the average of a statistical mixture of **5**, **7**, and **8**.[31] Also, the observed enantiomeric excess corresponds to the average value, when the different reaction rates of the diastereomeric complexes are taken into consideration. ^{31}P NMR analysis of the rhodium complexes derived from **4a** showed that the most stable complex is formed by ligand **5**, the one that also induces the highest enantioselectivity. Using a 4-fold excess of **4a**, a mixture of rhodium hydride complexes derived only from **5** and **8** are formed in a ratio of 2.65:1. This explains the increased enantiomeric excess when 4.4 equiv of **4a** is used (entry 18). The observed turnover frequency of 11 mol mol^{-1} h^{-1} and ee of 57% are in agreement with preferred complexation of **5** compared to **8**. Since no rhodium complexes derived from **7** are observed, the ee increases with increasing ligand to rhodium ratio. Likewise, it seems reasonable to assume that ligand **3a**, with adaptable conformations in the diaryl substituents, preferentially forms the most stable catalyst complex that also induces the highest enantioselectivity.

Conclusions

Variation of the *ortho* substituents on the bisphenol or bisnaphthol moieties in diphosphites **3**−**8** has a large effect on the asymmetric induction of the rhodium-catalyzed asymmetric hydroformylation of styrene. The highest enantiomeric excesses were found using trimethylsilyl substituents both for ligands **3** and **4**. Application of the diastereomerically pure ligands **5**−**8** clearly showed chiral cooperativity of the central backbone and the biaryl substituents. The highest ee of 86% using the diastereomer **5** is in the same range as the ee found for **3a**, which has rotational freedom around the biaryl axis.

The formation of only one diastereomer of hydridorhodium diphosphite dicarbonyl complexes [HRhL∩L-$(CO)_2$] of ligands **3a**−**c** was observed in ^{31}P NMR spectra. Apparently, the low-energy barrier for interconversion in atropisomers **3a**−**c** results in the formation of the most stable conformation in HRhL∩L$(CO)_2$ complexes. The high enantioselectivity of 87% found using ligand **3a** suggests that the preferentially formed

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(28) Van Rooy, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 835.

(29) Comparison of data should be interpreted with care since the reaction conditions for the $C(CH_3)_3$-substituted ligand are not the same. However, the reported TOF of 166 mol mol^{-1} h^{-1} at 40 °C in ref 11b Table 1 exceeds the TOFs reported for the trialkylsilyl-substituted analogues at 50 °C, which justifies the comparison of TOFs.

(30) van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 34.

(31) The formation of the HRhL∩L$(CO)_2$ complex using 1 equiv of ligand **4a** results in the formation of a statistical mixture of diasteroisomeric complexes (ratio **5**:**7**:**8** = 1:1:2). At 25 °C this gives a calculated TOF of (1 × 17 + 1 × 28 + 2 × 4)/4 = 13 mol mol^{-1} h^{-1}, whereas the observed value for **4a** was 14 mol mol^{-1} h^{-1}. The calculated ee amounts to (1 × 17 × 69 + 1 × 28 × 38 + 2 × 4 × 23)/(1 × 17 + 1 × 28 + 2 × 4) = 46%, whereas the observed value was 47%.

complex has the required conformation for optimal chiral cooperativity that induces the highest ee, as was observed for the complex derived from diastereomerically pure ligand **5**.

Experimental Section

General Considerations. Chemicals were obtained from Acros Chimica and Aldrich Chemical Co. All reactions were carried out in oven-dried glasswork using standard Schlenk techniques under an atmosphere of argon. Toluene was distilled from sodium/benzophenone. Triethyl amine and CH_2Cl_2 were distilled from CaH_2. PCl_3 was distilled before use. For column chromatography silica gel 60 (230−400 mesh) purchased from Merck was used. Melting points were determined on a Gallenkamp MFB-595 melting point apparatus in open capillaries and are uncorrected. NMR spectra were obtained on a Bruker AMX 300 spectrometer. ^{31}P and ^{13}C spectra were measured ^1H-decoupled unless otherwise stated. TMS was used as a standard for ^1H and ^{13}C NMR and H_3PO_4 for ^{31}P NMR. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrophotometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at room temperature (22 °C). Gas chromatographic analyses were run on an Interscience HR GC Mega 2 apparatus (split/splitless injector, J&W Scientific, DB1 30 m column, film thickness 3.0 μm, carrier gas 70 kPa He, FID detector) equipped with a Hewlett-Packard Data system (Chrom-Card). Enantiomeric excesses were measured after reduction of the aldehydes with $NaBH_4$ to the corresponding alcohols on a Carlo Erba Vega 6000 gas chromatograph (split/splitless injector, SGE 50 m chiral β-cyclodextrin column, FID detector, equipped with a Shimadzu C-R 5A integrator). Mass spectra were measured on a HP 5890/5971 GC−mass spectrometer. Hydroformylation reactions were carried out in a homemade 200 mL stainless steel autoclave. Syn gas 3.0 was purchased from Praxair. Elemental analyses were performed by the Department of Micro-Analyses at the University of Groningen and on a Elementar Vario EL analyzer from FOSS-electric Benelux. 3,3′-Dibromo-2,2′-dimethoxy-1,1′-biphenyl was prepared according to a literature procedure.[32] FAB-mass spectra were recorded by the Institute of Mass Spectroscopy of the University of Amsterdam on a JEOL JMS- SX/SX102A.

Catalysis. In a typical experiment, the autoclave was dried under reduced pressure at 50 °C for 1 h and filled with Rh(acac)$(CO)_2$ (0.020 mmol, 5 mL of a 4.0 mM stock solution in toluene), diphosphite ligand (0.022 mmol, P/Rh ratio of 2.2), and toluene (5.0 mL). Subsequently the autoclave was purged three times with syn gas ($CO:H_2 = 1:1$) and pressurized to the appropriate initial pressure. After heating the autoclave to the reaction temperature, the reaction mixture was stirred for 15 h to form the active catalyst. Styrene (2.29 mL, 20.0 mmol, filtered over neutral, activated aluminum oxide), the internal standard decane (5.0 mmol, 0.98 mL, dried on magnesium sulfate), and toluene (6.73 mL, total solvent volume 20 mL) were brought into the autoclave. During the reaction several samples were taken from the reaction vessel. After the desired reaction time the autoclave was cooled, depressurized, and vented with nitrogen. The reaction mixture was directly vacuum distilled to remove the catalyst and analyzed by GC. A sample of the reaction mixture was dissolved in ethanol. Sodium borohydride was added and the reaction mixture was stirred for 90 min at room temperature. After quenching the reaction mixture with water, the mixture was extracted two times with ethyl acetate/hexane (1/1). The organic layers were combined and dried on magnesium sulfate. About 20 μL of reduced reaction mixture was dissolved in ethanol (10 mL) and analyzed by GC for determination of the enantiomeric excess.

Preparation of HRhL∩L$(CO)_2$ Complexes. In a typical experiment a 5 mL vessel was filled with Rh(acac)$(CO)_2$ (0.0291 mmol), diphosphite ligand (0.0291 mmol), and toluene-d_8 (1 mL) and placed into the autoclave. Subsequently the autoclave was purged three times with syn gas ($CO:H_2 = 1:1$) and pressurized to the appropriate pressure (15−20 bar). After a reaction time of 15 h at 50 °C, the autoclave was cooled and depressurized. Shorter reaction times resulted in incomplete conversions and gave intermediate RhL∩L(acac) and RhL∩L(acac)(CO) species with characteristic rhodium−phosphorus coupling constants of about 300 Hz.[6,7,10b] Under atmospheric conditions NMR tubes were filled and immediately analyzed. No decomposition of HRhL∩L$(CO)_2$ could be observed during analysis. Typical IR data are given for complexes of **3a** (Rh-CO, 2066, 2016; Rh-H, 1995 cm^{-1}) and **3c** (Rh-CO, 2071, 2016; Rh-H, 1982 cm^{-1}).[10a,b]

3,3′-Dibromo-2,2′-bisphenol. This compound was prepared according to a modified literature procedure.[33] 3,3′-Dibromo-2,2′-dimethoxy-1,1′-biphenyl (40 mmol, 14.86 g) was dissolved in 57% HI (194 mmol, 43.52 g) and stirred for 4 h at reflux temperature. An additional amount of 57% HI (97 mmol) was added and the reaction mixture was refluxed overnight. The dark brown reaction mixture was extracted with CH_2Cl_2 (4 × 75 mL). The organic layers were combined and washed with 200 mL (0.1 M) NaS_2O_3 to yield a colorless organic phase. The organic layer was dried on $MgSO_4$. Evaporation of the solvent gave 12 g of crude product which was purified by column chromatography (10% EtOAc/toluene (v/v), $R_f = 0.40$). Yield: 74% (29.6 mmol, 10.18 g). Mp: 124−125 °C. ^{13}C NMR ($CDCl_3$): δ 149.3 (C arom), 132.2 (CH arom), 130.9 (CH arom), 125.4 (C arom), 121.8 (CH arom), 111.2 (C arom). ^1H NMR ($CDCl_3$): δ 7.55 (dd, 2H, arom, $^3J = 7.9$ Hz, $^4J = 1.6$ Hz), 7.23 (dd, 2H, arom, $^3J = 7.7$ Hz, $^4J = 1.6$ Hz), 6.92 (dd, 2H, arom, $^3J = 7.9$ Hz, $^3J = 7.7$ Hz), 5.92 (s, 2H, OH. Anal. Calcd for $C_{12}H_8O_2Br_2$: C, 41.90; H, 2.35. Found: C, 42.12; H, 2.50. MS: $m/z = 344$ (M^+).

2,2′-Bis(1-ethoxyethoxy)-1,1′-biphenyl. This compound was prepared *in situ* according to a literature procedure.[19] 2,2′-Bisphenol (8.0 mmol, 1.49 g) was azeotropically dried with toluene (3 × 1 mL) and dissolved in a solution of pyridinium *p*-toluenesulfonate (0.8 mmol, 0.21 g) in CH_2Cl_2 (65 mL). Ethyl vinyl ether (24.0 mmol, 2.29 mL) was slowly added at room temperature and the mixture stirred for 72 h. The reaction mixture was poured into water and extracted with diethyl ether. The organic phase was washed with brine and dried on $MgSO_4$. Evaporation of the solvent gave 2,2′-bis(1-ethoxyethoxy)-1,1′-biphenyl as a diastereomeric mixture in quantitative yield. The product was used in the subsequent reactions without further purification.

3,3′-Bis(trimethylsilyl)-2,2′-bis(1-ethoxyethoxy)-1,1′-biphenyl. 2,2′-Bis(1-ethoxyethoxy)-1,1′-biphenyl (8.0 mmol) was azeotropically dried with toluene (3 × 1 mL) and dissolved in Et_2O (25 mL). A solution of *n*-BuLi in hexane (32 mmol, 2.5 M, 12.8 mL) was slowly added at room temperature and the reaction mixture was stirred overnight. The white precipitate was cautiously washed with hexanes (2 × 5 mL) and dissolved in THF (25 mL). At −78 °C a solution of $SiMe_3Cl$ (16 mmol, 2.04 mL) in THF (20 mL) was added slowly. The reaction mixture was warmed to room temperature overnight. The reaction mixture was quenched with H_2O (25 mL) and extracted with Et_2O (3 × 25 mL). The organic layers were combined, dried on $MgSO_4$, and evaporated to dryness. The product was purified by column chromatography (2% EtOAc/PE 60−80 °C (v/v), $R_f = 0.40$). Yield: 42% (3.35 mmol, 1.59 g) of a yellow oil. ^1H NMR ($CDCl_3$): δ 7.43 (dd, $^3J = 7.2$ Hz, $^4J = 1.7$ Hz, 2H, arom), 7.27 (m, 2H, arom), 7.12 (dd, $^3J = 14$ Hz, $^3J = 6.3$ Hz, 2H, arom), 4.63 (q, $^3J = 5.0$ Hz, 2H, CH_3CH_2), 3.73 (q, $^3J = 7.1$ Hz, 2H, CH_3CH_2), 3.14 (m, H, CH), 2.94 (m, H, CH), 1.16 (d, $^3J = 5.0$ Hz, 6H, CH_3), 0.86 (d, $^3J = 6.9$ Hz, 6H, CH_3) 0.35 (m, 18H, $Si(CH_3)_3$).

3,3′-Bis(trimethylsilyl)-2,2′-bisphenol (1a). 3,3′-Bis(trimethylsilyl)-2,2′-bis(1-ethoxyethoxy)-1,1′-biphenyl (3.36 mmol) was deprotected with pyridinium *p*-toluenesulfonate according to a literature procedure.[19] The product was purified by column chromatography (7% EtOAc/PE 60−80 °C (v/v), $R_f =$

(32) Lingenfelter, D. S.; Helgeson, R. C.; Cram, D. J. *J. Org. Chem.* **1981**, *46*, 393.

0.42). Mp: 99−100 °C. Yield: 75% (2.52 mmol, 0.83 g) of a white powder. ^{1}H NMR ($CDCl_3$): δ 7.45 (dd, ^3J = 7.2 Hz, ^4J = 1.7 Hz, 2H, arom), 7.26 (dd, ^3J = 7.4 Hz, ^4J = 1.8 Hz, 2H, arom), 7.04 (dd, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 2H, arom), 5.29 (s, 2H, OH), 0.34 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 158.6 (C, arom), 136.7 (CH, arom), 132.8 (CH, arom), 127.5 (C, arom), 121.9 (C, arom), 121.7 (C, arom), −0.3 (CH_3, $Si(CH_3)_3$). MS: m/z = 330 (M^+). Mp: 94.0−95.0 °C. Anal. Calcd for $C_{18}H_{26}O_2Si_2$: C, 65.40; H, 7.93. Found: C, 65.72; H, 8.10.

3,3′-Bis(triethylsilyl)-2,2′-bisphenol (1b). To a solution of 3,3′-dibromo-2,2′-bisphenol (4.5 mmol, 1.55 g) in DMF (30 mL) and imidazole (13.5 mmol, 0.92 g) was added triethylsilyl chloride (11.3 mmol, 1.89 mL). The reaction mixture was stirred over night and worked up following a standard literature procedure.[17a] The crude triethylsilyl ether was purified by column chromatography (hexane/CH_2Cl_2 = 2/1 (v/v), R_f = 0.90). Yield: 68% (3.1 mmol, 1.77 g) of a white solid. Mp: 56.5−58.0 °C. ^{13}C NMR ($CDCl_3$): δ 152.2 (C arom), 133.3 (CH arom), 131.1 (CH arom), 122.6 (C arom), 122.5 (CH arom), 117.0 (C arom), 7.2 (CH_2CH_3), 5.8 (CH_2CH_3). ^{1}H NMR ($CDCl_3$): δ 7.54 (dd, 2H, arom, ^3J = 7.9 Hz, ^4J = 1.6 Hz), 7.10 (dd, 2H, arom, ^3J = 7.5 Hz, ^4J = 1.7 Hz), 6.87 (dd, 2H, arom, ^3J = 7.7 Hz, ^3J = 7.8 Hz), 0.79 (t, 18H, CH_3), 0.36 (m, 12H, CH_2). MS: m/z = 573 (M^+). Anal. Calcd for $C_{24}H_{36}Br_2O_2Si_2$: C, 50.35; H, 6.34. Found: C, 50.49; H, 6.35.

The triethylsilyl ether (3.1 mmol, 1.77 g) was azeotropically dried with toluene (3 × 1 mL) and dissolved in THF (40 mL). *t*-BuLi (1.7 M in pentane, 9.3 mmol, 5.47 mL) was added in 10 min at 0 °C. The reaction mixture was additionally stirred for 1 h at room temperature and worked up following a literature procedure.[17a] Yield: 66% (2.05 mmol, 2.05 g) of a white solid. ^{13}C NMR ($CDCl_3$): δ 158.8 (C arom), 137.5 (CH arom), 132.5 (CH arom), 124.5 (C arom), 121.8 (C arom), 121.5 (CH arom), 8.2 (CH_2CH_3), 4.0 (CH_2CH_3). ^{1}H NMR ($CDCl_3$): δ 7.43 (dd, 2H, arom, ^3J = 7.3 Hz, ^4J = 1.7 Hz), 7.25 (dd, 2H, arom, ^3J = 7.5 Hz, ^4J = 1.7 Hz), 7.03 (dd, 2H, arom, ^3J = 7.4 Hz, ^3J = 7.4 Hz), 5.25 (s, 2H, OH), 0.97 (m, 18H, CH_3), 0.90 (m, 12H, CH_2). MS: m/z = 414 (M^+). Anal. Calcd for $C_{24}H_{38}O_2Si_2$: C, 69.50; H, 9.24. Found: C, 69.60; H, 9.08. Mp: 51.5−53.0 °C.

3,3′-Bis(*tert*-butyldimethylsilyl)-2,2′-bisphenol (1c). This compound was prepared as described for **1b**. The crude *tert*-butyldimethylsilyl ether was purified by column chromatography (hexanes/CH_2Cl_2 = 2/1 (v/v), R_f = 0.90). Yield: 96% (4.82 mmol, 2.76 g) of a white powder. Mp: 102−103 °C. ^{13}C NMR ($CDCl_3$): δ 150.3 (C arom), 132.9 (CH arom), 132.5 (C arom), 131.2 (CH arom), 122.0 (CH arom), 116.3 (C arom), 25.7 ($C(CH_3)_3$), 18.3 ($C(CH_3)_3$), −3.5 ($SiCH_3$), −4.4 ($SiCH_3$). ^{1}H NMR ($CDCl_3$): δ 7.52 (dd, 2H, arom, ^3J = 8.5 Hz, ^4J = 1.6 Hz), 7.23 (dd, 2H, arom, ^3J = 7.5 Hz, ^4J = 1.5 Hz), 6.88 (dd, 2H, arom, ^3J = 7.8 Hz, ^3J = 7.8 Hz), 0.92 (s, 18H, *t*-Bu), −0.03 (s, 6H, CH_3), −0.49 (s, 6H, CH_3). HRMS (FAB+) m/z = 571.0691 (calcd 573.0680). Anal. Calcd for $C_{24}H_{36}Br_2O_2Si_2$: C, 50.35; H, 6.34. Found: C, 50.72; H, 6.42.

Data for **1c**. Compound **1c** was purified by column chromatography (EtOAc/PE 60−80 °C = 2/1 (v/v), R_f = 0.79). Yield: 90% (4.31 mmol, 1.78 g) of a white solid. Mp: 61.0−62.5 °C. ^{13}C NMR ($CDCl_3$): δ 158.0 (C arom), 137.3 (CH arom), 131.9 (CH arom), 124.1 (C arom), 121.4 (C arom), 120.6 (CH arom), 26.9 ($C(CH_3)_3$), 17.5 ($C(CH_3)_3$), −4.8 ($SiCH_3$). ^{1}H NMR ($CDCl_3$): δ 7.44 (dd, 2H, arom, ^3J = 7.3 Hz, ^4J = 1.6 Hz), 7.24 (dd, 2H, arom, ^3J = 7.4 Hz, ^4J = 1.6 Hz), 7.02 (dd, 2H, arom, ^3J = 7.4 Hz, ^3J = 7.4 Hz), 5.26 (s, 2H, OH), 0.92 (s, 18H, *tert*-Bu), 0.34 (s, 12H, CH_3). MS: m/z = 427 ($M + H)^+$. Anal. Calcd for $C_{24}H_{38}O_2Si_2$: C, 69.50; H, 9.24. Found: C, 69.38; H, 9.01.

3,3′-Bis(triphenylsilyl)-2,2′-bisphenol (1d). This compound was prepared as described for **1b**. The crude triphenylsilyl ether was purified by column chromatography (hexanes/CH_2Cl_2 = 2/1 (v/v), R_f = 0.86). Yield: 76% (4.41 mmol, 3.79 g) of a white powder. Mp: 167.7−168.9 °C. ^{1}H NMR (acetone-d_6): δ 7.62 (dd, 2H, arom, ^3J = 8.1 Hz, ^4J = 1.5 Hz), 7.58−7.73 (m, 28H, arom), 7.25 (dd, 2H, arom, ^3J = 9.3 Hz, ^4J = 2.0 Hz), 6.66−6.56 (m, 4H, arom). ^{13}C NMR ($CDCl_3$): δ 151.0 (C, arom), 136.2 (CH, arom), 134.5 (C, arom), 133.8 (CH, arom), 133.3 (C, arom), 131.1 (CH, arom), 130.4 (CH, arom), 128.1 (CH, arom), 123.2 (CH, arom), 117.0 (C, arom). MS: m/z = 860 (M^+). Anal. Calcd for $C_{48}H_{36}Br_2O_2Si_2$: C, 66.97; H, 4.21. Found: C, 67.25; H, 4.01.

Data for **1d**. Compound **1d** was purified by column chromatography (hexanes/CH_2Cl_2 = 1/1 (v/v), R_f = 0.42). Yield: 98% (1.96 mmol, 1.38 g) of a white powder. Mp: 167.5−169.0 °C. ^{1}H NMR (acetone-d_6): δ 7.73 (dd, 12H, arom, ^3J = 7.9 Hz, ^4J = 1.5 Hz), 7.62 (dd, 2H, arom, ^3J = 7.7 Hz, ^4J = 1.4 Hz), 7.56−7.43 (m, 18H, arom), 7.25 (dd, 2H, arom, ^3J = 7.3 Hz, ^4J = 1.7 Hz), 7.10 (dd, 2H, arom, ^3J = 7.4 Hz, ^3J = 7.4 Hz), 2.96 (s, 2H, OH). ^{13}C NMR ($CDCl_3$): δ 158.7 (C, arom), 139.4 (CH, arom), 137.0 (CH, arom), 134.9 (CH, arom), 134.7 (C, arom), 130.4 (CH, arom), 128.7 (CH, arom), 125.1 (C, arom), 122.1 (CH, arom), 121.6 (C, arom). MS: m/z = 725 ($M + Na)^+$. Anal. Calcd for $C_{48}H_{38}O_2Si_2$: C, 82.01; H, 5.45. Found: C, 81.55; H, 5.74.

Compound 3a. 3,3′-Bis(trimethylsilyl)-2,2′-bisphenol (**1a**) (1.25 mmol, 0.41 g) was azeotropically dried with toluene (3 × 1 mL), dissolved in toluene (10 mL), and added slowly to a solution of PCl_3 (2.00 mmol, 175 μL) and Et_3N (5.0 mmol, 0.52 mL) in toluene (10 mL) at 0 °C. Subsequently the reaction mixture was stirred 4 h at room temperature. The formed amine salts were removed by filtration. Evaporation to dryness gave the crude phosphorochloridite, which was used without further purification and was dissolved in toluene (10 mL) and Et_3N (5.0 mmol, 0.52 mL). To this solution was added (2*R*,4*R*)-pentane-2,4-diol (0.57 mmol, 59 mg, azeotropically dried with 3 × 1 mL toluene) in toluene (10 mL) at room temperature. The reaction mixture was stirred overnight, filtrated, and evaporated to dryness. The product was purified by column chromatography (10% EtOAc/PE 60−80 °C (v/v), R_f = 0.63). Yield: 81% (0.46 mmol, 0.38 g) of a white solid. Mp: 56−57 °C. $[\alpha]^{20}_D$ = 30° (c = 0.10, CH_2Cl_2). Anal. Calcd for $C_{41}H_{58}O_6P_2Si_4$: C, 59.96; H, 7.12. Found: C, 59.50; H, 7.17. ^{31}P−^{1}H NMR (benzene-d_6): δ 145.1 (m, $^3J_{PH}$ = 5.5 Hz, J_{PP} = 5.2 Hz). ^{13}C NMR (benzene-d_6): δ 154.6 (t, C arom, $^3J_{PC}$ = 6.8 Hz), 154.4 (t, C arom, $^3J_{PC}$ = 5.4 Hz), 135.0 (CH arom), 134.9 (CH arom), 132.2 (CH arom), 132.1 (CH arom), 131.7 (C arom), 131.6 (C arom), 131.3 (t, C arom, $^3J_{PC}$ < 2.0 Hz), 131.2 (t, C arom, $^3J_{PC}$ < 2.0 Hz), 124.5 (CH arom), 124.4 (CH arom), 69.6 (CH), 46.4 (b, CH_2), 22.1 (CH_3), 0.2 ($Si(CH_3)_3$). ^{1}H NMR (benzene-d_6): δ 7.40−7.38 (m, 4H, arom), 7.19−7.16 (m, 4H, arom), 7.03−6.97 (m, 4H, arom), 4.45 (m, 2H, CH), 1.92 (t, 2H, CH_2, ^3J = 6.5 Hz), 1.03 (d, 6H, CH_3, ^3J = 6.1 Hz), 0.41 (s, 18 H, $Si(CH_3)_3$), 0.39 (s, 18 H, $Si(CH_3)_3$).

Compound 3b. This compound was prepared as described for **3a**. The product was purified by column chromatography (2.0% EtOAc/5% Et_3N/PE 60−80 °C (v/v/v), R_f = 0.82) to yield 73% (0.73 mmol, 0.72 g) of a colorless oil, which was stored as a stock solution in benzene at −20 °C. $[\alpha]^{20}_D$ = 70.7° (c = 2.47, C_6H_6). Anal. Calcd for $C_{53}H_{82}O_6P_2Si_4$: C, 64.46; H, 8.17. Found: C, 64.50; H, 8.47. ^{31}P−^{1}H NMR ($CDCl_3$): δ 147.1 (m, $^3J_{PH}$ = 7.0, J_{PP} = 9.0 Hz). ^{13}C NMR ($CDCl_3$): δ 155.2 (t, C arom), 154.8 (t, C arom), 136.5 (CH arom), 136.4 (CH arom), 132.69 (CH arom), 132.67 (CH arom), 132.0 (t, C arom), 131.7 (t, C arom), 129.6 (C arom), 129.5 (C arom), 124.9 (CH arom), 124.7 (CH arom), 70.1 (t, CH), 47.2 (CH_2), 23.1 (CH_3), 8.1 (CH_2CH_3), 4.5 (CH_2CH_3). ^{1}H NMR ($CDCl_3$): δ 7.42 (dd, 4H, arom, ^3J = 7.3 Hz, ^4J = 1.0 Hz), 7.38 (dd, 4H, arom, ^3J = 7.6 Hz, ^4J = 1.0 Hz), 7.38 (dd, 2H, arom, ^3J = 7.4 Hz, ^3J = 7.4 Hz), 7.23 (dd, 2H, arom, ^3J = 7.4 Hz, ^3J = 7.4 Hz), 4.39 (m, 2H, CH), 1.84 (t, 2H, CH_2, ^3J = 6.4 Hz), 1.11 (d, 6H, CH_3, ^3J = 6.2 Hz), 0.93 (m, 60H, CH_2CH_3).

Compound 3c. This compound was prepared as described for **3a**.The product was purified by column chromatography (2.5% EtOAc/5% Et_3N/PE 60−80 °C (v/v/v), R_f = 0.74). Yield: 81% (0.81 mmol, 0.80 g) of a white solid. Mp: 65−67 °C. $[\alpha]^{20}_D$ = −27.0° (c = 0.10, CH_2Cl_2). ^{31}P−^{1}H NMR ($CDCl_3$): δ 139.4 (d, $^3J_{PH}$ = 8.5 Hz). ^{13}C NMR (benzene-d_6): δ 154.9 (m, C arom), 136.4 (CH arom), 136.3 (CH arom), 132.3 (CH arom), 132.1 (CH arom), 131.6 (m, C arom), 128.9 (C arom), 128.8 (C arom),

124.0 (CH arom), 123.9 (CH arom), 69.4 (d, CH, $^2J_{PC}$ = 5.2 Hz), 45.5 (CH_2), 26.6 ($C(CH_3)_3$), 26.5 ($C(CH_3)_3$), 21.3 (CH_3), 17.4 ($C(CH_3)_3$), 17.3 ($C(CH_3)_3$), −3.5 ($Si(CH_3)_3$), −3.7 ($Si(CH_3)_3$). ^{1}H NMR ($CDCl_3$): δ 7.46 (dd, 2H, arom, ^3J = 7.3 Hz, ^4J = 1.7 Hz), 7.42 (dd, 2H, arom, ^3J = 7.3 Hz, ^4J = 1.7 Hz), 7.35 (dd, 2H, arom, ^3J = 5.0 Hz, ^4J = 1.7 Hz), 7.33 (dd, 2H, arom, ^3J = 5.1 Hz, ^4J = 1.7 Hz), 7.21 (dd, 2H, arom, ^3J = 7.5 Hz, ^3J = 7.4 Hz), 7.18 (dd, 2H, arom, ^3J = 7.5 Hz, ^3J = 7.4 Hz), 3.96 (m, 2H, CH), 1.69 (t, 2H, CH_2, ^3J = 7.1 Hz), 0.84 (s, 18H, $C(CH_3)_3$), 0.83 (s, 18H, $C(CH_3)_3$), 0.66 (d, 6H, CH_3, ^3J = 6.1 Hz), 0.45 (s, 6H, CH_3), 0.40 (s, 6H, CH_3), 0.39 (s, 6H, CH_3), 0.36 (s, 6H, CH_3). MS: m/z = 1012 $(M + Na)^+$. Anal. Calcd for $C_{53}H_{82}O_6P_2Si_4$: C, 64.33; H, 8.36. Found: C, 64.77; H, 8.57.

Racemic (*R*/*S*)-(±)-2,2′-bis(1-ethoxyethoxy)-1,1′-binaphthyl. This compound was prepared *in situ* according to a literature procedure.[19] Racemic (*R*/*S*)-(±)-2,2′-bisnaphthol (15.0 mmol, 4.30 g) was azeotropically dried with toluene (3 × 5 mL) and dissolved in a solution of pyridinium *p*-toluenesulfonate (1.5 mmol, 0.40 g) in CH_2Cl_2 (125 mL). Ethyl vinyl ether (45.0 mmol, 4.30 mL) was slowly added at room temperature and the mixtured stirred for 72 h. The reaction mixture was poured into water and extracted with diethyl ether. The organic phase was washed with brine and dried on $MgSO_4$. Evaporation of the solvent gave (*R*/*S*)-(±)-2,2′-bis-(1-ethoxyethoxy)-1,1′-binaphthyl in quantitative yield. A complex ^{1}H NMR spectrum was obtained for the diastereomeric mixture. The product was used in the subsequent reactions without further purification.

(*R*)-(+)- and (*S*)-(−)-2,2′-Bis(1-ethoxyethoxy)-1,1′-binaphthyl. These compounds were prepared according to the procedure as described for racemic (*R*/*S*)-(±)-2,2′-bis(1-ethoxyethoxy)-1,1′-binaphthyl in a quantitative yield. Data for the (*S*)-enantiomer: Yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.92 (d, ^3J = 9.0 Hz, 2H, arom), 7.67 (d, ^3J = 8.2 Hz, 2H, arom), 7.58 (dd, ^3J = 8.9 Hz, ^4J = 2.2 Hz, 1H, arom), 7.57 (d, ^3J = 9.0 Hz, 1H, arom), 7.35 (dd, ^3J = 7.1 Hz, ^3J = 7.1 Hz), 7.17 (m, 4H, arom), 5.20 (m, 1H), 5.09 (m, 1H), 3.45 (m, 2H), 3.27 (m, 1H), 3.16 (m, 1H), 1.19 (m, 3H), 1.06 (m, 6H), 0.97 (m, 3H). The (*R*)-enantiomer gave identical chemical shifts. The product was used in the subsequent reactions without further purification.

Racemic (*R*/*S*)-(±)-3,3′-Bis(trimethylsilyl)-2,2′-bis(1-ethoxyethoxy)-1,1′-binaphthyl. This compound was prepared according to the procedure described for 3,3′-bis-(trimethylsilyl)-2,2′-bis(1-ethoxyethoxy)-1,1′-biphenyl. Yield: 71% (2.87 mmol, 1.65 g). A complex ^{1}H NMR spectrum was obtained for the diastereomeric mixture. The product was used in the subsequent reactions without further purification.

(*R*)-(+)- and (*S*)-(−)-3,3′-Bis(trimethylsilyl)-2,2′-bis(1-ethoxyethoxy)-1,1′-binaphthyl. These compounds were prepared according to the procedure as described for 3,3′-bis-(trimethylsilyl)-2,2′-bis(1-ethoxyethoxy)-1,1′-biphenyl. Data for the (*S*)-enantiomer: Yield: 88% (1.75 mmol, 1.01 g). ^{1}H NMR ($CDCl_3$): δ 8.06 (d, ^4J = 2.9 Hz, 2H, arom), 7.89 (dd, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 2H, arom), 7.37 (m, 2H, arom), 7.28 (m, 4H, arom), 4.33 (m, 1H), 4.07 (m, 1H), 3.80 (m, 1H), 3.10 (m, 1H), 2.97 (m, 1H), 2.68 (m, 1H), 1.07 (m, 3H, CH_3), 0.94 (m, 3H, CH_3), 0.74 (m, 6H, CH_3), 0.42 (m, 18H, $Si(CH_3)_3$).

Racemic (*R*/*S*)-(±)-3,3′-Bis(trimethylsilyl)-2,2′-bisnaphthol ((*R*/*S*)-2a). Racemic (*R*/*S*)-(±)-3,3′-bis(trimethylsilyl)-2,2′-bis(1-ethoxyethoxy)-1,1′-binaphthyl (2.87 mmol, 1.65 g) was deprotected with pyridinium *p*-toluene sulfonate according to a literature procedure.[19] The product was purified by column chromatography (2.5% EtOAc/PE 60−80 °C (v/v), R_f = 0.31). Mp: 158−160 °C. Yield: 66% (1.93 mmol, 0.83 g) of a white powder. ^{13}C NMR ($CDCl_3$): δ 158.4 (C arom), 139.2 (CH arom), 135.7 (C arom), 130.7 (C arom), 130.3 (C arom), 130.0 (CH arom), 129.0 (CH arom), 125.4 (CH arom), 125.1 (CH arom), 111.0 (C arom), 0.57 ($Si(CH)_3$). ^{1}H NMR ($CDCl_3$): δ 8.07 (s, 2H, arom), 7.89 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 2H, arom), 7.35 (ddd, ^3J = 6.6 Hz,^3J = 6.6 Hz, ^4J = 1.5 Hz, 2H, arom), 7.29 (ddd, ^3J = 6.7 Hz,^3J = 6.7 Hz, ^4J = 1.6 Hz, 2H, arom), 7.09 (d, ^3J = 8.2 Hz, 2H, arom), 4.86 (s, 2H, OH), 0.41 (s, 18H, $Si(CH_3)_3$) (lit.[34] ^{1}H NMR 8.07, 7.89, 7.35, 7.28, 7.09, 5.2, 0.41).

(*R*)-(+)- and (*S*)-(−)-3,3′-Bis(trimethylsilyl)-2,2′-bisnaphthol ((*R*)-2a) and ((*S*)-2a). These compounds were prepared according to the procedure as described for (*R*/*S*)-**2a**. (*R*)-(−)-3,3′-Bis(trimethylsilyl)-2,2′-bis(1-ethoxyethoxy)-1,1′-binaphthyl (1.75 mmol, 1.01 g) was deprotected with pyridinium *p*-toluenesulfonate according to a literature procedure.[19] The product was purified by column chromatography (5.0% EtOAc/PE 60−80 °C (v/v), R_f = 0.24). Yield: 97% (1.69 mmol, 0.73 g) of a white powder. ^{1}H NMR ($CDCl_3$): δ 8.08 (s, 2H, arom), 7.89 (dd, ^3J = 8.0 Hz, ^4J = 1.1 Hz, 2H, arom), 7.36 (ddd, ^3J = 6.8 Hz,^3J = 6.8 Hz, ^4J = 1.1 Hz, 2H, arom), 7.29 (ddd, ^3J = 8.6 Hz,^3J = 8.6 Hz, ^4J = 1.4 Hz, 2H, arom), 7.09 (dd, ^3J = 8.2 Hz, ^4J = 1.1 Hz, 2H, arom), 5.24 (s, 2H, OH), 0.41 (s, 18H, $Si(CH_3)_3$). $[\alpha]^{20}_D$ = +142° (c = 0.52, THF) [lit.[17a] $[\alpha]^{20}_D$ +143° (c = 0.985, THF)]. Mp: 70.5−73 °C (lit.[17a] mp 68−71 °C). The same route has been followed for the (*S*)-enantiomer.

Racemic (*R*/*S*)-(±)-3,3′-Dibromo-2,2′-bisnaphthol. This compound was prepared according to a literature procedure.[17a,32] Mp: 158−160 °C. ^{1}H NMR ($CDCl_3$): δ 8.26 (s, 2H, arom), 7.82 (d, 2H, arom, ^3J = 8.0 Hz), 7.39 (ddd, 2H, arom, ^3J = 7.9 Hz, ^3J = 7.9 Hz, ^4J = 1.1 Hz), 7.31 (ddd, 2H, arom, ^3J = 6.8 Hz, ^3J = 6.8 Hz, ^4J = 1.2 Hz), 7.10 (d, 2H, arom, ^3J = 8.3 Hz), 5.55 (s, 2H, OH) [lit.[34] ^{1}H NMR 8.35, 7.9, 7.40, 7.30, 7.00, 8.45 (OH)]. ^{13}C NMR ($CDCl_3$): δ 148.7 (C, arom), 133.5 (CH, arom), 130.4 (C, arom), 128.3 (CH, arom), 125.6 (CH, arom), 125.3 (CH, arom), 115.3 (C, arom), 112.9 (C, arom).

Racemic (*R*/*S*)-(±)-3,3′-Bis(triethylsilyl)-2,2′-bisnaphthol ((*R*/*S*)-2b). This compound was prepared according to a literature procedure for analogous compounds.[17a] Yield: 70% after purification by column chromatography (10% EtOAc/PE 60−80 °C (v/v), R_f = 0.54). Mp: 134−136 °C. ^{1}H NMR ($CDCl_3$): δ 8.07 (s, 2H, arom), 7.89 (d, 2H, arom, ^3J = 7.7 Hz), 7.36 (ddd, 2H, arom, ^3J = 6.7 Hz, ^3J = 6.7 Hz, ^4J = 1.0 Hz), 7.29 (ddd, 2H, arom, ^3J = 6.8 Hz, ^3J = 6.7 Hz, ^4J = 1.3 Hz), 7.09 (d, 2H, arom, ^3J = 8.2 Hz), 5.22 (s, 2H, OH), 1.10−0.87 (m, 30H, $Si(CH_2CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 157.8 (C, arom), 139.8 (CH, arom), 134.9 (C, arom), 130.0 (C, arom), 129.2 (CH, arom), 128.3 (CH, arom), 126.9 (C, arom), 124.6 (CH, arom), 124.3 (CH, arom), 110.1 (C, arom), 8.4 (CH_2, $SiEt_3$), 4.2 (CH_3, $SiEt_3$). Anal. Calcd for $C_{32}H_{42}O_2Si_2$: C, 74.65; H, 8.23. Found: C, 73.86; H, 8.30.

Racemic (*R*/*S*)-(±)-3,3′-Bis(*tert*-butyldimethylsilyl)-2,2′-bisnaphthol ((*R*/*S*)-2c). This compound was prepared according to a literature procedure.[17a] Mp: 217.5−218.5 °C. ^{1}H NMR ($CDCl_3$): δ 8.08 (s, 2H, arom), 7.89 (d, 2H, arom, ^3J = 8.0 Hz, ^4J = 1.2 Hz), 7.35 (ddd, 2H, arom, ^3J = 6.8 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz), 7.29 (ddd, 2H, arom, ^3J = 6.7 Hz, ^3J = 6.6 Hz, ^4J = 1.4 Hz), 7.09 (d, 2H, arom, ^3J = 8.2 Hz), 5.22 (s, 2H, OH), 0.95 (s, 18H, Si*t*-Bu), 0.43 (s, 6H, $SiCH_3$), 0.42 (s, 6H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 157.8 (C, arom), 140.1 (CH, arom), 134.9 (C, arom), 129.8 (C, arom), 129.3 (CH, arom), 128.3 (CH, arom), 127.4 (C, arom), 124.5 (CH, arom), 124.3 (CH, arom), 110.3 (C, arom), 27.8 (CH3, tert-Butyl), 18.3 (CH_3, *t*-Bu), −4.4 (CH_3, $Si(CH_3)_2$(*t*-Bu)), −4.5 (CH_3, $Si(CH_3)_2$(*t*-Bu)). MS: m/z = 514 (M^+). Anal. Calcd for $C_{32}H_{42}O_2Si_2$: C, 74.65; H, 8.23. Found: C, 74.57; H, 8.30.

Compound 4a. Compound (*R*/*S*)-**2a** (1.05 mmol) was azeotropically dried with toluene (3 × 1 mL), dissolved in toluene (10 mL) and added slowly to a solution of PCl_3 (1.32 mmol, 115 μL) and Et_3N (3.0 mmol, 0.31 mL) in toluene (10 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature. The formed amine salts were removed by filtration. Evaporation to dryness gave the crude phosphorochloridite, which was used without further purification and dissolved in toluene (10 mL) and Et_3N (3.0 mmol, 0.31 mL). To this solution was added (2*R*,4*R*)-pentane-2,4-diol (0.48 mmol, 50 mg, azeotropically dried with toluene 3 × 1 mL) in

(33) Adams, R.; Kornblum, N. *J. Am. Chem. Soc.* **1941**, *63*, 188.
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toluene (10 mL) at room temperature. The reaction mixture was stirred overnight, filtrated, and evaporated to dryness. The diastereomeric mixture was purified by column chromatography (10% EtOAc/PE 60−80 °C (v/v), $R_f = 0.46$). Yield: 87% (0.41 mmol, 0.42 g) of a white solid. $^{31}P-^{1}H$ NMR (benzene-d_6): **5** = δ 146.1 (m, $J_{PP} = 13$ Hz, $^3J_{PH} = 7.2$ Hz), **7** = δ 144.7 (d, $^3J_{PH} = 7.3$ Hz), **8** = δ 144.42 (d, $^3J_{PH} = 8.5$ Hz) and 144.24 (d, $^3J_{PH} = 7.3$ Hz).

Compound 4b. This compound was prepared as described for **3a**. The diastereomeric mixture was purified by column chromatography (1% Et_3N/15% EtOAc/PE 60−80 °C (v/v/v), $R_f = 0.72$). Yield: 47% (0.22 mmol, 0.26 g) of a white solid. Mp: 106.5−107.5 °C. $^{31}P-^{1}H$ NMR (benzene-d_6): δ 148.2 (b), 146.9 (d, $^3J_{PH} = 8.5$ Hz), 145.8 (d, $^3J_{PH} = 8.5$ Hz), 144.9 (d, $^3J_{PH} = 8.5$ Hz). MS: $m/z = 1212$ $(M + Na)^+$. Anal. Calcd for $C_{69}H_{90}O_6P_2Si_4$: C, 69.65; H, 7.63. Found: C, 70.31; H, 7.96.

Compound 4c. This compound was prepared as described for **3a**. The diastereomeric mixture was purified by column chromatography (1% Et_3N/15% EtOAc/PE 60−80 °C (v/v/v), $R_f = 0.75$). Yield: 76% (0.53 mmol, 0.80 g) of a white solid. $^{31}P-^{1}H$ NMR (benzene-d_6): δ 139.9 (d, $^3J_{PH} = 7.3$ Hz), 138.7 (d, $^3J_{PH} = 9.7$ Hz), 137.9 (d, $^3J_{PH} = 8.5$ Hz), 136.8 (d, $^3J_{PH} = 9.7$ Hz). Anal. Calcd for $C_{69}H_{90}O_6P_2Si_4$: C, 69.65; H, 7.63. Found: C, 70.37; H, 8.03.

Compound 5. This compound was prepared as described for **3a**. (*S*)-(−)-3,3′-Bis(trimethylsilyl)-2,2′-bisnaphthol (1.23 mmol, 0.53 g) was used for the synthesis of **5**. The product was purified by column chromatography (5% EtOAc/PE 60−80 °C, (v/v), $R_f = 0.39$). Yield: 96% (0.48 mmol, 0.50 g) of a white solid. Mp: 124−126 °C. Anal. Calcd for $C_{57}H_{66}O_6P_2Si_4$: C, 67.02; H, 6.51. Found: C, 67.11; H, 6.95. $[\alpha]^{20}_D = 51.6°$ ($c = 0.10$, CH_2Cl_2). ^{31}P NMR (benzene-d_6): δ 146.1. ^{13}C NMR (benzene-d_6): δ 152.7 (t, C arom, $J_{PC} = 6.0$ Hz), 152.1 (t, C arom, $J_{PC} = 5.0$ Hz), 137.8 (CH arom), 136.7 (CH arom), 134.6 (C arom), 134.3 (C arom), 132.5 (C arom), 132.4 (C arom), 131.3 (C arom), 130.8 (C arom), 128.7 (CH arom), 128.5 (CH arom), 126.9 (CH arom), 126.7 (CH arom), 126.6 (CH arom), 126.4 (CH arom), 124.8 (CH arom), 124.7 (CH arom), 123.5 (t, C arom, $J_{PC} = 5.5$ Hz), 122.6 (t, C arom, $J_{PC} = 3.0$ Hz), 69.5 (CH), 47.3 (CH_2), 22.2 (CH_3), 0.2 ($Si(CH_3)_3$), 0.1 ($SiCH_3)_3$). ^1H NMR (benzene-d_6): δ 8.08 (s, 2H, arom), 8.07 (s, 2H, arom), 7.69 (d, 2H, arom, $^3J = 7.6$ Hz), 7.66 (d, 2H, arom, $^3J = 7.6$ Hz), 7.31 (d, 2H, arom, $^3J = 8.5$ Hz), 7.25 (d, 2H, arom, $^3J = 8.5$ Hz), 7.12 (dd, 2H, arom, $J = 7.6$ Hz, $J = 7.3$ Hz), 7.10 (dd, 2H, arom, $J = 7.4$ Hz, $J = 7.5$ Hz), 6.87 (dd, 2H, arom, $J = 7.6$ Hz, $J = 7.7$ Hz), 6.85 (dd, 2H, arom, $J = 7.7$ Hz, $J = 7.4$ Hz), 4.48 (m, 2H, CH), 1.90 (t, 2H, CH_2, $^3J = 6.1$ Hz), 0.69 (d, 6H, CH_3, $^3J = 6.5$ Hz), 0.50 (s, 36 H, $Si(CH_3)_3$).

Compound 6. This compound was prepared as described for **3a**. (2*S*,4*S*)-Pentane-2,4-diol has been used for the synthesis of **6**. The product was purified by column chromatography (1% Et_3N/5% EtOAc/PE 60−80 °C, (v/v), $R_f = 0.27$). Yield: 73% (0.51 mmol, 0.53 g) of a white solid. Mp: 140−142 °C. Anal. Calcd for $C_{57}H_{66}O_6P_2Si_4$: C, 67.02; H, 6.52. Found: C, 67.24; H, 6.81. $[\alpha]^{20}_D = 64.7°$ ($c = 0.10$, CH_2Cl_2). $^{31}P-^{1}H$ NMR (benzene-d_6): δ 144.6 (d, $^3J_{PH} = 8.5$ Hz). ^{13}C NMR (benzene-d_6): δ 152.4 (d, C arom, $^3J_{PC} = 3.0$ Hz), 152.4 (d, C arom, $^3J_{PC} = 1.5$ Hz), 137.3 (CH arom), 136.9 (CH arom), 134.5 (C arom), 134.3 (C arom), 132.5 (C arom), 132.3 (C arom), 131.3 (C arom), 130.0 (C arom), 128.5 (CH arom), 128.3 (CH arom), 126.9 (CH arom), 126.7 (CH arom), 124.8 (CH arom), 124.7 (CH arom), 123.3 (CH arom), 123.2 (CH arom), 122.7 (C arom,), 122.6 (C arom), 70.5 (CH), 45.4 (CH_2), 21.8 (CH_3), 21.7 (CH_3), 0.3 (2 $Si(CH_3)_3$), 0.0 ($SiCH_3)_3$), −0.1 ($SiCH_3)_3$). ^1H NMR (benzene-d_6): δ 8.14 (s, 2H, arom), 8.05 (s, 2H, arom), 7.71 (d, 2H, arom, $^3J = 8.2$ Hz), 7.66 (d, 2H, arom, $^3J = 8.2$ Hz), 7.30 (d, 2H, arom, $^3J = 8.5$ Hz), 7.22 (d, 2H, arom, $^3J = 8.5$ Hz), 7.13 (dd, 2H, arom, $J = 7.6$ Hz, $J = 9.0$ Hz), 7.10 (dd, 2H, arom, $J = 9.0$ Hz, $J = 8.3$ Hz), 6.86 (dd, 2H, arom, $J = 7.9$ Hz, $J = 7.7$ Hz), 6.83 (dd, 2H, arom, $J = 7.7$ Hz, $J = 7.4$ Hz), 4.02 (m, 2H, CH), 1.72 (t, 2H, CH_2, $^3J = 7.0$ Hz), 0.69 (d, 6H, CH_3, $^3J = 6.1$ Hz), 0.51 (s, 18 H, $Si(CH_3)_3$), 0.44 (s, 18 H, $Si(CH_3)_3$).

Compound 7. This compound was prepared as described for **3a**. (2*R*4*R*)-Pentane-2,4-diol and (*R*)-(+)-3,3′-bis(trimethylsilyl)-2,2′-bisnaphthol have been used as starting compounds. Enantiomers **6** and **7** show similar NMR spectroscopic data. Yield: 70% (0.49 mmol, 0.51 g) of a white solid. Mp: 141−143 °C. Anal. Calcd for $C_{57}H_{66}O_6P_2Si_4$: C, 67.02; H, 6.52. Found: C, 67.17; H, 6.61. $[\alpha]^{20}_D = -63.8°$ ($c = 0.10$, CH_2Cl_2).

Compound 8. Compound (*R*)-**2a** (1.63 mmol, 0.70 g) was azeotropically dried with toluene (3 × 1 mL), dissolved in toluene (10 mL), and added slowly to a solution of PCl_3 (1.80 mmol, 157 μL) and Et_3N (7.5 mmol, 0.78 mL) in toluene (10 mL) at 0 °C. Subsequently the reaction mixture was stirred for 4 h at 50 °C. The formed amine salts were removed by filtration. Evaporation to dryness gave the crude phosphorochloridite (^{31}P NMR ($CDCl_3$): δ 177) which was used without further purification and was dissolved in toluene (10 mL) and Et_3N (5.0 mmol, 0.52 mL). To this solution was added (2*R*,4*R*)-pentane-2,4-diol (1.63 mmol, 0.17 g, azeotropically dried with 3 × 1 mL toluene) in toluene (10 mL) at −55 °C. The reaction mixture was stirred overnight at room temperature, filtrated, and evaporated to dryness. The monophosphite (*R*,2*R*,4*R*) was purified by column chromatography (10% EtOAc/PE 60−80 °C (v/v), $R_f = 0.48$). Yield: 61% (1.00 mmol, 0.56 g) of a white solid. ^{31}P NMR (benzene-d_6): δ 150.12 (s). The product was dissolved in toluene (10 mL) and Et_3N (5.0 mmol). To this solution was added an *in situ* prepared solution of (*S*)-(−)-3,3′-bis(trimethylsilyl)-2,2′-bisnaphthol phosphorochloridite (1.00 mmol) at room temperature. The reaction mixture was stirred overnight, filtrated, and evaporated to dryness. The product was purified by column chromatography (15% EtOAc/2% Et_3N/PE 60−80 °C (v/v/v), $R_f = 0.79$). Yield: 84% (0.84 mmol, 0.87 g) of a white solid. Mp: 122−124 °C. Anal. Calcd for $C_{57}H_{66}O_6P_2Si_4$: C, 67.02; H, 6.52. Found: C, 67.20; H, 6.54. $[\alpha]^{20}_D = 0.00°$ ($c = 0.10$, CH_2Cl_2). ^{31}P NMR (benzene-d_6): δ 144.4 (s) and 144.2 (s). ^1H NMR (benzene-d_6): δ 8.06 (m, 4H, arom), 7.65 (m, 4H, arom), 7.30 (m, 4H, arom), 7.10 (m, 4H, arom), 6.83 (m, 4H, arom), 4.16 (m, 1H, CH), 3.96 (m, 1H, CH), 2.06 (m, 1H, CH_2), 1.77 (m, 1H, CH_2), 0.99 (d, 3H, CH_3, $^3J = 2.5$ Hz), 0.85 (d, 3H, CH_3, $^3J = 2.6$ Hz), 0.52 (s, 9 H, $Si(CH_3)_3$), 0.49 (s, 9 H, $Si(CH_3)_3$), 0.46 (s, 9 H, $Si(CH_3)_3$), 0.43 (s, 9 H, $Si(CH_3)_3$).

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