New Chiral Phosphine−Phosphite Ligands in the Enantioselective Rhodium-Catalyzed Hydroformylation of Styrene

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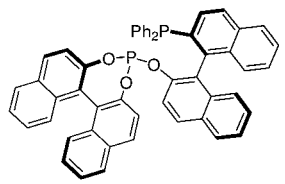
A series of chiral phosphine−phosphite ligands **1a**−**g** have been synthesized from monophosphines **2**−**4**, enantiomerically pure propene oxide or styrene oxide, and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite or enantiomerically pure 3,3′-bis(trimethylsilyl)-2,2′-binaphthol phosphorochloridites. These phosphine−phosphites have been used in the rhodium-catalyzed asymmetric hydroformylation of styrene. The structures of the active catalysts, [HRh(L−L)$(CO)_2$] complexes (L−L = ligands **1a**−**g**), have been studied using high-pressure NMR and IR spectroscopy. The obtained spectroscopic data show that the ligands coordinate in an equatorial−apical fashion to the rhodium center with the phosphine in apical position. Systematic variation in configuration of the stereocenters at both the ligand bridge and the phosphine moiety revealed a remarkable cooperative effect on the selectivity of the hydroformylation reaction. Under mild reaction conditions ee's of 63% and regioselectivities up to 92% toward 2-phenylpropanal were obtained (25−60 °C, 20 bar of syn gas CO:H_2 [1:1]) for ligands **1**. The absolute configuration of the product is governed by the stereogenic center of the backbone of the ligand. There is a large cooperative effect, however, from the phosphine moiety. Spectroscopic data, in combination with the obtained results in catalysis, suggest that phosphine−phosphite ligands (L−L) containing the conformationally flexible and axially chiral biphenyl moiety exist predominantly as single atropisomers in the HRh(L−L)$(CO)_2$ complexes. Comparison of the bisphenol and binaphthol substituents suggests that the high enantiomeric excesses obtained with the former are caused by the preferential formation of the most selective diastereomer.

Introduction

Hydroformylation is an important and thus extensively studied industrial process.[1−4] Improvement of rates and selectivities and mechanistic aspects receive a great deal of attention.[5,6] Asymmetric hydroformylation is a potentially powerful synthetic tool for the synthesis of several chiral building blocks that can be used as precursors for high-value-added compounds such as pharmaceuticals, agrochemicals, flavors, and fragrances.[7−11]

In general, chiral diphosphine−Rh(I) complexes show high catalytic activity and chemoselectivity. The enantiomeric excesses obtained so far, however, do not exceed 60%.[12] Chiral diphosphite−Rh(I) complexes show high enantioselectivities,[13,14] but the scope is limited. Takaya et al. have reported a hydroformylation catalyst precursor based on [Rh(acac)$(CO)_2$] modified with a chiral phosphine−phosphite ligand, BINAPHOS,[15,16] which combines the advantages of both ligand types; high ee's were obtained in the hydroformylation of styrene and other olefins, combined with excellent chemo- and regioselectivity.[17]



BINAPHOS

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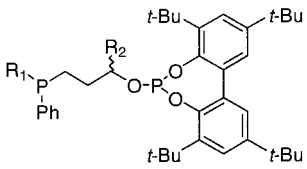
Most of the research published to date is dedicated to ligands having stereogenic elements attached to the donor atom(s). Ligands having a stereogenic donor atom, for instance a stereogenic phosphine, are rare, and DIPAMP is one of the few examples.[18] Jugé et al. have developed a method for the synthesis of enantiomerically pure, borane-protected stereogenic phosphines of the type P(Ph)(R)(Me)(BH_3).[19] It is a useful chiral building block, which can be applied in the synthesis of chiral ligands containing stereogenic P atoms. Following this method, Mezzetti et al. synthesized (*S,S*)-Me_2Si-(CH_2P(1-Np)(Ph))$_2$, which gave ee's up to 97.7% in the catalytic hydrogenation of dehydroamino acids.[20] Although high enantioselectivities have been obtained, catalytic applications of bidentate ligands containing stereogenic phosphorus atoms are still rare.[21−31]

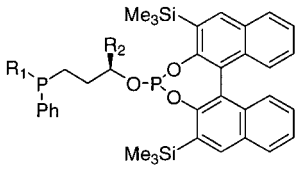
Previous work in our group and in the literature shows the possibility of chiral cooperativity between stereocenters in a ligand. For instance, diphosphite ligands containing biaryl moieties with bulky substituents show hindered rotation around the biaryl axis.[14,17] Although the additional stereocenter originating from the atropisomeric biaryl substituents may lead to several diastereomers, high enantioselectivities are obtained in the hydroformylation reaction. It was found that the low-energy barrier for interconversion in atropisomers resulted in the formation of a single diastereomeric $HRh(CO)_2$(diphosphite) complex. This complex also gives rise to high enantioselectivities.

Herrmann et al. have published molecular modeling studies of the BINAPHOS−rhodium complex,[32] but the mechanistic aspects of the asymmetric hydroformylation reaction are still not understood well enough to be used for the prediction of the enantioselectivities.

Encouraged by the success of BINAPHOS, the success of ligands containing stereogenic phosphorus atoms, and the cooperative effect found in bulky phosphite ligands, we designed a series of chiral phosphine−phosphite ligands that allowed a systematic approach to study the asymmetric induction of a ligand in the hydroformylation reaction.



1a (S_P,S_C) R_1=1-Napht, R_2=Ph
1b (S_P,S_C) R_1=2-Anisyl, R_2=Ph
1c (S_P,R_C) R_1=1-Napht, R_2=Ph
1d (-,S_C) R_1=Ph, R_2=Me
1e (-,S_C) R_1=Ph, R_2=Ph



1f (S_P,S_C,*R*) R_1=1-Napht, R_2=Ph
1g (S_P,S_C,*S*) R_1=1-Napht, R_2=Ph

In this paper we describe the synthesis of novel chiral phosphine−phosphite ligands. The designed ligands consist of a phosphine moiety with a stereogenic phosphorus atom. The configuration of the phosphorus atom is expected to be important for the course of the catalytic reaction, since it is in close vicinity of the metal center. Furthermore, the ligands contain a bridge having a stereocenter and a bulky phosphite moiety. The stereogenic phosphorus moiety, the stereocenter in the backbone, and the configuration of the biaryl moiety can result in several diastereomers. Systematic variation of the stereocenters provides information about the effect of the different stereocenters on the enantioselectivity. The presence of bulky substituents on aromatic biphenyl positions has already shown to have a significant effect on the catalyst performance.[13,14,33−38] Having two different donor atoms, the ligand is anticipated to coordinate as follows: the phosphine, the better σ-donor, will coordinate in an apical position, and the phosphite, the better π-acceptor, will coordinate in an equatorial position.[39] This was confirmed by high-pressure NMR and IR studies of $RhH(CO)_2$(phosphine−phosphite) complexes under catalytic conditions.[40−45]

Results and Discussion

Ligand Synthesis. Ligands **1a**−**e** were synthesized in three steps starting from the corresponding monophosphines **2**−**4** (Scheme 1). Methyldiphenylphosphine was protected by reaction with BH_3·SMe_2 to obtain

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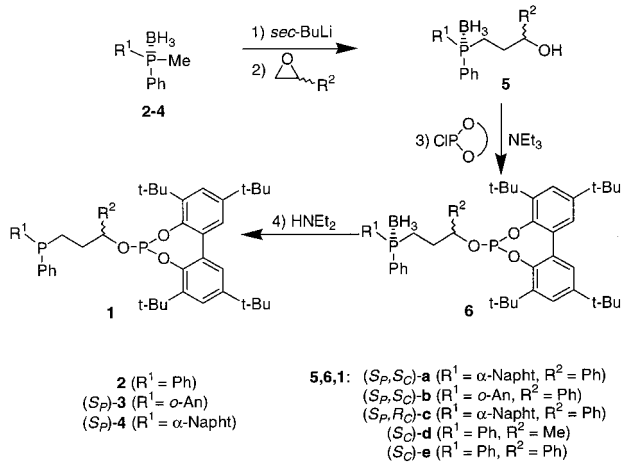
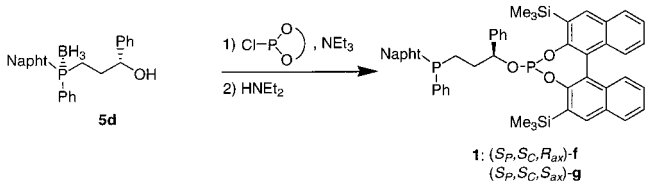
Scheme 1



monophosphine **2** as a crystalline product.[46−49] The boronato group was used both to avoid oxidation of the phosphine and to activate the methylphosphine toward lithiation.[50] Stereogenic monophosphines **3** and **4** were synthesized as enantiomerically pure, crystalline products using the methodology of Jugé[19] and Mezzetti,[20] respectively. After metalation of these phosphines, **2**−**4**, using *sec*-BuLi in THF at −40 °C, they reacted with enantiomerically pure propene oxide or styrene oxide to yield phosphino alcohols **5a**−**e**.[46−49] Phosphino alcohols **5a**−**e** were coupled with bisphenol phosphorochloridite in the presence of triethylamine.[33,51] Filtration over a short silica column, to remove hydrolyzed phosphorochloridite, gave pure phosphine−phosphites **6a**−**e** as colorless oils. Compounds **2**−**6** show broad signals in the ^{31}P NMR indicative of a phosphine−borane complex.[21,52,53] Phosphine−phosphite borane adducts **6** were immediately deprotected overnight at 50 °C using diethylamine. After filtration, the phosphine−phosphites **1** were obtained in moderate to good yields (37−95%). From ^{1}H NMR and ^{31}P NMR we concluded that in none of the reactions were the stereocenters in the ligands affected, since no formation of diastereomers was observed. The existence of a single peak for each phosphorus atom of **1a**−**e** in the ^{31}P NMR suggests the rapid isomerization in the biphenyl moiety, which results in an averaged configuration on the NMR time scale.[14,17] In none of the preceding reactions is the configuration at the P atom affected. As borane decomplexation reactions are known to occur with retention of configuration at the phosphorus atom,[19,54,55] the absolute configuration at the phosphorus atom is assigned as *S*.

To study the influence of the biaryl moiety on the catalyst, bulky binaphthol-based ligands **1f**,**g** were prepared (Scheme 2). The interconversion around the binaphthyl bond is energetically highly unfavorable, and stable diastereomeric phosphine−phosphite ligands have been obtained in diastereomerically pure form. Ligands **1f** and **1g** were synthesized in a similar way as described for ligands **1a**−**e**. A literature method was applied for the synthesis of enantiomerically pure (*R*)- and (*S*)-3,3′-bis(trimethylsilyl)-2,2′-binaphthol phosphorochloridites.[14] Reaction with phosphino alcohol **5a** and decomplexation of the BH_3 group gave phosphine−phosphites **1f** and **1g** as white solids.

Scheme 2



[RhH(CO)$_2$(L−L)] Complexes. The coordination mode of the ligand in the active complex has been studied using IR and NMR under 20 bar of syn gas.[34−37,44,56,57] Hydridorhodium phosphine−phosphite dicarbonyl complexes [RhH(CO)$_2$(L−L)] were prepared from Rh(acac)(CO)$_2$ and ligands **1**. The spectroscopic data are shown in Table 1. The IR spectrum of RhH(CO)$_2$(**1a**) in cyclohexane shows absorptions at 2021 (medium) and 1974 (strong) cm^{-1} due to a symmetric and an antisymmetric stretch vibration of two equatorially coordinated CO ligands. The Rh−H vibration was not observed in the spectrum. Upon deuteration, there is no shift observed in the CO absorptions.[44,58,59] This is characteristic of a coordination fashion in which the hydride and both CO ligands of RhH(CO)$_2$(L−L) are orientated cis to one another. Similar data were observed for ligands **1b**−**g**.

The ^{31}P NMR spectrum of RhH(CO)$_2$(**1a**) shows signals at 6.91 and 163.89 ppm attributed to the phosphine and the phosphite, respectively. For the Rh−H coupling constant a value of 9 Hz is found, whereas $J\{P^1-H\}$ and $J\{P^2-H\}$ are found to be 102 and <2 Hz, respectively. The coupling constant of P^1−Rh is 101 Hz and P^2−Rh is 237 Hz. The coupling constant $J\{P^1-P^2\}$ is 24.3 Hz. From these results and from literature it is expected that the structure of the HRh(CO)$_2$(P^1-P^2) is a trigonal bipyramid (Chart 1).[7−11]

The value found for the P^1−H coupling of 102 Hz is typical of a complex containing an apical hydride and an apical phosphine. The magnitude of the coupling constant of P^2−H of 2 Hz is similar to that reported for an apical hydride with an equatorial phosphite.[34−36] A coupling constant of 106 Hz in trigonal bipyramidal HRh(CO)$_2$(DPEphos) has been found for an apical phosphine,[58,59] whereas for apical phosphite complexes of trigonal bipyramidal HRh(CO)$_2$(diphosphite), coupling constants of 160 Hz have been reported.[15,60,61]

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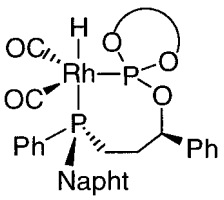
Table 1. Spectral Data of the Complexes RhH(CO)$_2$(phosphine−phosphite) under 20 bar Syn Gas

	NMR[a,b]									IR[c,d]	
	P^1 = phosphine			P^2 = phosphite				hydride			
ligand	δ(P^1)	J{P^1−H}	J{P^1−Rh}	δ(P^2)	J{P^2−H}	J{P^2−Rh}	J{P^1−P^2}	δ(H)	J{H−Rh}	ν(CO)	ν(CO)
Binaphos	26.92	23.2	119	184.86	159.9	181.6	39.7	−8.85	9.8	1974	2018
1a (*S*,*S*)	6.91	102	101	163.89	<2	237	24.3	−9.58	9.0	1974	2021
1b (*S*,*S*)	10.56	114	97	162.71	<3.5	239	40.7	−9.40	9.2	1972	2016
1c (*S*,*R*)	22.20	102	99	159.89	<2	237	34.0	−9.47	9.0	1974	2018
1d (-,*S*)	18.14	90	104	162.59	15.5	229	20.8	−9.45	9.1	1973	2019
1e (-,*S*)	16.60	96	103	163.37	15.7	231	31.4	−9.02	9.1	1975	2020
1f (*S*,*S*,*R*)	3.75	105	100	171.70	*e*	236	41.6	−9.75	*e*	1979	2020
1g (*S*,*S*,*S*)	7.07	94	103	171.36	<2	238	11.9	−9.90	8.2	1973	2021

[a] HRh(P−P)(CO)$_2$ complexes prepared in benzene-d_6 at 50 °C. ^{31}P and ^{1}H spectra recorded in benzene-d_6 at room temperature. [b] Chemical shifts (δ) in ppm; coupling constants (J) in hertz. [c] HRh(P−P)(CO)$_2$ complexes prepared in cyclohexane at 50 °C, and IR spectra recorded at 50 °C. [d] Absorptions (ν) in cm^{-1}. [e] Broadened multiplet.

Chart 1. Structure of HRh(L−L)(CO)$_2$



Upon selective decoupling of the phosphine and the phosphite in the ^{1}H NMR, the coupling constants of 102 and 2 Hz disappeared, respectively. From these NMR data we conclude that the hydride orientation is trans to the phosphine (P^1) and cis to the phosphite (P^2). The magnitude of J{Rh−H}, 9 Hz, confirms the equatorial apical coordination; that is, a coupling constant between a rhodium and an apical hydride having a phosphine or a phosphite trans is around 9 Hz, whereas a coupling constant between rhodium and an apical hydride having a CO ligand trans is less than 4 Hz. The obtained coupling constants are indicative of a structure close to an ideal trigonal bipyramid. For ligands **1d** and **1e** J{P^1−H} of 15 Hz is larger than expected for perfect equatorial coordination. This can be due to distortion of the trigonal bipyramidal structure or due to an equilibrium of the complex between P^1-equatorial-P^2-apical coordination and P^1-apical-P^2-equatorial coordination.

The HP-IR spectrum shows only two vibrations in the Rh−CO region, indicative of a single species, unless the absorptions coincide. From molecular modeling calculations it is expected that Rh−CO absorptions of complexes with P^1-equatorial-P^2-apical coordination or P^1-apical-P^2-equatorial will coincide.[62] We assume that the large magnitude of J{P^1−H} for ligands **1d** and **1e** is caused by distortion of the trigonal bipyramidal structure. From NMR spectroscopy it is concluded that in the RhH(CO)$_2$(L−L) complexes, prepared from phosphine−phosphite ligands **1a**−**g**, the phosphine, the best σ-donor, occupies an apical position and the phosphite, the best π-acceptor, occupies an equatorial position.[39] This is in contrast with the coordination mode found for the [RhH(CO)$_2$(L−L) complex of BINAPHOS, in which the phosphine occupies an equatorial position and the phosphite an apical position. Despite the structural similarity of our ligands **1** and BINAPHOS, the coordination fashion is different. Apparently, this is due to steric factors. The CO absorption bands of rhodium dicarbonyl complexes of BINAPHOS at 2018 (medium) and 1974 (strong) that previously were assigned to Rh−H and Rh−CO absorptions, respectively, are similar to the analogous complexes of ligand **1** and containing BINAPHOS in an apical−equatorial position. As expected, deuteration of the complex did not shift or decrease the CO absorptions. A small absorption at 2058 did disappear, which was assigned to the Rh−H vibration. Interestingly, the complexes derived from ligands **1a**−**c** exist as single species, as shown by HP NMR. Variable-temperature (295−163 K) ^{31}P and ^{1}H NMR experiments did not demonstrate fluxional processes. The spectra were recorded under 15 bar of syngas in acetone-d_6/THF-d_8 = 1:1. At very low temperature (163 K) ^{31}P and ^{1}H NMR spectra showed the same coupling constants as at room temperature, except for a small increase of the phosphite−hydride coupling from 2 to 8 Hz. This small change in J{P^2−H} is attributed to small conformational changes in the backbone of the ligand on cooling. Upon selective decoupling of the phosphine signal the ^{1}H NMR spectrum showed total disappearance of the large phosphine−hydride coupling of 102 Hz. This confirms the formation of only one complex with the phosphine at axial position trans to the hydride. Although rapid atropisomerization of the biphenyl moiety might still be possible, we assume that the biphenyl moiety is fixed in the most stable conformation, as already suggested by us before.[14] The interconversion of the biphenyl moiety from *R* to *S* seems to be inhibited by the coordination to the Rh(I) center or by the ligand backbone. Ligands **1f** and **1g** each give rise to a single Rh complex, as can be concluded from HP NMR and HP-IR.

Asymmetric Hydroformylation of Styrene. Complexes RhH(CO)$_2$(ligand **1**) have been used as catalysts in the asymmetric hydroformylation of styrene. The results are given in Table 2. 2-Phenylpropanal **8** (branched aldehyde) was obtained with moderate enantioselectivity (Scheme 3). Regioisomer **9** (linear aldehyde) was formed in relatively small amounts. Styrene as a substrate has a preference for the formation of the branched aldehyde due to the stability of the intermediate benzylic rhodium species, induced by the formation of a stable η^3-complex.[2] Other products, resulting from hydrogenation or polymerization of styrene, were not observed.

The effect of the temperature and the ligand-to-rhodium ratio on the enantioselectivity was investigated

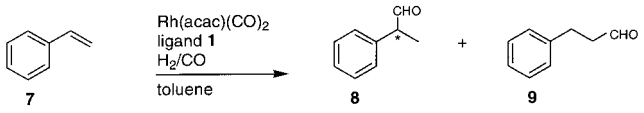
(61) Hyde, E. M.; Swain, J. R.; Verkade, J. G.; Meakin, P. *J. Chem. Soc., Dalton Trans.* **1976**, 1196.
(62) Bo, C. Unpublished result and results in ref 59.

Table 2. Asymmetric Hydroformylation of Styrene Catalyzed by $HRh(CO)_2$(1) at 50 °C under 20 bar of Syn Gas[a]

entry no.	ligand	T, °C	time, h	L/Rh [c]	conv, % [d]	b/l [e]	TOF [f]	ee, % [g]
1	(S_P,S_C)-**1a**	50	24	4	55	11	45	63 (*S*)
2	(S_P,S_C)-**1a**	40	24	4	13	15	10	60 (*S*)
3	(S_P,S_C)-**1a**	25	237	4	29	15	2	59 (*S*)
4	(S_P,S_C)-**1a**	60	5	4	41	8	153	46 (*S*)
5	(S_P,S_C)-**1a**	50	4	1	50	10	88	6 (*S*)
6	(S_P,S_C)-**1a**	50	6	2	16	16	95	34 (*S*)
7	(S_P,S_C)-**1a**	50	6	5	12	18	39	59 (*S*)
8	(S_P,S_C)-**1a**	50	6	10	14	*h*	42	41 (*S*)
9	(S_P,S_C)-**1a**	50[b]	5	2	5	*h*	17	51 (*S*)
10	(S_P,S_C)-**1b**	50	25	4	24	20	18	57 (*S*)
11	(S_P,S_C)-**1b**	50[b]	3	5	2	*h*	12	48 (*S*)
12	(S_P,R_C)-**1c**	50	15	4	20	25	28	22 (*R*)
13	(S_P,R_C)-**1c**	50	6	5	7	*h*	24	33 (*R*)
14	(S_P,R_C)-**1c**	50	6	10	7	*h*	24	28 (*R*)
15	(S_C)-**1d**	50[b]	17	4	41	18	49	9 (*R*)
16	(S_C)-**1e**	50	25	4	69	2	56	18 (*S*)
17	(S_P,S_C,R_{ax})-**1f**	50	18	4	95	9	111	40 (*S*)
18	(S_P,S_C,S_{ax})-**1g**	50	19	4	26	8	25	4 (*S*)

[a] Styrene to catalyst molar ratio is 2000. [b] Catalyst formation period 1−3 h. [c] Ligand-to-rhodium ratio. [d] Percent conversion of styrene. [e] Branched to linear aldehydes ratio. [f] TOF in mol styrene (mol Rh)$^{-1}$ h^{-1} determined at the end of the reaction time by GC. [g] Enantiomeric excess. Absolute configurations are drawn in parentheses. [h] Could not be determined, because peak was too small compared to styrene peak.

Scheme 3



using ligands **1a**, **1b**, and **1c** (runs 1−15). The ratio of H_2 and CO was kept constant.[17] $Rh(acac)(CO)_2$ was the catalyst precursor of choice, since other precursors were reported to give lower enantioselectivities.[17] A satisfactory branched over linear ratio (>92%) and a moderate ee (63%, 55% conversion) were achieved in toluene, under H_2/CO = 10 bar/10 bar at 50 °C for 24 h (run 1).

Variation of the temperature showed that at 50 °C the highest enantioselectivity was found. The ee of the product decreases with increasing temperature (run 4). At lower temperature the ee does not change significantly (runs 2 and 3). The enantioselectivity of the reaction is constant in time; even after a very long reaction period of almost 10 days (run 3) the ee remains constant. At higher temperature the activity increases, as can be seen from the increase of the initial turnover frequencies from 2 to 45 mol mol^{-1} h^{-1} (runs 1−3). All the other reactions were performed at 50 °C, because at this temperature the optimum rate and enantioselectivity were found.

Variation of the ligand-to-rhodium ratio shows that for ligand **1a** the optimum ee is reached at a ligand-to-rhodium ratio of 4−5 (runs 5−8). At lower ligand-to-rhodium ratios there may still be unmodified rhodium species present at the concentrations used (runs 5 and 6). At higher ligand-to-rhodium ratios the ee decreases probably due to monodentate coordination of more than one ligand to the rhodium center. This trend was also found for ligands **1b** (runs 9−11) and **1c** (runs 12−15).[39] Therefore, all other ligands are tested with a ligand-to-rhodium ratio of 4 (runs 15−18).

The ligands were compared under "standard" conditions, i.e., a temperature of 50 °C and a ligand-to-rhodium ratio of 4. The fastest ligand, **1a**, also gives the highest ee of 63%. Use of ligands **1b** and **1c** resulted in lower initial turnover frequencies, whereas ligands **1d** and **1e** showed almost equal activity as **1a**, but did not yield high enantioselectivities (9% and 18%, respectively). Ligand **1f** consisting of a stereogenic binaphthol with bulky trimethylsilyl substituents at the ortho-positions results in a high reaction rate and moderate enantioselectivity (run 17). Due to the conformation of the binaphthol group, ligand **1f** probably causes less steric hindrance at the rhodium complex compared to $RhH(CO)_2$(ligand **1a**), and therefore, it is more reactive. Inversion of the stereocenter of the binaphthol moiety in ligand **1g** resulted in a lower reaction rate and low enantioselectivity (run 18).

The results of ligands **1** in the hydroformylation of styrene can be summarized as follows:

(1) A large group attached to the backbone is important to obtain a high ee. The phenyl group of ligand **1e** has a larger influence than the methyl group of ligand **1d**.

(2) Introduction of a phosphine with a stereogenic phosphorus atom (**1a** and **1b**) enhances the ee remarkably. The naphthyl group of ligand **1a** and the *o*-anisyl group of ligand **1b** have a large effect on the enantioselectivity. Apparently, the combination of the substituent at the stereogenic phosphine and the stereocenter in the backbone creates a complex that induces enantioselectivity. The stereogenic phosphine is important, since the corresponding achiral ligand **1e** does not yield a high enantioselectivity.

(3) The absolute configuration of the major enantiomer of the product aldehyde is always *S* when the configuration of the stereocenter in the backbone is *S*. Inversion of the configuration of this carbon atom results in an inversion of the product aldehyde from *S* to *R*. Ligand **1d** is an exception to this rule. Although the absolute configuration at the stereocenters of ligands **1d** and **1c** is different, the methyl substituent at the stereocenter holds the same position as the phenyl substituent, resulting in the same enantiomer.[63] Thus, the sense of enantiofacial selection is predominantly controlled by the configuration of the stereocenter in the bridge. Ligand **1c** gives a lower ee due to a mismatched combination of the stereocenters at the phosphine moiety and the backbone.

(4) The use of ligand **1f** having a (*R*)-binaphthyl moiety results in an ee of 40% (*S*), whereas the use of diastereomer **1g** having a (*S*)-binaphthyl moiety results in an ee of 4% (*S*). In the HP NMR spectra of [HRh(ligand **1a**)$(CO)_2$], the formation of only one diastereomer was observed. Therefore, comparing the results obtained with ligands **1a**, **1f**, and **1g**, we assume that the fast interchanging atropisomers of ligand **1a** adopt predominantly the same conformation as ligand **1f**. Thus, the conformation of the biphenyl moiety at the phosphite is controlled by the substituent at the stereocenter in the backbone.

(5) The stereogenic group at the backbone controls not only the configuration of the biaryl moiety at the

(63) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

phosphite but also the configuration of the product. Since the phosphite is coordinated in an equatorial position, the equatorially coordinated group is important for obtaining high enantioselectivities. This is in accordance with the results of Takaya et al., who also found that for BINAPHOS the equatorially coordinating moiety, the phosphine in this instance, has the largest influence.[17]

Conclusions

A series of novel ligands containing a stereogenic phosphine moiety and a phosphite moiety with axial chirality controlled by a stereocenter in the backbone have been prepared and used as ligands in the rhodium-catalyzed hydroformylation reaction. The ligands were synthesized conveniently in eight steps and derivatized systematically. In the [HRh(ligand **1**)$(CO)_2$] complexes the ligands coordinate in an equatorial−apical coordination fashion with the phosphine moiety in the apical position. We have shown that the equatorially coordinated group, i.e., the phosphite moiety, is important for obtaining high enantioselectivity. This is in accordance with the results of Takaya et al., who found that also for BINAPHOS the equatorially coordinating group has the largest influence. Good enantioselectivities were obtained in the asymmetric hydroformylation of styrene. To obtain high ee's, however, it is necessary to have two stereocenters in the ligand. The experiments done using the ligands containing stereogenic binaphthol groups show a cooperative effect of the binaphthol moiety and the group attached to the stereocenter in the backbone.

Experimental Section

General Methods. Chemicals were obtained from Acros Chimica and Aldrich Chemical Co. All reactions were carried out in flame-dried glasswork using standard Schlenk techniques under an atmosphere of argon. Toluene was distilled from sodium. THF and Et_2O were distilled from sodium/benzophenone. Triethylamine and diethylamine 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. Compounds **3** and **4** were synthesized following the procedures of Mezzetti[20] and Jugé,[19] respectively. Melting points were determined on a Gallenkamp MFB-595 melting point apparatus in open capillaries and are uncorrected. NMR spectra were obtained on Bruker AMX 300 and DRX 300 spectrometers. ^{31}P and ^{13}C spectra were measured ^1H-decoupled unless stated otherwise. TMS was used as a reference 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. HP-IR spectra were measured using a 20 mL homemade stainless steel autoclave equipped with mechanical stirring and ZnS windows. Hydroformylation reactions were carried out in a homemade 200 mL stainless steel autoclave. Syn gas (CO/H_2, 1:1, 99.9%) was purchased from Air Liquide. D_2 was purchased from Hoekloos. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

Gas chromatographic analyses were run on an Interscience HR GC Mega 2 apparatus (split/splitless injector, J&W Scientific, DB-1 J&W 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 with $NaBH_4$ to the corresponding alcohols on a Carlo Erba Vega 6000 gas chromatograph, J&W Scientific, CycloSil-B(JW) column, film thickness 0.25 μm, carrier gas 80 kPa He, FID detector equipped with a Hewlett-Packard data system (Chrom-Card). FAB exact mass spectra were recorded by the Institute of Mass Spectroscopy of the University of Amsterdam on a JEOL JMS-SX/SX102A spectrometer. Elemental analyses were carried out on an Elementar Vario EL apparatus.

Hydroformylation Experiments. Hydroformylation reactions were carried out in an autoclave, equipped with glass inner beaker, a substrate inlet vessel, a liquid sampling valve, and a magnetic stirring rod. The temperature was controlled by a thermocouple. In a typical experiment, the autoclave was filled with the phosphine−phosphite ligand (0.040 mmol, P/Rh ratio of 8). Subsequently, the autoclave was purged two times with 20 bar of syn gas ($CO:H_2 = 1:1$), and $Rh(acac)(CO)_2$ (0.010 mmol, 5.0 mL of a 2.0 mM stock solution in toluene) and toluene (5.0 mL) were added. The autoclave was purged again with syn gas and pressurized to the appropriate initial pressure. After heating the autoclave to the reaction temperature, the reaction mixture was stirred for 18 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), and toluene (6.73 mL, total solvent volume 20.0 mL) were purged with syn gas and brought into the autoclave. During the reaction several samples were taken from the reaction vessel. After the desired reaction time the autoclave was cooled and depressurized. The toluene was evaporated, and the residue was distilled under vacuum to remove the catalyst. A sample of the reaction mixture was dissolved in ethanol. Sodium borohydride was added, and the reaction mixture was stirred for 2 h at room temperature. After quenching the reaction mixture with water, the mixture was extracted two times with ethyl acetate/petroleum ether 60−80 °C (1:1). The combined organic layers were dried over magnesium sulfate and concentrated in vacuo. About 40 μL of reduced reaction mixture was dissolved in ethanol (10 mL) and analyzed by GC for determination of the enantiomeric excess.

HP NMR Experiments. In a typical experiment the NMR tube was filled with a solution of $Rh(CO)_2(acac)$ (5.0 mg, 0.019 mmol), ligand (0.019 mmol), and benzene-d_6 (1.5 mL). The tube was purged two times with 15 bar of H_2/CO (1:1), pressurized with 20 bar of H_2/CO (1:1), and left overnight at 50 °C. After cooling to room temperature the NMR spectra were recorded.

Variable Temperature HP NMR Experiments. For variable-temperature high-pressure NMR experiments (295−163 K) the $HRh(L-L)(CO)_2$ complex was prepared in a mixture of acetone-d_6/THF-d_8 = 1:1.

HP-FT-IR Experiments. In a typical experiment the HP-IR autoclave was filled with a solution of $Rh(CO)_2(acac)$ (3.87 mg, 0.015 mmol), ligand (0.015 mmol), and cyclohexane (15 mL). The autoclave was purged two times with 15 bar of H_2/CO (1:1), pressurized with 20 bar of H_2/CO (1:1), and heated to 50 °C. Catalyst formation was followed in time by FT-IR and was usually complete within 1 h.

Compound 5a. Phosphine−borane **4** (0.599 g, 2.27 mmol), azeotropically dried with toluene (2 × 5 mL), was dissolved in THF (5 mL), and the solution was cooled to −25 °C. *sec*-BuLi (1.68 mL of a 1.35 M/L cyclohexane solution) was added to this solution, and stirring was continued for 10 min. The cooling bath was removed, and the solution was stirred at room temperature for 1 h. This solution was added dropwise to a solution of (*R*)-phenyl oxirane (0.26 mL, 2.27 mmol) in THF (5 mL) at −60 °C. The reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was quenched with water and extracted with Et_2O (2 × 30 mL). The combined extracts were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (eluent: 1: toluene, 2: 10% EtOAc in toluene), giving **5a** (0.635 g, 1.65 mmol, 73%) as a white solid. Anal. Calcd for $C_{25}H_{26}BOP$: C, 78.14; H, 6.82. Found: C, 78.10; H, 6.91. ^1H NMR ($CDCl_3$): δ 8.07−8.00 (m, 2H, Ar−H), 7.91−7.88 (m, 2H, Ar−H), 7.59−7.20 (m, 13H, Ar−H), 4.69 (dd, 1H, J = 5.4 and

7.1 Hz, C*H*OH), 2.52 (m, 2H, PCH_2CH_2), 1.94 (m, 2H, PCH_2-CH_2), 1.90−0.50 (m, 3H, BH_3). ^{31}P NMR ($CDCl_3$): δ 17.20 (br d). ^{13}C NMR ($CDCl_3$): δ 143.15 (q), 133.96 (d, $J_{CP} = 10.6$ Hz), 133.77 (d, $J_{CP} = 6.8$ Hz, q), 132.89 (d, $J_{CP} = 6.0$ Hz, q), 132.70, 131.48 (d, $J_{CP} = 9.1$ Hz), 130.71, 130.49 (q), 129.08, 128.70 (d, $J_{CP} = 10.5$ Hz), 128.38, 127.64, 126.57, 126.19 (d, $J_{CP} = 6.0$ Hz), 126.06, 125.62, 124.67, 124.14 (q), 74.13 (d, $J_{CP} = 14.2$ Hz, CH), 31.76 (CH_2), 21.65 (d, $J_{CP} = 38.2$ Hz, CH_2). Mp: 113−114 °C. $[\alpha]_D^{25} = -25.8$ (*c* 1.11, $CHCl_3$). MS HR-FAB [found 383.1743; $C_{25}H_{25}B_1O_1P_1$ ($M^{\bullet+} - H$) requires 383.1736].

Compound 5b. This compound was prepared as described for **5a**. Phosphine−borane **3** and (*R*)-phenyl oxirane have been used for the synthesis of **5b**. The product was purified by column chromatography (eluent: 1: toluene, 2: 10% EtOAc in toluene), giving **5b** (0.560 g, 1.54 mmol, 96%) as a white solid. Anal. Calcd for $C_{22}H_{26}BO_2P$: C, 72.55; H, 7.20. Found: C, 72.28; H, 7.29. ^1H NMR ($CDCl_3$): δ 7.96 (ddd, 1H, $J = 1.5$, 7.5 and 13.5 Hz, Ar−H), 7.64 (m, 2H, Ar−H), 7.49 (m, 1H, Ar−H), 7.44−7.24 (m, 8H, Ar−H), 7.05 (dt, 1H, $J = 1.4$ and 7.4 Hz, Ar−H), 6.85 (dd, 1H, $J = 3.3$ and 8.4 Hz, Ar−H), 4.66 (t, 1H, $J = 6.4$ Hz, C*H*OH), 3.52 (s, 3H, OCH_3), 2.48 (m, 2H, PCH_2CH_2), 2.12 (m, 1H, PCH_2CH_2), 1.82 (m, 1H, PCH_2CH_2), 1.90−0.50 (m, 3H, BH_3). ^{31}P NMR ($CDCl_3$): δ 16.58 (br s). ^{13}C NMR ($CDCl_3$): δ 161.12 (CH_3OC_q), 143.47 (q), 136.29 (d, $J_{CP} = 14.1$ Hz), 133.53, 131.35 (d, $J_{CP} = 9.3$ Hz), 130.18, 130.06 (d, $J_{CP} = 57.7$ Hz, q), 128.30, 128.07 (d, $J_{CP} = 10.1$ Hz), 127.53, 125.76, 120.98 (d, $J_{CP} = 12.2$ Hz), 115.65 (d, $J_{CP} = 52.1$ Hz, q), 110.80, 74.43 (d, $J_{CP} = 15.0$ Hz), 54.98, 32.19, 19.82 (d, $J_{CP} = 40.1$ Hz). Mp: 102−103 °C. $[\alpha]_D^{25} = -15.1$ (*c* 1.25, $CHCl_3$). MS HR-FAB [found 363.1660; $C_{22}H_{25}B_1O_2P_1$ ($M^{\bullet+} - H$) requires 363.1685].

Compound 5c. This compound was prepared as described for **5a**. Phosphine−borane **4** and (*S*)-phenyl oxirane have been used for the synthesis of **5c**. The product was purified by column chromatography (eluent: 1: toluene, 2: 10% EtOAc in toluene), giving **5c** (0.873 g, 2.27 mmol, 100%) quantitatively as a white solid. Anal. Calcd for $C_{25}H_{26}BOP$: C, 78.14; H, 6.82. Found: C, 77.90; H, 7.04. ^1H NMR ($CDCl_3$): δ 8.03 (m, 2H, Ar−H), 7.90 (m, 2H, Ar−H), 7.59−7.20 (m, 13H, Ar−H), 4.69 (dd, 1H, $J = 5.4$ and 7.1 Hz, C*H*OH), 2.52 (m, 2H, PCH_2CH_2), 1.94 (m, 2H, PCH_2CH_2), 1.90−0.50 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$): δ 143.14 (q), 134.03 (d, $J_{CP} = 11.1$ Hz), 133.75 (d, $J_{CP} = 6.9$ Hz, q), 132.90 (d, $J_{CP} = 5.5$ Hz, q), 132.73, 131.04 (d, $J_{CP} = 9.0$ Hz), 130.69, 130.00 (q), 129.08, 128.68 (d, $J_{CP} = 9.8$ Hz), 128.37, 127.61, 126.62, 126.20, 126.07, 125.58, 124.74 (d, $J_{CP} = 12.2$ Hz), 123.86 (q), 74.04 (d, $J_{CP} = 14.1$ Hz), 31.82, 21.65 (d, $J_{CP} = 38.40$ Hz). ^{31}P NMR ($CDCl_3$): δ 17.10 (br d, $J_{PB} = 48$ Hz). Mp: 121−122 °C. $[\alpha]_D^{25} = +23.9$ (*c* 1.01, $CHCl_3$). MS HR-EI [found 384.1786; $C_{49}H_{60}O_3P_2$ ($M^{\bullet+}$) requires 384.1814].

Compound 5d. This compound was prepared as described for **5a**. Phosphine−borane **2** and (*S*)-propene oxide have been used for the synthesis of **5d**. The product was purified by column chromatography (eluent: 1: toluene, 2: 10% EtOAc in toluene), giving **5d** (0.362 g, 1.33 mmol, 57%) as a colorless oil. ^1H NMR ($CDCl_3$): δ 7.68 (m, 4H, Ar−H), 7.42 (m, 6H, Ar−H), 3.79 (m, 1H, C*H*OH), 2.47 (m, 1H, PCHC*H*), 2.22 (m, 1H, PCHC*H*), 1.64 (m, 2H, PCH_2), 0.98 (d, 3H, $J = 6.3$ Hz, CH_3), 1.90−0.50 (m, 3H, BH_3). ^{31}P NMR ($CDCl_3$): δ 16.6 (br d, $J = 67$ Hz). ^{13}C NMR ($CDCl_3$): δ 131.98 (d, $J_{CP} = 8.7$ Hz), 131.88 (d, $J = 7.6$ Hz), 131.03, 129.55 (d, $J = 24.9$ Hz, q), 128.98 (q), 128.55 (d, $J_{CP} = 8.4$ Hz, 2C), 67.74 (d, $J_{CP} = 14.3$ Hz), 31.91, 23.12, 21.49 (d, $J_{CP} = 38.7$ Hz). $[\alpha]_D^{25} = -15.1$ (*c* 1.25, $CHCl_3$). MS HR-FAB [found 258.1179; $C_{16}H_{19}OP$ ($M^{\bullet+} - BH_3$) requires 258.1174].

Compound 5e. This compound was prepared as described for **5a**. Phosphine−borane **2** and (*R*)-phenyl oxirane have been used for the synthesis of **5e**. The product was purified by column chromatography (eluent: 1: toluene, 2: 10% EtOAc in toluene), giving **5e** (1.56 g, 4.67 mmol, 100%) quantitatively as a white solid. Anal. Calcd for $C_{21}H_{24}BOP$: C, 75.47; H, 7.24. Found: C, 75.38; H, 7.32. ^1H NMR ($CDCl_3$): δ 7.67−7.61 (m, 4H, Ar−H), 7.50−7.40 (m, 6H, Ar−H), 7.34−7.28 (m, 5H, Ar−H), 4.75 (dd, 1H, $J = 6.1$ and 6.4 Hz, C*H*OP), 2.42 (m, 1H, PCHC*H*), 2.24 (m, 1H, PCHC*H*), 1.97 (m, 2H, PCH_2), 1.60−0.40 (m, 3H, BH_3). ^{31}P NMR ($CDCl_3$): δ 16.80 (br d, $J_{PB} = 58$ Hz). ^{13}C NMR ($CDCl_3$): δ 143.30 (q), 131.98 (d, $J_{CP} = 9.1$ Hz), 131.91 (d, $J_{CP} = 9.1$ Hz), 131.01 (2 × s), 129.47 (d, $J = 24.2$ Hz, q), 128.90 (d, q), 128.71, 128.58, 128.40, 127.63, 125.64, 73.99 (d, $J_{CP} = 14.0$ Hz), 31.89, 21.31 (d, $J_{CP} = 38.3$ Hz). Mp: 92−93 °C; $[\alpha]_D^{25} = -36.6$ (*c* 0.98, $CHCl_3$). MS HR-FAB [found 334.1658; $C_{21}H_{24}B_1O_1P_1$ ($M^{\bullet+}$) requires 335.1658].

Compound 6a. Alcohol **5a** (0.605 g, 1.58 mmol) was azeotropically dried with toluene (2 × 5 mL) and dissolved in toluene (20 mL) and NEt_3 (0.46 mL, 3.3 mmol), and the solution was cooled to −20 °C. A solution of 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite (0.787 g, 1.66 mmol) in toluene (5 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was filtered over Celite and concentrated in vacuo. Filtration over a short column of silica (eluent: toluene) afforded **6a** (1.22 g, 1.48 mmol, 94%) as a foam. ^{31}P NMR ($CDCl_3$): 143.60 (s), 17.29 (br s). MS HR-FAB [found 823.4614; $C_{53}H_{66}B_1O_3P_2$ ($M^{\bullet+} + H$) requires 823.4580]. Compound **6a** was used immediately without further purification.

Compound 6b. This compound was prepared as described for **6a**. Phosphino alcohol **5b** and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite have been used for the synthesis of **6b**. Filtration over a short column of silica (eluent: toluene) afforded **6b** (1.10 g, 1.37 mmol, 100%) quantitatively as a foam. ^{31}P NMR ($CDCl_3$): δ 144.11 (s) and 16.98 (br s). MS HR-FAB [found 803.4467; $C_{50}H_{66}B_1O_4P_2$ ($M^{\bullet+} + H$) requires 803.4529]. Compound **6b** was used immediately without further purification.

Compound 6c. This compound was prepared as described for **6a**. Phosphino alcohol **5c** and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite have been used for the synthesis of **6c**. Filtration over a short column of silica (eluent: toluene) afforded **6c** (1.86 g, 2.27 mmol, 100%) quantitatively as a foam. ^{31}P NMR ($CDCl_3$): δ 143.65 (s), 17.29 (br s). MS HR-FAB [found 823.4627; $C_{53}H_{66}B_1O_3P_2$ ($M^{\bullet+} + H$) requires 823.4580]. Compound **6c** was used immediately without further purification.

Compound 6d. This compound was prepared as described for **6a**. Phosphino alcohol **5d** and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite have been used for the synthesis of **6d**. Filtration over a short column of silica (eluent: toluene) afforded **6d** (0.550 g, 0.77 mmol, 65%) as a foam. ^{31}P NMR ($CDCl_3$): δ 145.43 (s), 16.66 (br s). Compound **6d** was used immediately without further purification.

Compound 6e. This compound was prepared as described for **6a**. Phosphino alcohol **5e** and 3,3′,5,5′-tetra(*tert*-butyl)-2,2′-bisphenol phosphorochloridite have been used for the synthesis of **6e**. Filtration over a short column of silica (eluent: toluene) afforded **6e** (1.64 g, 2.13 mmol, 97%) as a foam. ^{31}P NMR ($CDCl_3$): δ 143.46, 17.10 (br s). MS HR-FAB [found 773.4435; $C_{49}H_{64}B_1O_3P_2$ ($M^{\bullet+} + H$) requires 773.4424]. Compound **6e** was used immediately without further purification.

Compound 1a. Phosphine−borane **6a** (1.15 g, 1.40 mmol) was dissolved in diethylamine (20 mL) and stirred overnight at 50 °C. The reaction mixture was concentrated in vacuo. Filtration over silica (eluent: toluene) gave **1a** (1.02 g, 1.26 mmol, 90%) as a white solid. Anal. Calcd for $C_{54}H_{62}O_3P_2$: C, 78.68; H, 7.73. Found: C, 78.75; H, 7.65. ^1H NMR ($CDCl_3$): δ 8.41 (dd, 1H, $J = 4.4$ and 8.0 Hz, Ar−H), 7.82 (dd, 2H, $J = 6.8$ and 7.5 Hz, Ar−H), 7.43−7.11 (m, 18H, Ar−H), 5.18 (m, 1H, C*H*OP), 2.06 (m, 2H, PCH_2 C*H*H′), 1.88 (m, 2H, PCH_2 C*H*H′), 1.38 (s, 9H, *tert*-butyl), 1.34 (s, 9H, *tert*-butyl), 1.28 (s, 9H, *tert*-butyl), 1.24 (s, 9H, *tert*-butyl). ^{31}P NMR ($CDCl_3$): δ 143.75 (s) and −26.75 (s). ^{13}C NMR ($CDCl_3$): δ 146.10 (q), 145.84 (q), 140.65 (q), 139.95 (q), 139.68 (q), 135.43 (d, $J = 20.4$ Hz, q), 134.40 (q), 133.33, 132.57 (2 × d, $J_{CP} = 26.4$ Hz, q), 132.36 (d,

J_{CP} = 18.9 Hz, q), 129.59−123.83 (CH−arom.), 78.59 (dd, J_{CP} = 8.7 and 15.2 Hz), 34.97 (q), 34.42 (q), 34.23 (d, CH_2), 31.33, 30.72 (d, J = 7.7 Hz), 22.18 (d, J_{CP} = 12.2 Hz, CH_2). Mp: 91.5−92.5 °C. $[\alpha]_D^{25}$ = +63.1 (*c* 1.0, $CHCl_3$). MS HR-FAB [found 809.4196; $C_{54}H_{63}O_3P_2$ ($M^{\bullet+}$ + H) requires 809.4252].

Compound 1b. This compound was prepared as described for **1a**. Phosphine−borane **6b** has been used for the synthesis of **1b**. Filtration over silica (eluent: toluene) gave **1b** (0.99 g, 1.25 mmol, 96%) as a white solid. Anal. Calcd for $C_{50}H_{62}O_4P$: C, 76.11; H, 7.93. Found: C, 76.07; H, 8.06. ^{1}H NMR ($CDCl_3$): δ 7.52 (d, 1H, J = 2.2 Hz, Ar−H), 7.41−7.12 (m, 14H, Ar−H), 6.92−6.76 (m, 3H, Ar−H), 5.16 (m, 1H, C*H*OH), 3.69 (s, 3H, OCH_3), 1.99 (m, 2H, PCH_2 CH*H*′), 1.79 (m, 2H, PCH_2 C*H*H′), 1.37 (s, 9H, *tert*-butyl), 1.34 (s, 9H, *tert*-butyl), 1.28 (s, 9H, *tert*-butyl), 1.25 (s, 9H, *tert*-butyl). ^{31}P NMR ($CDCl_3$): δ 144.13 (s) and −24.81 (s). ^{13}C NMR ($CDCl_3$): δ 160.99 (q), 146.05 (q), 145.80 (q), 140.80 (q), 139.96 (q), 139.68 (q), 137.12 (q), 132.75 (d, J = 19.6 Hz), 132.52 (d, J = 19.6 Hz), 131.94−110.04 (CH−arom.), 78.80 (dd, J_{CP} = 8.8 and 15.7 Hz), 55.13, 34.98, 34.68 (d), 34.41, 31.32, 30.81, 30.69, 21.01 (d, J_{CP} = 11.6 Hz). Mp: 79.0−80.5 °C. $[\alpha]_D^{25}$ = +41.8 (*c* 1.11, $CHCl_3$). MS HR-FAB [found 788.4174; $C_{50}H_{63}O_4P_2$ ($M^{\bullet+}$ + H) requires 759.4202].

Compound 1c. This compound was prepared as described for **1a**. Phosphine−borane **6c** has been used for the synthesis of **1c**. Filtration over silica (eluent: toluene) gave **1c** (1.83 g, 2.26 mmol, 100%) as a white solid. Anal. Calcd for $C_{54}H_{62}O_3P_2$: C, 78.68; H, 7.73. Found: C, 78.32; H, 7.90. ^{1}H NMR ($CDCl_3$): δ 8.43 (m, 1H, Ar−H), 7.82 (dd, 2H, J = 8.0 and 10.6 Hz, Ar−H), 7.49−7.38 (m, 4H, Ar−H), 7.30−7.15 (m, 14H, Ar−H), 5.24 (m, 1H, C*H*OP), 2.16−1.83 (m, 4H, PCH_2CH_2), 1.40 (s, 9H, *tert*-butyl), 1.36 (s, 9H, *tert*-butyl), 1.31 (s, 9H, *tert*-butyl), 1.27 (s, 9H, *tert*-butyl). ^{31}P NMR ($CDCl_3$): δ 143.81 (s), −27.26 (s). ^{13}C NMR ($CDCl_3$): δ 149.62 (q), 146.16 (q), 145.91 (q), 145.22 (q), 142.82 (q), 140.59 (q), 140.01 (q), 139.72 (q), 137.51 (d, J_{CP} = 12.8 Hz, q), 135.38 (d, J_{CP} = 21.1 Hz, q), 134.89 (d, J_{CP} = 16.6 Hz, q), 133.33 (d, J_{CP} = 4.5 Hz, q), 132.81 (q), 132.60 (d, J_{CP} = 18.9 Hz, CH), 132.39 (q), 132.30 (q), 129.47−123.70 (CH−arom.), 78.60 (dd, J_{CP} = 8.4 and 15.3 Hz), 35.02 (q), 34.46 (q), 34.24 (d, J = 8.7 Hz, CH_2), 31.42, 30.80 (d, J = 11.8 Hz), 22.32 (d, J_{CP} = 12.2 Hz, CH_2). Mp: 91−91.5 °C. $[\alpha]_D^{25}$ = −25.8 (*c* 0.96, $CHCl_3$). MS HR-FAB [found 809.4210; $C_{53}H_{63}O_3P_2$ ($M^{\bullet+}$ + H) requires 809.4252].

Compound 1d. This compound was prepared as described for **1a**. Phosphine−borane **6d** has been used for the synthesis of **1d**. Filtration over silica (eluent: toluene) gave **1d** (1.83 g, 2.26 mmol, 100%) as a white solid. Anal. Calcd for $C_{44}H_{58}O_3P_2$: C, 75.83; H, 8.39. Found: C, 75.80; H, 8.49. ^{1}H NMR ($CDCl_3$): δ 7.45 (dd, 2H, J = 2.4 and 4.1 Hz, Ar−H), 7.42−7.37 (m, 10H, Ar−H), 7.32−7.29 (dd, 2H, J = 2.4 and 4.1 Hz, Ar−H), 4.53 (ddq, 1H, J = 6.1, 6.1 and 14.5, C*H*OP), 2.18 (ddd, 1H, J = 5.7, 11.5 and 13.2 Hz, PCH_2CHH′), 2.04 (ddd, 1H, J = 5.7, 10.8 and 13.8 Hz, PCH_2CHH′), 1.74 (m, 2H, PCH_2), 1.49 (s, 9H, *tert*-butyl), 1.46 (s, 9H, *tert*-butyl), 1.37 (s, 9H, *tert*-butyl), 1.37 (s, 9H, *tert*-butyl), 1.25 (d, 3H, J = 6.1 Hz, CH_3). ^{31}P NMR ($CDCl_3$): δ 145.68 (s), −15.19 (s). ^{13}C NMR ($CDCl_3$): δ 160.98 155.31 (d, J_{CP} = 8.3 Hz), 142.37 (d, J_{CP} = 13.6 Hz), 141.71, 141.62, 141.56, 141.49, 140.52, 136.46 (d, J_{CP} = 14.3 Hz), 133.55, 131.19 (d, J_{CP} = 9.8 Hz), 130.45, 130.07, 129.68, 128.82, 128.11, 128.07, 128.02, 127.93, 127.76, 126.88, 125.09, 120.91 (d, J_{CP} = 9.8 Hz), 114.76, 113.96 (d, J_{CP} = 14.3 Hz), 112.65 (d, J_{CP} = 13.6 Hz), 110.57, 78.28 (dd, J_{CP} = 10.8 and 17.7 Hz), 55.39, 54.69, 35.03, 31.63, 30.60, 29.49, 21.24, 19.32 (d, J_{CP} = 39.9 Hz). Mp: 64−65 °C. $[\alpha]_D^{25}$ = −10.6 (*c* 1.01, $CHCl_3$). MS HR-FAB [found 697.3957; $C_{44}H_{59}O_3P_2$ ($M^{\bullet+}$ + H) requires 697.3939].

Compound 1e. This compound was prepared as described for **1a**. Phosphine−borane **6e** has been used for the synthesis of **1e**. Filtration over silica (eluent: toluene) gave **1e** (1.35 g, 1.78 mmol, 86%) as a white solid. Anal. Calcd for $C_{49}H_{60}O_3P_2$: C, 77.54; H, 7.97. Found: C, 77.36; H, 8.06. ^{1}H NMR ($CDCl_3$): δ 7.39 (dd, 2H, J = 2.4 and 4.6 Hz, Ar−H), 7.27−7.24 (m, 13H, Ar−H), 7.19 (d, 1H, J = 2.3 Hz, Ar−H), 7.16 (d, 1H, J = 2.4 Hz, Ar−H), 7.12 (m, 2H, Ar−H), 5.17 (m, 1H, C*H*OP), 2.01 (m, 2H, PCH_2CH_2), 1.77 (m, 2H, PCH_2CH_2), 1.38 (s, 9H, *tert*-butyl), 1.35 (s, 9H, *tert*-butyl), 1.29 (s, 9H, *tert*-butyl), 1.27 (s, 9H, *tert*-butyl). ^{31}P NMR ($CDCl_3$): δ 143.88 (s) and −15.29 (s). ^{13}C NMR ($CDCl_3$): δ 146.10 (q), 145.84 (q), 140.59 (q), 139.97 (d, q), 139.66 (q), 138.19 (q), 137.91 (d, q), 132.74 (q), 132.51 (d, J_{CP} = 18.9 Hz, Ar−C), 132.32 (d, J_{CP} = 18.9 Hz, Ar−C), 132.32 (q), 128.30, 128.17, 128.08, 127.99, 127.64, 126.98, 126.24 (d, J_{CP} = 9.1 Hz), 123.96 (d, J_{CP} = 17.4 Hz), 78.61 (dd, J_{CP} = 8.5 and 14.8 Hz), 34.99 (q), 34.42 (q), 34.03 (CH_2), 31.36, 31.33, 30.80 (d, J = 3.2 Hz), 30.70, 22.72 (d, J = 12.2 Hz, CH_2), 31.32, 30.76 (d, J_{CP} = 10.7 Hz), 29.49, 20.60 (d, J_{CP} = 37.9 Hz). Mp: 178−179 °C. $[\alpha]_D^{25}$ = +40.0 (*c* 1.01, $CHCl_3$). MS HR-FAB [found 759.4080; $C_{49}H_{61}O_3P_2$ ($M^{\bullet+}$ + H) requires 759.4096].

Compound 1f. Alcohol **5a** (0.220 g, 0.573 mmol) was azeotropically dried with toluene (2 × 2 mL) and dissolved in toluene (10 mL) and NEt_3 (0.160 mL, 1.16 mmol), and the solution was cooled to −20 °C. A solution of freshly prepared (*R*)-3,3′-bis(trimethylsilyl)-2,2′-binaphthol phosphorochloridite (0.573 mmol) in toluene (5 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature overnight. The reaction mixture was filtered over Celite and concentrated in vacuo. Filtration over a short column of silica (eluent: toluene) afforded **6f** as a foam. ^{31}P NMR ($CDCl_3$): 143.67 (s), 18.20 (br s). Phosphine−borane **1f** was subsequently prepared as described for **1a**. The product was purified by column chromatography (toluene) giving **1f** (0.200 g, 0.242 mmol, 42%) as a foam. Anal. Calcd for $C_{51}H_{50}O_3P_2Si_2$: C, 73.88; H, 6.08. Found: C, 73.47; H, 6.39. ^{1}H NMR ($CDCl_3$): δ 8.35 (dd, 1H, J = 4.5 and 7.6 Hz, Ar−H), 8.00−7.75 (m, 6H, Ar−H), 7.46−7.04 (m, 20H, Ar−H), 4.72 (m, 1H, C*H*OP), 1.80 (m, 2H, PCH_2CH_2), 1.52 (m, 2H, PCH_2CH_2), 0.35 (s, 9H, $Si(CH_3)_3$), 0.20 (s, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ 145.20 (s) and −26.48 (s). Mp: 101−102 °C. $[\alpha]_D^{25}$ = −350 (*c* 1.01, $CHCl_3$). MS HR-FAB [found 829.2876; $C_{51}H_{51}O_3P_2Si_2$ ($M^{\bullet+}$ + H) requires 829.2852].

Compound 1g. This compound was prepared as described for **1f**. Phosphino alcohol **5e** and (*S*)-3,3′-bis(trimethylsilyl)-2,2′-binaphthol phosphorochloridite (0.573 mmol) have been used for the synthesis of **6e**. Filtration over a short column of silica (eluent: toluene) afforded **6g** as a foam. ^{31}P NMR ($CDCl_3$): 143.67 (s), 18.23 (br s). Phosphine−borane **1g** was subsequently prepared as described for **1a**. The product was purified by column chromatography (toluene) giving **1g** (0.245 g, 0.296 mmol, 52%) as a foam. Anal. Calcd for $C_{51}H_{50}O_3P_2Si_2$: C, 73.88; H, 6.08. Found: C, 71.76; H, 6.71. ^{1}H NMR ($CDCl_3$): δ 8.37 (dd, 1H, J = 4.5 and 8.1 Hz, Ar−H), 8.08−7.78 (m, 6H, Ar−H), 7.47−7.03 (m, 18H, Ar−H), 6.82 (m, 2H, Ar−H), 4.95 (m, 1H, C*H*OP), 2.10 (m, 2H, PCH_2CH_2), 1.77 (m, 2H, PCH_2CH_2), 0.30 (s, 9H, $Si(CH_3)_3$), 0.17 (s, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): 143.88 (s) and −27.09 (s). Mp: 97.5−98.5 °C. $[\alpha]_D^{25}$ = +353 (*c* 1.01, $CHCl_3$). MS HR-FAB [found 829.2870; $C_{51}H_{51}O_3P_2Si_2$ ($M^{\bullet+}$ + H) requires 829.2852].

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