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Highly Regio- and Enantioselective Hydroformylation of Vinyl Esters Using Bidentate Phosphine,P-Chiral Phosphorodiamidite Ligands

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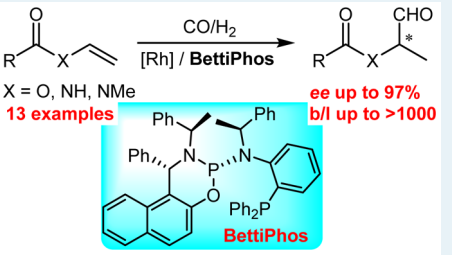
Supporting Information

ABSTRACT: Hybrid bidentate phosphine-phosphorodiamidite ligands based on a chiral Betti base backbone and diphenylphosphinoaniline derivatives have been prepared (BettiPhos). The ligands possess a stereogenic P atom at the phosphorodiamidite moiety, whose configuration can be largely controlled by the synthetic route and the choice of base and solvent. The new ligands were applied in the rhodium-catalyzed asymmetric hydroformylation (AHF) of vinyl esters and vinyl amides. Very high enantioselectivities of up to 97% ee accompanied by excellent regioselectivities (up to b/l > 1000) were obtained using the BettiPhos ligand (S_C,S_C,R_P,S_C)-**4b** bearing an additional chiral group at the aniline nitrogen. The catalyst resting state [RhH(CO)$_2${(S_C,S_C,R_P,S_C)-**4b**}] was investigated by high pressure-NMR studies, revealing an equatorial−apical coordination of the bidentate ligand where the two phosphorus donors rapidly exchange their positions through an intermediate with the ligand bound via the phosphine group only.



KEYWORDS: *asymmetric catalysis, hybrid phosphorus ligands, hydroformylation, rhodium, P-stereogenic ligands*

INTRODUCTION

Hydroformylation allows atom-efficient and direct formation of aldehydes from olefins and synthesis gas and has become a powerful synthetic tool for the preparation of these key organic intermediates.[1] Nowadays, hydroformylation is the largest application of homogeneous catalysis on an industrial scale with a capacity of more than 10 million tons of oxo products per year and is almost exclusively targeted to the production of the linear isomer.[2] In contrast, the regio- and stereoselective synthesis of chiral branched aldehydes is far less established,[1] although these compounds are of special interest for the preparation of a variety of biologically active compounds and fine chemicals, such as chiral alcohols, acids, amines, diols, and amino alcohols.[3,4]

Among the reported ligands for asymmetric hydroformylation (AHF), only very few are capable of giving high chemo-, regio-, and enantioselectivity at the same time. For example, diphosphite ligands such as (*S*,*S*)-Chiraphite[5] and (*S*,*S*)-Kelliphite[6] and diphosphine ligands such as (*S*,*S*,*S*)-Bisdiazaphos[7,4c,d] and (*R*,*R*)-Ph-BPE[8] provided good to high enantioselectivities of 82−96% ee for styrene or vinyl acetate but only in a few cases have high regioselectivities (92−99%) been obtained as well.[9] Recently, the AHF of *Z*-enamides and various enol esters with a very high level of stereocontrol using (*S*,*S*,*S*)-Bisdiazaphos was demonstrated.[4c,d] Very recently, Vidal-Ferran reported that very high regio- and enantioselectivity can be achieved using bidentate phosphite ligands with a polyether backbone tunable through the addition of "regulating agents".[10]

Since the seminal report of Takaya and Nozaki in 1993 on the phosphine-phosphite ligand Binaphos,[11] hybrid bidentate ligands with two different phosphorus donors have been intensively investigated for AHF.[1,3f,12] Very high enantioselectivities were achieved in the AHF of various substrate using a Binaphos derivative (up to 98% ee)[11d,e] or the related phosphine-phosphoramidite ligand Yanphos (up to 98% ee).[13] Both ligands, however, do not excel in regioselectivity (89−95%). In contrast, the phospholane-phosphite Bobphos led to higher regioselectivities of 98−99% but lower enantioselectivities of 83−92% ee.[14]

Herein we report the synthesis of a new family of hybrid phosphine-phosphorodiamidite bidentate ligands bearing a stereogenic P atom (BettiPhos) and their application in the asymmetric hydroformylation of vinyl ester derivatives with exceptionally high regioselectivities (up to >99.9% corresponding to a b/l ratio >1000) accompanied by very high enantioselectivities (ee up to 97%). NMR investigations showed that in the resting state [HRh(CO)$_2$(P-P′)] the phosphine and the phosphorodiamidite moieties occupy the equatorial and apical positions (major isomer 60% at −70 °C) or vice versa (minor isomer 40% at −70 °C). The two structures interconvert rapidly through an intermediate where the ligand is bound via the phosphine group only.

RESULTS AND DISCUSSION

Synthesis of Phosphine-Phosphorodiamidites. The ligand synthesis was accomplished from (*R*,*R*)-, (*R*,*S*)-, or (*S*,*S*)-Betti base **1**[15,16] and 2-(diphenylphosphino)-*N*-phenyl-

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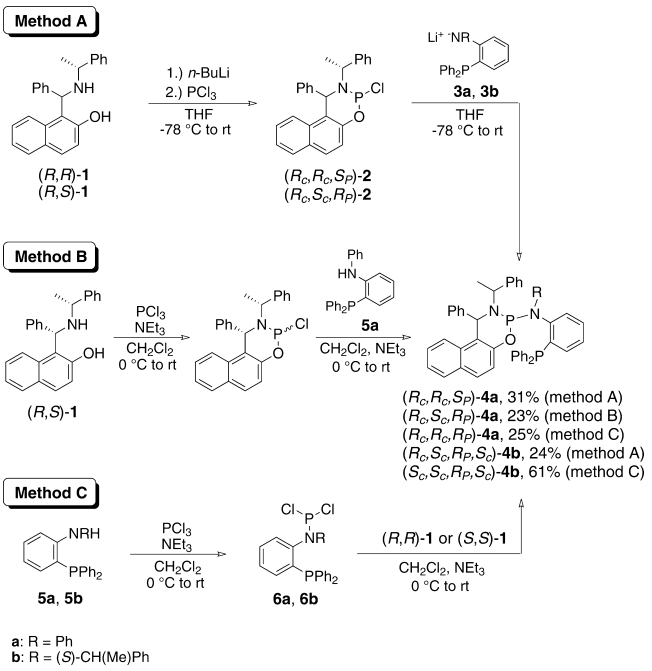
aniline **5a**[17] or (*S*)-2-(diphenylphosphino)-*N*-(1-phenylethyl)-aniline **5b**,[17] using a previously explored synthetic methodology.[16] The methods depicted in Scheme 1 via different routes, solvents, and bases provide good control of the configuration of the newly generated P-stereogenic center at the phosphorodiamidite moiety.

Scheme 1. Ligand Synthesis



Method A involves first the treatment of Betti base (*R*,*R*)-**1** or (*R*,*S*)-**1** with *n*-butyllithium in THF followed by the addition of PCl_3 and allows the stereoselective formation of phosphoramidochloridites (R_C,R_C,S_P)-**2** and (R_C,S_C,R_P)-**2**, respectively. The epimerically pure phosphoramidochloridites were then reacted with the lithiated 2-(diphenylphosphino)-*N*-phenylaniline **3a** or (*S*)-2-(diphenylphosphino)-*N*-(1-phenylethyl)aniline **3b** to give the desired phosphine-phosphorodiamidite ligands (R_C,R_C,S_P)-**4a** and (R_C,S_C,R_P,S_C)-**4b** in 31% and 24% yields, respectively, after recrystallization from toluene/ethanol (Scheme 1).

Method B follows a similar reaction sequence using, however, triethylamine as base and CH_2Cl_2 as solvent. This method was applied for the preparation of ligand (R_C,R_C,S_P)-**4a** from (*R*,*S*)-**1** and 2-(diphenylphosphino)-*N*-phenylaniline (**5a**). After recrystallization from toluene/ethanol, (R_C,R_C,S_P)-**4a** was obtained in 23% yield (Scheme 1).

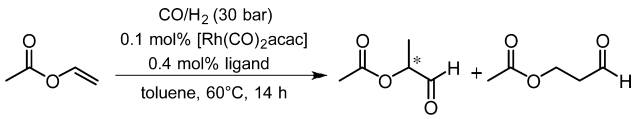
Method C, which comprises the in situ formation of dichloraminophosphines **6a**,**b**, was used for the synthesis of (R_C,R_C,R_P)-**4a** and (S_C,S_C,R_P,S_C)-**4b**, respectively. After purification by recrystallization from toluene/ethanol, the bidentate ligands were obtained in epimerically pure form and 25% and 61% yields, respectively (Scheme 1).

The absolute configuration of the phosphorodiamidite P atom of all BettiPhos ligands was assigned by comparison of the very characteristic chemical shifts in the ^{1}H, ^{13}C, and ^{31}P NMR spectra and coupling constants $J_{^1H,^{31}P}$ and $J_{^{13}C,^{31}P}$ to the related monodentate phosphorodiamidite ligands based on the same Betti base backbone, where the P configuration was unambiguously determined via X-ray crystal structure analysis.[16]

In the ^{31}P NMR, ligands (R_C,R_C,S_P)-**4a** and (R_C,S_C,R_P)-**4a** gave two sharp doublets for the phosphine and phosphoramidite moieties with through-space coupling constants $J_{P,P'}$ of 48.5 and 42.6 Hz, respectively. In contrast, broad signals were obtained for the phosphorodiamidite groups in (R_C,R_C,R_P)-**4a**, (S_C,S_C,R_P,S_C)-**4b**, and (R_C,S_C,R_P,S_C)-**4b** suggesting the presence of rotamers. Indeed, variable-temperature (VT) ^{31}P NMR showed for (S_C,S_C,R_P,S_C)-**4b** (see Figure S1 in the Supporting Information) two distinct sets of doublets of doublets at −40 °C with a ratio of 94:6 (major, δ_P −21.1 ppm, 140.6 ppm, $J_{P,P'}$ = 30.3 Hz; minor, δ_P −19.4 ppm, 130.7 ppm, $J_{P,P'}$ = 33.1 Hz). The conformers may originate from hindered rotation at the C−N bonds of the 1-phenylethyl groups both characterized by broad signals in the ^{1}H NMR even at −40 °C (see Figure S2 in the Supporting Information).

Rh-Catalyzed Asymmetric Hydroformylation. The BettiPhos ligands were applied in the asymmetric hydroformylation of vinyl acetate. The catalytic systems were prepared in situ by addition of the bidentate ligand to a solution of [$Rh(CO)_2(acac)$] in a Rh:L ratio of 1:4, and the reaction was carried out under standard conditions ($p(CO/H_2)$ 30 bar (ratio 1:1), T = 60 °C, t = 14 h). The results are summarized in Table 1.

Table 1. Rh-Catalyzed Asymmetric Hydroformylation of Vinyl Acetate Using Phosphine-Phosphorodiamidites 4[a]



entry	ligand	conversn[b] (%)	iso[c] (%)	ee[c] (%)
1	(R_C,R_C,R_P)-**4a**	13	98	32.6 (*S*)
2	(R_C,R_C,S_P)-**4a**	28	99	29.6 (*S*)
3	(R_C,S_C,R_P)-**4a**	30	99	34.5 (*R*)
4	(R_C,S_C,R_P,S_C)-**4b**	27	>99.9	83.4 (*R*)
5	(S_C,S_C,R_P,S_C)-**4b**	57	>99.9	93.8 (*R*)

[a]Conditions: substrate, 2 mmol; sub/Rh/L, 1000/1/4; toluene, 1 mL; $p(CO/H_2)$ = 30 bar (1:1); T = 60 °C, t = 14 h. [b]Determined by ^{1}H NMR. [c]Determined by chiral GC.

All ligands afforded moderately active hydroformylation catalysts exhibiting excellent regioselectivities. The relative configuration of the stereogenic phosphorus has little impact on the catalyst performance, and low enantioselectivities in favor of the *S*-aldehyde were obtained with both (R_C,R_C,R_P)-**4a** and (R_C,R_C,S_P)-**4a** (Table 1, entries 1 and 2). In contrast, the change of the stereochemistry of the Betti-base backbone in (R_C,S_C,R_P)-**4a** had a very significant effect and led to the preferential formation of the opposite enantiomer with a similar ee value (entry 3 vs entry 1). The enantioselectivity could be substantially increased using the ligands **4b** bearing an additional chiral moiety at the aniline nitrogen. In the presence of (R_C,S_C,R_P,S_C)-**4b**, 83.4% (*R*) ee and very high regioselectivity were achieved, albeit at low conversion (entry 4). Finally, the diastereomer (S_C,S_C,R_P,S_C)-**4b** based on Betti base (*S*,*S*)-**1** provided higher conversion (57%), a regioselectivity exceeding 99%, and 93.8% ee (entry 5).

Next, the reaction conditions for the AHF of vinyl acetate using BettiPhos (S_C,S_C,R_P,S_C)-**4b** were optimized (see Table S1 in the Supporting Information for full screening). For better

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Table 2. AHF of Vinyl Acetate Using (S_C,S_C,R_P,S_C)-4b[a]

entry	Sub/Rh	T (°C)	CO/H_2	L/Rh	conversn[b] (%)	b/l[c]	ee[c] (%)
1	1000	60	1	4	57	>1000	93.8
2	500	60	1	4	> 99	>1000	94.0
3	1000	80	1	4	> 99	>1000	66.6
4	500	45	1	4	54	497	95.1
5	1000	60	0.2	4	86	>1000	94.2
6	1000	60	1	2	67	76	64.4
7	1000	60	1	10	29	>1000	94.2
8	300	40	0.2	4	91	859	95.7
9	100	25	0.2	4	49	257	96.7
10[d]	4000	40	0.2	4	22	495	94.7

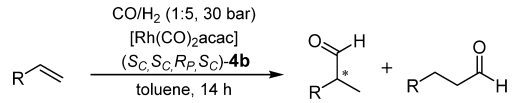
[a]Conditions unless specified otherwise: substrate, 2 mmol; toluene, 1 mL; $p(CO/H_2)$ = 30 bar; t = 14 h. [b]Determined by ^{1}H NMR. [c]Determined by chiral GC (R enantiomer always preferentially formed). [d]Reaction performed in 0.75 mL of substrate; p = 40 bar.

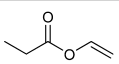
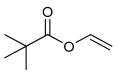
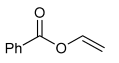
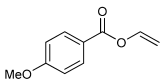
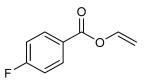
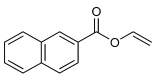
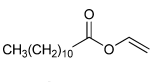
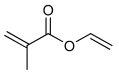
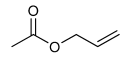
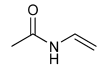
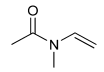
comparison the regioselectivities will be expressed as b/l ratios. The most important results are summarized in Table 2.

Increasing reaction temperature led to enhanced reaction rate and lower ee (Table 2, entry 3), whereas the regioselectivity remained excellent. An enantiomeric excess of 95.1% was achieved when the reaction was performed at 45 °C with b/l = 497 (Table 2, entry 4). No significant effect of the variation of the overall pressure was observed (see Table S1 in the Supporting Information), whereas an increased partial pressure of hydrogen (CO/H_2 = 1/5) accelerated the reaction according to the hydroformylation kinetic law (Table 2, entry 5 vs 1).[2a] The variation of the ligand/Rh ratio strongly affected the outcome of the reaction. When only 2 equiv of ligand was used, ee and b/l values dropped dramatically at a slightly increased reaction rate (Table 2, entry 6). The use of 10 equiv of ligand provided excellent regio- and enantioselectivity, albeit at the expense of activity (Table 2, entry 7). When the AHF was carried out at lower temperature, substrate/Rh ratio, and CO partial pressure, the enantioselectivity could be further increased. For instance, 95.7% ee was obtained at 40 °C with 91% conversion and b/l = 859 (Table 2, entry 8). This result represents the best compromise in terms of catalyst activity and regio- and enantioselectivity. Furthermore, the catalyst was also active at 25 °C, providing 96.7% ee, albeit at slightly reduced regioselectivity (b/l = 257) (Table 2, entry 9). When the reaction was performed in neat substrate at 40 °C, 22% conversion was achieved within 14 h with 94.7% ee and b/l = 495 (Table 2, entry 10). This corresponds to TOF_{av} = 63 h^{-1}. Attempts to preform the catalyst and then conduct AHF led to a racemic product mixture, because irreversible catalyst decomposition occurs upon releasing syngas before introducing the substrate.[18]

A series of vinyl esters and vinyl amides were hydroformylated using BettiPhos (S_C,S_C,R_P,S_C)-**4b** under the optimized conditions identified above. The results are summarized in Table 3. In the AHF of vinyl propionate ee values of up to 95.5% were obtained, although a somewhat reduced branched/linear ratio of 121 was found in comparison to the vinyl acetate (Table 3, entries 1 and 2). The use of vinyl pivalate as substrate resulted again in excellent regioselectivities with b/l values up to 451 and 94.6% ee. Interestingly, the catalyst activity was not negatively affected by the increased steric bulk of the *tert*-butyl group in the substrate (Table 3, entries 3 and 4). A comparable enantiomeric excess of 94.7% was achieved using vinyl benzoate as substrate, albeit at reduced yet high regioselectivity (b/l = 100) (Table 3, entries 5 and 6). For vinyl 4-methoxybenzoate again excellent regioselectivity

Table 3. AHF of Vinylic Substrates using (S_C,S_C,R_P,S_C)-4b[a]



Nr	Substrate	Sub/Rh	T (°C)	conv.[b] (%)	b/l[c]	ee[c] (%)
1		1000	60	62	73	94.0 (+)
2		300	40	97	121	95.5 (+)
3		1000	60	>99	292	94.2 (+)
4		300	40	97	451	94.6 (+)
5		1000	60	81	56	92.3 (+)
6		300	40	86	100	94.7 (+)
7		1000	60	89	271	91.0 (+)
8		300	40	60	>1000	91.3 (+)
9		1000	60	56	>1000	91.7 (+)
10		300	40	73	>1000	92.1 (+)
11		1000	60	95	61	81.7 (-)
12		300	40	80	81	88.0 (-)
13		1000	60	57	333	94.5 (+)
14		300	40	68	477	95.1 (+)
15		1000	60	23	158	94.0 (+)
16		300	40	35	381	95.8 (+)
17		100	60	3	<0.1	n.d.
18		100	80	>99	0.1	5 (-)
19		1000	60	31	10	63 (+)
20		300	40	22	25	82 (+)
21		1000	60	22	5	51 (+)
22		300	40	7	6	83 (+)

[a]Conditions: substrate, 2 mmol; Rh/L, 1/4; toluene, 1 mL; $p(CO/H_2)$ = 30 bar (1/5); t = 14 h. [b]Determined by ^{1}H NMR. [c]Determined by chiral GC.

(b/l > 1000) was observed, leading practically to a single regioisomer, accompanied by a slightly reduced enantioselectivity of 91.3% ee (Table 3, entries 7 and 8). Comparable results were obtained for vinyl 4-fluorobenzoate with 73% conversion, b/l > 1000, and 92.1% ee (Table 3, entry 10). The AHF of vinyl 2-naphthoate resulted in up to 88% ee and b/l =

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81 at 80% conversion (Table 3, entries 11 and 12). The long-chain vinyl laurate underwent hydroformylation with up to 95.1% ee and excellent regioselectivity (b/l = 477) (Table 3, entries 13 and 14). When vinyl methacrylate was used as substrate, the exclusive hydroformylation of the vinyl group was observed, whereas the conjugated double bond was untouched (>99% chemoselectivity in ^{1}H NMR). Enantioselectivities of up to 95.8% ee and a b/l ratio of 381 were obtained in this transformation (Table 3, entries 15 and 16). In contrast to the smooth hydroformylation of vinyl esters under mild conditions, the AHF of allyl acetate required elevated temperatures and afforded the desired aldehyde in only a poor enantiomeric excess of 5% (Table 3, entries 17 and 18).

Finally, vinylamides were hydroformylated with BettiPhos (S_C,S_C,R_P,S_C)-**4b**. Vinylacetamide and *N*-methyl vinylacetamide underwent hydroformylation with 82% and 83% ee, respectively (Table 3, entries 19−22). The conversions obtained were somewhat lower in comparison to the previously investigated vinyl ester substrates, and also the regioselectivities were significantly lower (b/l = 25 and 6, respectively), but still represent one of the best reported examples so far.[19]

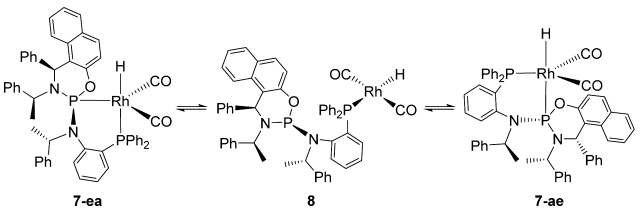
Investigations on Catalyst Resting State [RhH(CO)$_2$(P-P′)]. The coordination mode of the ligand in the catalytic resting state is believed to play an important role for stereocontrol in the AHF.[3d,f] For instance, the high level of enantioselectivity obtained with Binaphos was correlated with the equatorial−apical coordination mode adopted by the ligand in the resting state [HRh(CO)$_2$(P-P′)].[11b,g] A recent NMR study showed, however, that the major species with the phosphine at the equatorial position and the phosphite group in the apical position is in rapid equilibrium with the isomer with reverse coordination with a ratio of up to 3:1 in CD_2Cl_2 at −90 °C.[11k]

The coordination mode of the BettiPhos ligand in [HRh(CO)$_2$(P-P′)] was investigated via high pressure (HP) NMR. In a HP NMR tube (sapphire tube with a non-magnetic titanium head), the complex [Rh{(S_C,S_C,R_P,S_C)-**4b**}(acac)] was generated in situ from [Rh(CO)$_2$(acac)] and the ligand. In the ^{31}P NMR, this precursor displays two sets of doublets of doublets (δ_P = 34.4 ppm, dd, $J_{P,Rh}$ = 187.9 Hz, $J_{P,P'}$ = 86.6 Hz; $\delta_{P'}$ = 153.9 ppm, dd, $J_{P',Rh}$ = 264.7 Hz, $J_{P,P'}$ = 86.6 Hz). The HP NMR tube was then pressurized with CO/H_2 (30 bar), leading to the quantitative formation of the catalyst resting state [HRh(CO)$_2${(S_C,S_C,R_P,S_C)-**4b**}] with the following resonances in ^{31}P NMR: δ_P 19.3 ppm, dd, $J_{P,Rh}$ = 112.3 Hz, $J_{P,P}$ = 59.4 Hz; δ_P 167.1 ppm, dd, $J_{P,Rh}$ = 174.6 Hz, $J_{P,P}$ = 59.4 Hz. A single hydride species was visible in the ^{1}H NMR at −9.2 ppm (ddd, $^1J_{H,Rh}$ = 12.0 Hz, $^2J_{H,P}$ = 66.7 Hz, $^2J_{H,P}$ = 87.0 Hz; see Figure S3 in the Supporting Information). Selective decoupling of each inequivalent P nucleus allowed us to unequivocally associate the $^2J_{H,P}$ coupling constants of 87.0 and 66.7 Hz to the phosphorodiamidite and diphenylphosphine groups, respectively (see Figure S4 in the Supporting Information). The chemical shifts of the phosphorus signals as well as the $^1J_{H,Rh}$ and $J_{P,Rh}$ coupling constants are in the expected range for a trigonal-bipyramidal structure with equatorial−apical coordination of the ligand. The similar $^2J_{H,P}$ values, however, are indicative of a weighted average of cis and a trans coupling and do not support the presence of a single isomer.[20] This observation rather suggests the presence of an equilibrium of two stereoisomeric Rh complexes [HRh(CO)$_2${(S_C,S_C,R_P,S_C)-**4b**}] (each with equatorial−apical coordination of the BettiPhos ligand) which is not resolved on the NMR time scale at room temperature, as already observed for Binaphos.[11k]

This hypothesis was verified by conducting VT HP NMR experiments. Indeed, when the temperature was decreased, the hydride signal in the ^{1}H NMR broadened and then sharpened again to give two resolved but still slightly broad doublets at −70 °C (δ_H −9.0 and −9.1 ppm) exhibiting coupling constants of $^2J_{H,P}$ = 121 Hz (phosphine group) and $^2J_{H,P}$ = 194 Hz (phosphorodiamidite group), respectively (see Figures S5 and S6 in the Supporting Information). Additionally, a new broad doublet signal ($^2J_{H,P}$ = 118 Hz, phosphine group) appeared at −7.9 ppm at $T \leq -50$ °C.[21] The large coupling constants observed are characteristic for H,P-trans coupling, whereas the small H,P-cis and the H−Rh couplings were not resolved. The ratio of the hydride signals accounts for 37% (−7.9 ppm), 26% (−9.0 ppm), and 37% (−9.1 ppm). The ^{31}P NMR spectra varied accordingly upon a decrease in temperature. Three distinct broad peaks for the phosphine at δ_P 14.7, 21.7, and 29.2 ppm as well as for the phosphoramidite group at δ_P 170.9, 161.0, and 129.0 ppm were visible at −70 °C (see Figures S7−S9 in the Supporting Information). When the sample was heated again, these signals disappeared and signals were observed at room temperature that were identical with those found before the sample was cooled.

These observations strongly support the presence in solution of the two stereoisomeric Rh species **7-ea** and **7-ae** (Scheme 2),

Scheme 2. Equilibrium of Diastereomeric [HRh(CO)$_2${(S_C,S_C,R_P,S_C)-4b}] with Equatorial−Apical κ^2(P,P′) Coordination in 7 and κ^1(P,P′) in 8



both exhibiting an equatorial−apical coordination of the bidentate ligand where the phosphine group of (S_C,S_C,R_P,S_C)-**4b** occupies the axial position and the phosphorodiamidite the equatorial position (**7-ea**, $\delta_{phosphine}$(−70 °C, CD_2Cl_2) 21.7 ppm, $\delta_{phosphorodiamidite}$ 161.0 ppm) and vice versa (**7-ae**, $\delta_{phosphine}$ 14.7 ppm, $\delta_{phosphorodiamidite}$ 170.9 ppm) with an approximate ratio of 40:60. The additional NMR signals appearing at lower temperatures should arise from the square-planar species **8**, where only the phosphine group at δ_P 29.2 ppm is coordinated to the Rh trans to the hydride and with a pendant phosphorodiamidite group characterized by the chemical shift δ_P 129.0 ppm upfield with respect to that observed in the free ligand (δ_P 140.5 ppm). The species **8** may serve as an intermediate in the isomerization of **7-ea** and **7-ae**.

At this stage it is not possible to distinguish which isomer(s) is/are responsible for the highly enantioselective turnovers in the AHF. However, following the analogy with Binaphos,[11] the stereoisomer **7-ae** with the phosphorodiamidite trans to the hydride would be the most plausible candidate.

CONCLUSIONS

New hybrid phosphine-phosphorodiamidite bidentate BettiPhos ligands based on a chiral Betti-base backbone and diphenylphosphinoaniline derivatives have been prepared. The

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ligands possess a stereogenic P atom in the phosphorodiamidite moiety, whose configuration can be controlled to a large extent by the synthetic route. The BettiPhos ligands were applied in the rhodium-catalyzed asymmetric hydroformylation, combining very high enantioselectivities (up to 97%) with exceptional regioselectivities (up to b/l > 1000) for a variety of vinyl esters. Thus, the highly modular BettiPhos ligands define a new lead structure for the AHF of vinyl esters, providing synthetically useful selectivities.

In the resting state [$HRh(CO)_2${(S_C,S_C,R_P,S_C)-**4b**}], the ligand exhibits an equatorial−apical coordination with the two P moieties rapidly exchanging their positions through a square-planar intermediate where the ligand is bonded to the Rh via the phosphine donor only. These findings corroborate the assumption that an equatorial−apical coordination of the phosphorus ligand is a structural requirement for achieving highly enantioselective AHF, whereas a rigid environment is not and a fluxional behavior is tolerated.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b02846.

Experimental details, NMR spectra, and GC traces (PDF)

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Notes

The authors declare no competing financial interest.

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(21) Hydride signals in this region are commonly observed for Rh hydrido carbonyl complexes with ligands exhibiting a bis-equatorial coordination, as well as for complexes with monodentate ligands: see ref 5.

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