Phosphorus-Chiral Diphosphines as Ligands in Hydroformylation. An Investigation on the Influence of Electronic Effects in Catalysis

Ulrike Nettekoven,[†] Paul C. J. Kamer,[†] Michael Widhalm,[‡] and Piet W. N. M. van Leeuwen*,[†]

Institute of Molecular Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, and Institute of Organic Chemistry, University of Vienna, Währinger Strasse 38, 1090 Vienna, Austria

Received May 30, 2000

The phosphorus-chiral diphosphine 1,1′-bis(1-naphthylphenylphosphino)ferrocene (**1a**) and its new electronically modified derivatives **1b**−**d** bearing methoxy and/or trifluoromethyl groups in *para* positions of the phenyl rings were investigated as ligands in rhodium-catalyzed (asymmetric) hydroformylation. Depending on ligand basicity, high-pressure NMR and IR characterization of the respective (diphosphine) rhodium dicarbonyl hydride precursor complexes revealed subtle differences in the occupation of bis-equatorial (*ee*) and equatorial−apical (*ea*) coordination geometries. The high *ee*:*ea* ratio of the four complexes contrasted with the clear *ea* preference observed for the related achiral compound dppf (1,1′-bis(diphenylphosphino)ferrocene). In the hydroformylation of styrene the best result (50% ee) was obtained by employing the best π-acceptor ligand **1c**, incorporating two *p*-trifluoromethyl substituents. Substrate electronic variations using 4-methoxystyrene and 4-chlorostyrene showed a pronounced influence on turnover frequencies, branched/linear aldehyde product ratios, and enantiodiscrimination, whereas in the hydroformylation of 1-octene ligand electronic perturbations did affect only the rate, but not the selectivity of the reaction.

Introduction

The catalytic hydroformylation of alkenes ranks among the most widely industrially applied homogeneous processes. Its asymmetric variant has not yet reached that level of sophistication; nevertheless, or just for that reason, many efforts have been directed toward that goal during the past few years. Attractive features of the reaction, such as atom economy and potential catalyst recyclability as well as the need for optically active aldehyde products as intermediates for fine chemicals, are counterbalanced by several drawbacks, among which number unsatisfactory branched/linear ratios, modest reactivities and enantioselectivities, side reactions, and insufficient catalyst stability.[1]

Useful asymmetric systems developed to date include catalysts based on platinum(II) or rhodium(I), in which both of the metal centers have been modified by mono- or bidentate phosphorus ligands.[2] Although some of the highest enantiomeric excess (ee) values ever reported in asymmetric hydroformylation were obtained using platinum/stannous chloride catalysts,[3] these systems tend to suffer from low reaction rates, moderate branched/linear ratios, and product racemization. With respect to the mentioned criteria, rhodium(I)-based catalysts are considered superior, but catalyst stability and especially enantiodiscrimination are features that deserve improvement. The most successful ligands reported to date for rhodium-catalyzed asymmetric hydroformylation are bulky diphosphites based on enantiopure pentane-2,4-diols[4] on one hand and phosphine−phosphites bearing atropisomeric binaphthyl moieties on the other hand (Binaphos, 96% ee for the hydroformylation of styrene).[5]

Previously, a new class of rigid diphosphine ligands was developed in our group, based on 9,10-dimethylxanthene or related backbones and, consequently, bearing a large natural bite angle as a structural characteristic.[6] The coordination mode of these Xantphos-type ligands in rhodium(I) dicarbonyl hydride precursor complexes was shown to be preferentially bis-equatorial,

[†] University of Amsterdam.
[‡] University of Vienna.

(1) For reviews on hydroformylation see for example: (a) Tolman, C. A.; Faller, J. W. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; p 81. (b) Beller, M.; Cornils, B.; Frohning, C. D.; Kohlpaintner, C. W. *J. Mol. Catal. A: Chem.* **1995**, *104*, 17. (c) Frohning, C. D.; Kohlpaintner, C. W. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996; Vol. 1, p 27.

(2) For reviews on asymmetric hydroformylation see for example: (a) Agbossou, F.; Carpentier, J.-F.; Mortreux, A. *Chem. Rev.* **1995**, *95*, 2485. (b) Gladiali, S.; Bayon, J. C.; Claver, C. *Tetrahedron: Asymmetry* **1995**, *6*, 1453 and references therein.

(3) (a) Stille, J. K.; Su, H.; Brechot, P.; Parrinello, P.; Hegedus, L. S. *Organometallics* **1991**, *10*, 1183. (b) Cserépi-Szücs, S.; Bakos, J. *J. Chem. Soc., Chem. Commun.* **1997**, 635.

(4) (a) Babin, J. E.; Whiteker, G. T. PCT Int. Appl. WO 93 03839, 1993; *Chem. Abstr.* **1993**, *119*, 159872h. (b) Buisman, G. J. H.; van der Veen, L. A.; Klootwijk, A.; de Lange, W. G. J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Vogt, D. *Organometallics* **1997**, *16*, 2929.

(5) (a) Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033. (b) Nozaki, K.; Sakai, N.; Nanno, T.; Horiuchi, T.; Takaya, H. *J. Am. Chem. Soc.* **1997**, *119*, 4413 and references therein.

(6) Kranenburg, M.; van der Burgt, Y. E. M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 3081.

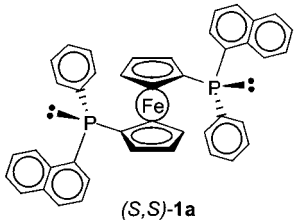
10.1021/om0004489 CCC: $19.00
Publication on Web 10/05/2000

which, at first, was assumed to be an explanation for the high selectivity toward linear aldehyde observed in the hydroformylation of 1-octene. When electronically modified Xantphos ligands were employed, the reactivity was (expectedly) found to depend on the electron donor and acceptor capacities of the substituents at the *para* position of the phenyl rings of the phosphines,[7] whereas the earlier reported correlation[8] between Hammett σ_p constants and the selectivity toward formation of the linear aldehyde did not apply.

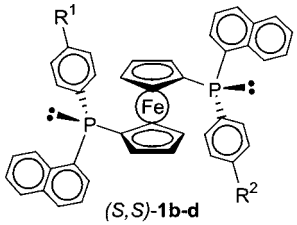
In contrast, Casey et al. reported on a distinct influence of ligand electronic effects on the linear/branched aldehyde product ratio in the hydroformylation of 1-hexene.[9] They stated that electron-withdrawing substituents on equatorially coordinated phosphines slightly favor formation of linear aldehydes, whereas electron-poor phosphines in the apical position are supposed to support strongly the opposite regiochemistry. This hypothesis was substantiated by the synthesis and application of electronically dissymmetric equatorial−apical coordinating ligands, which, due to the preference of electron-deficient phosphines for the equatorial coordination site, showed indeed a higher linear/branched ratio than their symmetric counterparts.[10]

Our interest was attracted by a possible extension of these results to asymmetric hydroformylation and the effects that might be encountered there. C_2-symmetrical diphosphines do not rank among the ligands inducing excellent enantioselectivities in that reaction; to the best of our knowledge, the highest ee values (60%) were obtained using bdpp (2,4-bis(diphenylphosphino)pentane).[11] This ligand was shown to coordinate to trigonal-bipyramidal rhodium(I) precursor complexes in a predominantly equatorial−apical fashion, which is ascribed to the small natural bite angle of around 90°. In contrast, the application of propeller-shaped diphosphine ligands displaying larger natural bite angles (>100°) in an asymmetric reaction variant has not been investigated in detail. To render this type of compound promising, we reasoned that chirality at the coordinating phosphines might, due to their proximity to the metal center, induce higher enantioselectivities than if incorporated in the backbone. Furthermore, provided that trigonal-bipyramidal intermediates are involved in the selectivity-determining step of the catalytic cycle, bis-equatorially coordinated structures of C_2-type symmetry are more desirable, since they leave only one equatorial coordination site accessible on which alkene complexation and subsequent hydride migratory insertion is to proceed. Thus, a reduction of competitive diastereomeric reaction pathways resulting therefrom is believed to confer high levels of enantiodiscrimination.[12]

The ligands we chose for our study were 1,1′-bis(1-naphthylphenylphosphino)ferrocene (**1a**) and electronically modified derivatives thereof, bearing methoxy and trifluoromethyl groups in *para* positions of the phenyl rings. Consequently, steric alterations imposed by the substituents should be negligible, allowing for an investigation of mainly electronic effects. Because of their analogy to the achiral dppf (1,1′-bis(diphenylphosphino)-ferrocene) ligand, bite angles of around 100° can be expected for this type of diphosphine,[13] which should favor the formation of bis-equatorially coordinated complexes. In this paper we report on the stereoselective synthesis of three new phosphorus-chiral, electronically varied ferrocenyldiphosphine ligands **1b**−**d** and their application in the asymmetric hydroformylation of styrene and derivatives. To evaluate ligand performances in comparative context with respect to linear/branched ratios, hydroformylation experiments employing 1-octene as the model substrate were conducted as well. High-pressure IR and NMR measurements are described, which enabled the characterization of catalytic intermediates. Their implications for the reaction cycle, the regiochemistry, and enantioselectivities will be discussed.



(S,S)-**1a**



(S,S)-**1b-d**

1b : $R^1 = R^2 = OCH_3$
1c : $R^1 = R^2 = CF_3$
1d : $R^1 = OCH_3$, $R^2 = CF_3$

Results and Discussion

Ligand Synthesis. Recently we described the preparation of a series of phosphorus-chiral enantiopure arylphenylferrocenyldiphosphines.[14] On employing the approach of Jugé et al.,[15] characterized by attachment of an optically active auxiliary, ephedrine, to a borane-protected phosphorus center, and its stepwise removal

(7) van der Veen, L. A.; Boele, M. D. K.; Bregman, F. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Schenk, H.; Bo, C. *J. Am. Chem. Soc.* **1998**, *120*, 11616.

(8) (a) Unruh, J. D.; Christenson, J. R. *J. Mol. Catal.* **1982**, *14*, 19. (b) Moser, W. R.; Papile, C. J.; Brannon, D. A.; Duwell, R. A.; Weininger, S. J. *J. Mol. Catal.* **1987**, *41*, 271.

(9) Casey, C. P.; Lin Paulsen, E.; Beuttenmueller, E. W.; Proft, B. R.; Petrovich, L. M.; Matter, B. R.; Powell, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 11817.

(10) Casey, C. P.; Lin Paulsen, E.; Beuttenmueller, E. W.; Proft, B. R.; Matter, B. R.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 63.

(11) (a) Masdeu-Bultó, A. M.: Orejón, A.; Castellanos, A.; Castillón, S.; Claver, C. *Tetrahedron: Asymmetry* **1996**, *7*, 1829. (b) Dieguez, M.; Pereira, M. M.; Masdeu-Bultó, A. M.; Claver, C.; Bayon, J. C. *J. Mol. Catal. A* **1999**, *143*, 111.

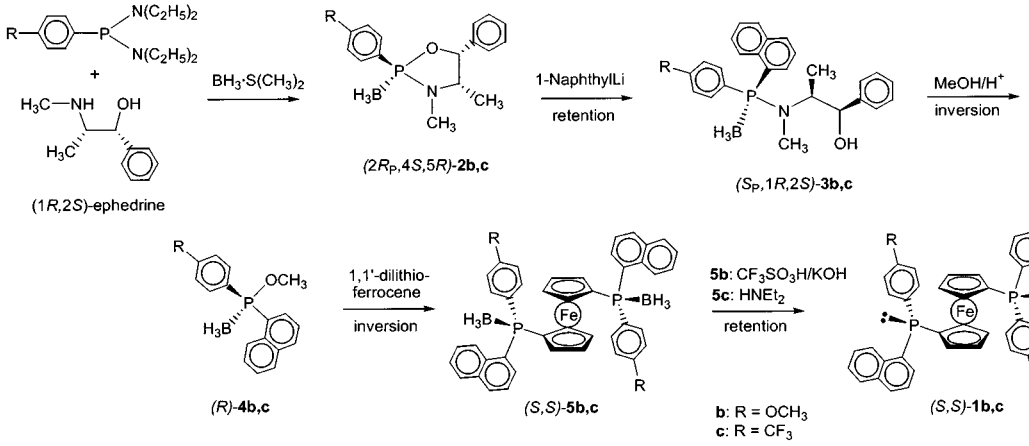
(12) Buisman, G. J. H.; Vos, E. J.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1995**, 409.

(13) For a compilation of crystal structure data of dppf complexes see for example: Gan, K.-S.; Hor, T. S. A. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995; Chapter 1.

(14) (a) Nettekoven, U.; Widhalm, M.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1997**, *8*, 3185. (b) Nettekoven, U.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Widhalm, M.; Spek, A. L.; Lutz, M. *J. Org. Chem.* **1999**, *64*, 3996.

(15) Jugé, S.; Stephan, M.; Laffitte, J. A.; Genêt, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357.

Scheme 1



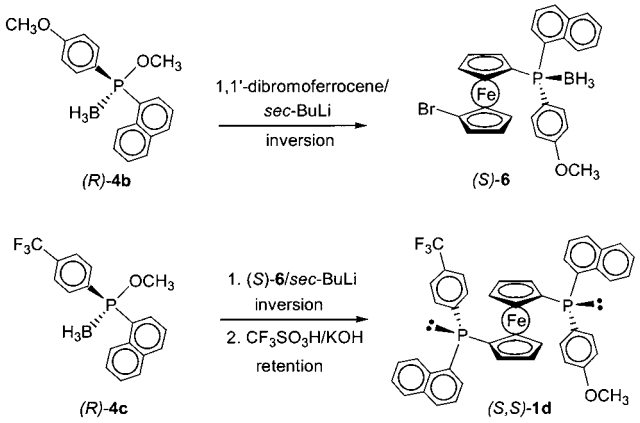
therefrom by nucleophilic substitutions, different methyl arylphenylphosphinite boranes of defined absolute configuration were obtained. Subsequently, we succeeded in the stereoselective coupling of the latter onto 1,1′-dilithioferrocene, which gave rise to the first phosphorus-chiral, enantiopure dppf analogues.

To allow for the introduction of the *para* substituents on the 1-naphthylphenylphosphino derivative **1a**, a slightly modified pathway had to be followed. Since the reaction sequence did not permit easy incorporation of electron-donating or -releasing groups at a final stage, the condensation reaction with the auxiliary had to be performed with the suitably substituted bis(diethylamino)phenylphosphines (Scheme 1).[16] These were synthesized by reaction of the respective Grignard reagents, derived from *p*-(trifluoromethyl)- and *p*-methoxybromobenzenes with bis(diethylamino)chlorophosphine. Subsequently, condensation with (1*S*,2*R*)-ephedrine at elevated temperatures, followed by complexation of the phosphorus centers using BH_3−dimethyl sulfide gave rise to single diastereomers of the respective oxazaphospholidine borane complexes **2b**,**c**.

For the unsubstituted phenyl derivative, the stereochemical course of the several steps during the condensation−substitution sequence has been confirmed by crystal structure analysis.[17] The presence of the *p*-methoxy or *p*-trifluoromethyl groups was assumed not to interfere severely during diastereo- and enantiodiscrimination; therefore, descriptors for the asymmetrically substituted phosphorus atoms were assigned in agreement with the literature findings.

Nucleophilic attack of 1-naphthyllithium proceeded in analogy to the described procedure,[14b] delivering the ring-opened phosphorus amide boranes **3b**,**c** in good yields. In comparison to the unsubstituted starting material, however, the observed diastereoselectivities were lower, resulting in 88−90% de of the products with configurationally retained phosphorus stereocenters. Nevertheless, separation of the isomers by column

Scheme 2



chromatography was achieved easily, thus permitting the use of stereohomogeneous starting materials for the next step.

Acidic methanolysis of the phosphorus amides was performed according to the literature and afforded the configurationally inverted phosphinite boranes **4b**,**c**. A considerably higher yield was obtained for the *p*-methoxy-substituted derivative.[18]

In the subsequent reaction, 1,1′-dilithioferrocene served as the nucleophile, stereoselectively replacing the methoxy groups at phosphorus and giving rise to the respective diphosphine diborane complexes **5b**,**c**. However, deprotection of the crude products using nitrogen bases such as diethylamine and morpholine proved successful only for the diborane **5c**. In the case of **5b**, decomplexation was accompanied by considerable epimerization at phosphorus, as recognized by formation of the *meso*-configured diphosphine. Repeated complexation of such a product mixture and comparison of its NMR data with those of the original diborane product indicated that racemization had indeed occurred during deprotection and did not result from unselective substitution. As an alternative method, acidic decomplexation was employed.[19] With this procedure no epimerization took place and, after column chromatographic purification, the diphosphine ligand **1b** was obtained in enantiopure

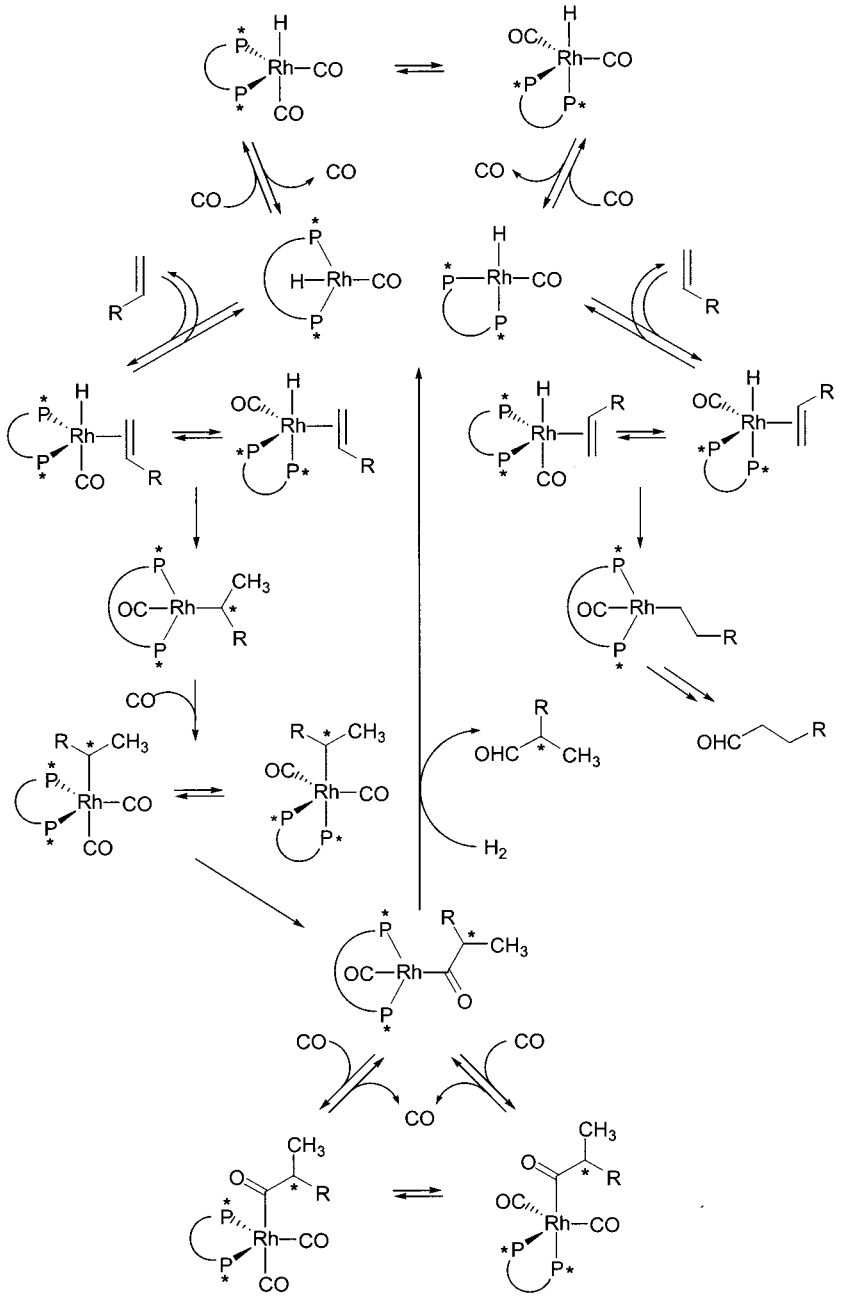
(16) In principle, a reversed sequence comprising of condensation of bis(diethylamino)(1-naphthyl)phosphine and ephedrine, followed by nucleophilic attack of *para*-substituted phenyllithium, should also be possible. Yet, purification of the bis(diethylamino)arylphosphine starting material by distillation was expected to be troublesome; therefore, this variant was not taken into further consideration.

(17) (a) Jugé, S.; Stephan, M.; Merdès, R.; Genêt, J. P.; Halut-Desportes, S. *J. Chem. Soc., Chem. Commun.* **1993**, 531. (b) Reference 14b.

(18) Addition of more than 1.1 equiv of sulfuric acid gave no improvement in the yield of the *p*-trifluoromethyl-substituted phosphinite−borane.

(19) McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319.

Scheme 3



form, as was diphosphine **1c** after removal of borane using diethylamine.

The synthesis of the electronically dissymmetric ligand **1d** was envisaged to proceed by stepwise introduction of the phosphine moieties to the ferrocene backbone (Scheme 2). In a first attempt, 1,1′-dibromoferrocene was lithiated using 1 equiv of *n*-butyllithium[20] and consecutively made to react with methyl 1-naphthyl-(4-(trifluoromethyl)phenyl)phosphinite−borane (**4c**). This procedure, however, resulted in a mixture of several products, including 1-bromo-1′-phosphinoferrocene−borane as well as heteroannularly unsubstituted ferrocenylphosphine−borane, both of which proved to be largely inseparable by low-pressure column chromatographic techniques. In a second approach, metalation was performed using *sec*-butyllithium and the resulting ferrocenyl nucleophile underwent reaction with the *p*-methoxyphenyl-substituted methyl phosphinite−borane **4b**. Although again amounts of monosubstituted ferrocene derivative were observed, the desired 1-bromo-1′-phosphinoferrocene−borane complex **6** was obtained as the main product and successfully purified by column chromatography. Subsequent lithiation of the latter by halogen−metal exchange employing *sec*-butyllithium and coupling to phosphinite−borane **4c** gave rise to the ferrocenyldiphosphine−diborane complex. Deprotection was achieved using trifluoromethanesulfonic acid and proceeded in a manner similar to that described for compound **5b**. Thus, the enantiomerically pure C_1-symmetrical ligand **1d** was isolated as an orange foam and constitutes one of the first examples

(20) (a) Lai, L.-L.; Dong, T.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2347. (b) Butler, I. R.; Davies, R. L. *Synthesis* **1996**, 1350.

Table 1. Selected NMR Data for (diphosphine)Rh(CO)$_2$H Complexes

complex	$\delta(^1H)$/ppm	$^1J_{H-Rh}$/Hz	$^2J_{H-P(av)}$/Hz	$\delta(^{31}P)$/ppm	$^1J_{P(av)-Rh}$/Hz	*ee*:*ea*
(**1a**)Rh(CO)$_2$H	−8.87	5.2	6.9	23.75	135.4	84:16
(**1b**)Rh(CO)$_2$H	−8.83	5.4	7.2	12.16	134.6	84:16
(**1c**)Rh(CO)$_2$H	−9.04	5.1	5.0	23.85	137.7	88:12
(**1d**)Rh(CO)$_2$H	−8.81	4.0	3.4 (P1)	17.45	136.1	
			9.3 (P2)	19.33		71:20:9[a]
(dppf)Rh(CO)$_2$H	−9.09	9.5	41.5	27.79	121.9	22:78

[a] Occupation of *ee* (*ee*-1 + *ee*-2), *ea*-1, and *ea*-2 coordination modes, respectively (Figure 1).

of a stereogenic diphosphine bearing two differently substituted phosphorus centers.

After suitable deprotection of diboranes **5b**−**d**, no signals indicating partial epimerization to the *meso* (type) compound were detected by NMR measurements. Nevertheless, the enantiomeric purity was checked by applying the NMR shift reagent *N*-(3,5-dinitrobenzoyl)-1-phenylethylamine[21] to diphosphine dioxides, derived from the respective ligands **1b**−**d**. Within the NMR integration errors of ±2%, no splitting of signals due to the presence of other diastereomeric adducts was observed.

High-Pressure NMR Measurements. A simplified mechanistic cycle for the generally accepted dissociative pathway of the diphosphine modified rhodium-catalyzed hydroformylation is depicted in Scheme 3.[22] The trigonal-bipyramidal rhodium diphosphine dicarbonyl hydride may be regarded as a precatalyst, from which CO decoordination is to occur, followed by alkene complexation to give again a five-coordinated intermediate. Under conditions of low pressure and temperature, consecutive hydride migratory insertion is assumed to be rate- and selectivity-determining,[23] as long as substrate isomerization indicating β-hydride elimination from the rhodium alkyl intermediates remains negligible.[24] Since they were the only observable monomeric species under catalytic conditions, the coordination mode of bidentate diphosphine ligands in rhodium dicarbonyl hydride complexes was found to influence the regiochemical outcome of the hydroformylation reaction (vide supra).

Concerning the issue of stereoselectivity, the situation is ambiguous. High enantioselectivities were obtained with bis-equatorially coordinating diphosphites[4] as well as equatorial−apically coordinating phosphine−phosphite[5] and, to a lesser degree, diphosphine chelates.[11] If the complexation mode of diphosphines in the trigonal-bipyramidal precursor complexes or alkene adducts was of any relevance to stereodiscrimination, subtle changes in the equilibrium population of the two isomers by ligand electronic perturbations should result in different ee values.

Therefore, the solution structures of rhodium dicarbonyl hydrides bearing dppf-analogues **1a**−**d** were determined by high-pressure NMR techniques. Because of the fast interconversion between bis-equatorial (*ee*) and equatorial−apical (*ea*) coordination fashions of chelating diphosphines, presumably proceeding via turnstile or Berry-type (pseudo)rotations,[25] averaged values for proton−phosphorus and phosphorus−rhodium coupling constants are generally obtained. At low temperatures the equilibrium may be frozen out, permitting the determination of individual constants for the coordination isomers and, subsequently, calculation of the *ee*:*ea* ratio for a given (diphosphine)Rh(CO)$_2$H complex or its iridium analogue.[26] For reasons of comparison, we were also interested in the behavior of the achiral ligand dppf, from which diphosphines **1a**−**d** are derived of. To this aim, experiments with dppf were included.

Reaction of ligands **1a**−**d** with Rh(CO)$_2$acac under 20 bar of syngas (H_2/CO = 1) at 40 °C resulted in exclusive formation of the respective diphosphine rhodium dicarbonyl hydride compounds. This was evidenced by the appearance of a triplet of doublets for the hydride signal in ^{1}H NMR and a doublet in the ^{31}P NMR (with exception of complexes incorporating ligand **1d**; vide infra). Unfortunately, for all of the complexes investigated, the dynamic equilibrium could not be frozen out completely at the lowest available temperature of −110 °C. Thus, equilibrium populations of bis-equatorial and equatorial−apical coordination modes were calculated assuming values of $^2J_{H-P(av)} = \pm 2$ Hz and $^2J_{H-P(av)} = 110$ Hz[27] for cis and trans hydride phosphorus coupling constants, respectively (Table 1).

The obvious trend observed for complexes of ligands **1a**−**d** is the dependence of the *ee*:*ea* distribution on ligand basicity. In agreement with previously reported work,[7] an increase in the electron-donating capacity within the ligand series was accompanied by a decrease in the *ee*:*ea* ratio. Among the complexes ligated by C_2-symmetrical diphosphines, the highest preference for the bis-equatorial coordination mode was, expectedly, measured for (**1c**)Rh(CO)$_2$H, displaying a value of 88:12. For the complexes incorporating ligands **1a**,**b**, the ratios were somewhat lower but, interestingly, almost equal. The electronic effect of the *p*-methoxy residues was found to be rather small, which should be mirrored in catalysis results (vide infra).

In the case of the complex (**1d**)Rh(CO)$_2$H, bearing the C_1-symmetrical ligand, the ^{31}P{^{1}H} spectrum showed two doublets of doublets, originating from direct rhodium−phosphorus coupling $^1J_{P(av)-Rh}$ as well as geminal coupling $^2J_{P1(av)-P2(av)}$ of the nonequivalent phosphines (Figure 1). In the ^{1}H spectrum, a very broad doublet

(21) Dunach, E.; Kagan, H. B. *Tetrahedron Lett.* **1985**, *26*, 2649.
(22) Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3133.
(23) Consiglio, G.; Pino, P. *Top. Curr. Chem.* **1982**, *105*, 77.
(24) (a) Lazzaroni, R.; Settambolo, R.; Raffaelli, A.; Pucci, S.; Vitulli, G. *J. Organomet. Chem.* **1988**, *339*, 357. (b) Lazzaroni, R.; Raffaelli, A.; Settambolo, R.; Bertozzi, S.; Vitulli, G. *J. Mol. Catal.* **1989**, *50*, 1.
(25) (a) Buisman, G. J. H.; van der Veen, L. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1997**, *16*, 5681. (b) Castellanos-Páez, A.; Castillón, S.; Claver, C.; van Leeuwen, P. W. N. M.; de Lange, W. G. J. *Organometallics* **1998**, *17*, 2543.
(26) (a) Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 725. (b) References 9 and 10.
(27) A value of 110 Hz was observed for *trans*-$^2J_{H-P(av)}$ in the rhodium dicarbonyl hydride complex of ligand **1d** at 193 K. This is in good agreement with data reported for comparably wide bite angle diphosphine rhodium or iridium compounds; see, for example refs 7 and 9. The common assumption of $^2J_{H-P(av)} = \pm 2$ Hz, however, may be subject to uncertainty.

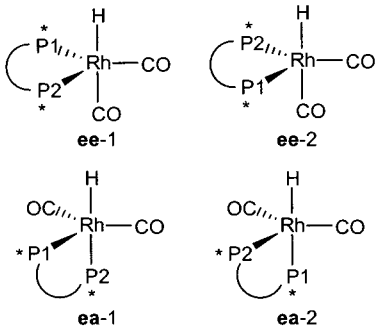


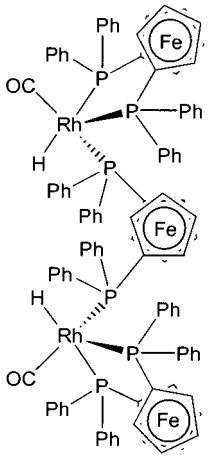
Figure 1. Possible coordination isomers of trigonal-bipyramidal rhodium dicarbonyl hydrides bearing P-chiral C_1-symmetrical diphosphines.

was observed at δ −8.94 ppm. Broad-band phosphorus decoupling enabled identification of the rhodium hydride coupling constant $^1J_{H-Rh}$ and, consequently, determination of $^2J_{H-P1(av)}$ and $^2J_{H-P2(av)}$. Considering the known preference of electron-poor donor ligands for equatorial coordination sites, the lower value of the averaged phosphorus hydride coupling constants of 3.4 Hz was assigned to the phosphine bearing the trifluoromethyl residue (P1), whereas the constant of 9.2 Hz implied an increased occupation of the apical coordination site and was therefore attributed to the methoxy-substituted phosphorus donor (P2). Calculation of the equilibrium concentrations gave a distribution of 71:20:9 between (not further discerned) *ee*, *ea*-1, and *ea*-2 coordination modes, respectively. Thus, the electronically dissymmetric diphosphine **1d** induced an *ee*:*ea* ratio in the dicarbonyl hydride complex, which ranks clearly below the values observed for either of the symmetrical donor ligands.

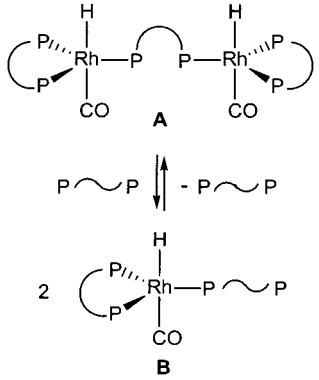
Interestingly, the achiral dppf chelate displayed a different coordination behavior. The NMR spectra indicated that under the conditions applied (20 bar of syngas, 1/1 CO/H_2, [Rh] = 8 mM) only when equimolar amounts of dppf and $Rh(CO)_2$acac were employed was the dicarbonyl hydride species formed as the main product. At higher ligand concentrations (dppf/$Rh(CO)_2$acac = 1.5−2; [dppf] = 12−16 mM), appearance of a broad doublet and, additionally, a broad singlet at δ 21.19 ppm indicated the prevailing species to be a dinuclear complex in which three phosphines are bound to each rhodium center by means of a bridging dppf molecule (Chart 1).[28,29] Such a structure had already been invoked by Unruh and Christenson in order to account for the observed increase of the linear/branched aldehyde ratio and the decrease in reaction rate utilizing 1.5 equiv or more of ligand per mole of rhodium in the hydroformylation of 1-hexene.[8a]

The chemical shift values are within the range previously observed for comparable trigonal-bipyramidal monocarbonyl rhodium hydrides;[30] the absence of additional distinct coupling patterns in ^1H as well as $^{31}P\{^1H\}$ NMR can be ascribed to a combination of rapid exchange between bridging and mononuclear tris(phosphine)-coordinated species (Scheme 4) and the mentioned *ee*:*ea* equilibration.

Chart 1



Scheme 4



A clearly lower *ee*:*ea* ratio was calculated for the chelating dppf ligand than for ligands **1a**−**d** in dicarbonyl hydride complexes. The smaller $^1J_{P(av)-Rh}$ coupling constant likewise suggested enhanced occupation of the apical coordination site,[31] whereas an expected small $^1J_{P(bridge)-Rh}$ coupling might not be resolved in the broad signal at δ 21.19 ppm. Consequently, tris(phosphine) carbonyl rhodium hydride species appeared to accommodate the bridging or monocoordinating dppf ligand in the equatorial position. The relatively large *ea* contribution to the averaged signals of the chelating donor seemed surprising, since spatial congestion in both complexes **A** and **B** is better released by tris-equatorial phosphine coordination. Nevertheless, the steric accessibility of the phosphines in dppf might, due to the presence of one five-membered ring, even surpass that of triphenylphosphine, which in combination with free rotation around the Cp−Fe−Cp axis could explain the enhanced formation of bridged *ea* chelated species. When these observations are compared with the high-pressure NMR structures incorporating diphosphines **1a**−**d**, replacement of a phenyl by a 1-naphthyl substituent seemed to introduce sufficient steric hindrance to prohibit formation of mono- or dinuclear tris(phosphine)-ligated species. Consequently, higher reactivities

(28) At dppf/rhodium ratios of up to 1.5, no signals stemming from noncoordinating phosphines were observed.

(29) Related observations of bridging phosphines in hydroformylation have been reported: (a) Reference 25b. (b) Freixa, Z.; Pereira, M. M.; Pais, A. A. C. C.; Bayón, J. C. *J. Chem. Soc., Dalton Trans.* **1999**, 3245.

(30) Hughes, O. R.; Young, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 6636.

(31) (a) Sanger, A. R. *J. Chem. Soc., Dalton Trans.* **1977**, 120. (b) Garrou, P. E.; Curtis, J. L. S.; Hartwell, G. E. *Inorg. Chem.* **1976**, *15*, 3094. (c) Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 7272.

Table 2. Selected IR Data (cm^{-1}) for (diphosphine)$Rh(CO)_2H$ Complexes

complex	ν_1	ν_2	ν_3	ν_4
(**1a**)$Rh(CO)_2H$	2041 (m)	1996 (m)	1991 (s)	1955 (m)
(**1b**)$Rh(CO)_2H$	2037 (m)	1993 (m)	1988 (s)	1952 (m)
(**1c**)$Rh(CO)_2H$	2043 (m)	2001 (m)	1996 (s)	1961 (m)
(**1d**)$Rh(CO)_2H$	2040 (m)	1997 (s)	1991 (s)	1957 (s)
(dppf)$Rh(CO)_2H$	2040 (w)	1996 (s)	1984 (w)	1955 (s)

and branched aldehyde selectivities were expected from catalysts derived from (**1a**−**d**) rhodium dicarbonyl hydrides.

High-Pressure IR Measurements. The presence of a dynamic equilibrium between *ee* and *ea* complexation modes in (**1a**−**e**)$Rh(CO)_2H$ compounds was corroborated by high-pressure IR spectroscopy. Each of the spectra of the respective complexes showed four absorption bands in the region between 2100 and 1900 cm^{-1}, which were attributed to carbonyl vibrations. In analogy to literature findings, the lowest frequency band ν_1 as well as ν_3 were assigned to the *ee* complex isomer, since upon H/D exchange only these bands were found to display a characteristic frequency shift in comparable diphosphine rhodium dicarbonyl hydrides.[7]

For the complexes bearing the structurally related ligands **1a**−**d**, a characteristic dependence of the vibration frequencies on ligand basicity was evidenced. With increasing electron acceptor properties of the phosphine a shift to higher wavenumbers was observed for all four absorption bands. **1a**−**c**-chelated complexes showed comparably strong ν_1 and ν_3 absorptions, whereas the ν_2 vibrations (partly hidden under ν_3) and the ν_4 bands appeared to be relatively weak. This trend was especially pronounced for the complex incorporating the bis-(*p*-(trifluoromethyl)phenyl)-substituted diphosphine **1c**, indicating this compound to exhibit the highest *ee* preference (Table 2). In contrast, the complex modified by ligand **1d** displayed a strong ν_2 vibration, clearly distinguishable from the ν_3 absorption band. Moreover, the intensity of the ν_4 vibration surpassed the otherwise strongest ν_3 absorption. Both observations conferred a higher equilibrium concentration of the *ea* coordination isomer in comparison to complexes bearing ligands **1a**−**c** (Figure 2).

Further evidence for this behavior was provided by the high-pressure IR spectrum of the rhodium dicarbonyl hydride ligated by dppf. NMR measurements suggested a pronounced contribution of the *ea* chelated trigonal-bipyramidal complex geometry to the equilibrium distribution and this was supported by the obtained IR data. Strong ν_2 and ν_4 vibrations but weak absorption bands of ν_1 and ν_3 are characteristics of a preferential *ea* complexation mode, which to a lesser degree were also recognizable in the spectra of the (**1d**)-$Rh(CO)_2H$ complex. Because of the low ligand and rhodium concentrations employed in IR experiments, the formation of the aforementioned tris(phosphine) carbonyl rhodium hydride species was less likely. A single CO resonance at about 1930 cm^{-1}, reported for mixtures of $[HRh(CO)(phosphine)_{1.5}]_2$ and $[HRh(CO)(phosphine)_3]$ with CO in a *trans* relationship to the hydride, was not observed.[30] Thus, the IR spectroscopic measurements on the respective (**1a**−**d**)$Rh(CO)_2H$ complexes were found to be in good agreement with the high-pressure NMR data, substantiating the *ee*:*ea* equilibrium distribution determined by the latter method.

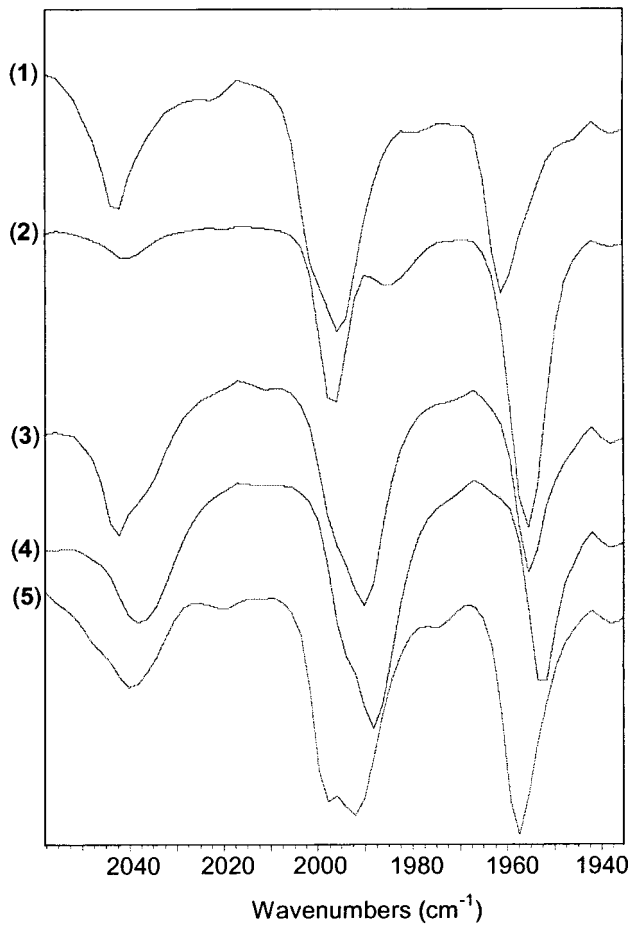
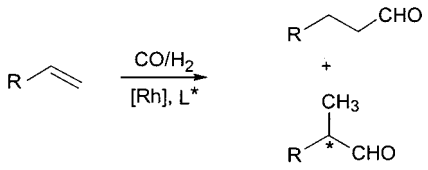


Figure 2. High-pressure IR spectra for diphosphine rhodium dicarbonyl hydride complexes (carbonyl region): (**1**) (**1c**)$Rh(CO)_2H$; (**2**) (**dppf**)$Rh(CO)_2H$; (**3**) (**1a**)$Rh(CO)_2H$; (**4**) (**1b**)$Rh(CO)_2H$; (**5**) (**1d**)$Rh(CO)_2H$.

Scheme 5



R = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, $CH_3(CH_2)_5$

Hydroformylation Results. Hydroformylation of styrene was carried out in toluene at a pressure of 20 bar of syngas (1/1 CO/H_2). In the first instance, the optimum reaction conditions were determined in experiments employing ligand **1a** at variable temperatures, ligand/rhodium ratios, and substrate concentrations (Scheme 5, Table 3).

To summarize, rather low reactivities and branched/linear ratios were obtained, indicating considerable steric congestion in the active catalyst species. ee values turned out to be moderate for the catalytic system investigated. Expectedly, an increase in enantioselectivities was observed on lowering the temperature; the limit for the reaction to proceed at acceptable rates, however, was above 30 °C. Equimolar amounts of rhodium precursor and ligand did not seem to give quantitative conversion to the diphosphine rhodium dicarbonyl hydride; the resulting low ee value can be ascribed to the presence of additional unsaturated

Table 3. Hydroformylation of Styrene (R = Ph) Using (*S,S*)-1a/Rh(CO)$_2$acac[a]

1a/ Rh(CO)$_2$acac	*T*/°C	% conversn	b:l ratio[b]	TOF[c]	% ee[d] (abs confign)
1.1	40	28	1.7	5	21 (*S*)
2.2	40	25	1.7	7	46 (*S*)
3	40	25	1.7	7	46 (*S*)
2.2	60	85	1.5	43	41 (*S*)
2.2	30	12	1.9	1	49 (*S*)
2.2[e]	40	21	1.7	10	32 (*S*)

[a] Reaction conditions: $CO/H_2 = 1$; pressure 20 bar, styrene/rhodium = 500; [Rh] = 2.30 mM in toluene. [b] Branched/linear product ratio. [c] Turnover frequency = (mol of aldehyde) (mol of Rh)$^{-1}$ h^{-1}. [d] Determined by chiral GC analysis of the corresponding alcohol. [e] Styrene/rhodium = 1000.

Table 4. Hydroformylation of (Substituted) Styrenes Using Different diphosphine/ Rh(CO)$_2$acac Species[a]

ligand	substrate R	*T*/°C	b:l ratio[b]	TOF[c]	% ee[d] (abs confign)
(*S,S*)-**1a**	Ph	40	1.7	7[e]	46 (*S*)
(*S,S*)-**1b**	Ph	40	1.7	6[e]	46 (*S*)
(*S,S*)-**1c**	Ph	40	1.5	12[e]	50 (*S*)
(*S,S*)-**1d**	Ph	40	1.7	11[e]	41 (*S*)
dppf	Ph	40	2.4	11[e]	
(*S,S*)-**1a**	4-MeOC$_6$H$_4$	60	1.2	42[f]	40 (*S*)
(*S,S*)-**1b**	4-MeOC$_6$H$_4$	60	1.2	24[f]	51 (*S*)
(*S,S*)-**1c**	4-MeOC$_6$H$_4$	60	1.1	71[f]	36 (*S*)
(*S,S*)-**1d**	4-MeOC$_6$H$_4$	60	1.1	55[f]	29 (*S*)
dppf	4-MeOC$_6$H$_4$	60	1.6	30[f]	
(*S,S*)-**1a**	4-ClC$_6$H$_4$	40	2.1	21[g]	37 (*S*)
(*S,S*)-**1b**	4-ClC$_6$H$_4$	40	2.4	15[g]	22 (*S*)
(*S,S*)-**1c**	4-ClC$_6$H$_4$	40	2.0	30[g]	22 (*S*)
(*S,S*)-**1d**	4-ClC$_6$H$_4$	40	2.3	22[g]	16 (*S*)
dppf	4-ClC$_6$H$_4$	40	2.6	3[h]	

[a] Reaction conditions: $CO/H_2 = 1$; pressure 20 bar, 2.2/1 ligand/rhodium, 500/1 styrene/rhodium; [Rh] = 2.30 mM in toluene. [b] Branched/linear product ratio. [c] Turnover frequency = (mol of aldehyde) (mol of Rh)$^{-1}$ h^{-1}. [d] Determined by chiral GC analysis of the corresponding alcohol. [e] Reactions were stopped at ~30% conversion. [f] Reactions were stopped at ~60% conversion. [g] Reactions were stopped at ~30% conversion. [h] Reactions were stopped at ~10% conversion.

catalytically active species. In contrast, the use of 2.2 equiv of **1a** sufficed for complete generation of the actual catalyst, since when 3 equiv were employed, no further improvement was obtained. A higher substrate/rhodium ratio was found to have a deleterious effect on enantiodiscrimination, which might be due to reduced catalyst stability at higher substrate concentrations.

Utilizing 2.2 equiv of diphosphine and a substrate/rhodium ratio of 500, hydroformylations with diphosphines **1a**−**d** as well as dppf-modified catalysts were carried out at 40 °C, the results of which are summarized in Table 4. In the presence of predominantly equatorial−apically coordinated catalysts, the use of styrene as a substrate is generally accompanied by relatively high branched/linear aldehyde ratios, a fact that is postulated to originate from an η^3-allyl type stabilization involving the phenyl ring of the branched rhodium alkyl species.[1a] However, a prevailingly bisequatorial coordination mode of the diphosphine ligand employed is associated with an increased preference for formation of the linear aldehyde,[9] which, indeed, is observed for ligands **1a**−**d**. As anticipated after inspection of the solution structures, the difference in performance of catalysts incorporating diphosphine **1a** and its *p*-methoxyphenyl derivative **1b** was small. A slight decrease in reaction rates was observed for the latter; nevertheless, the enantioselectivities proved to be equal. The presence of the *p*-trifluoromethyl groups of ligand **1c** in the catalyst affected turnover frequencies as well as optical induction. The first were found to be almost twice as high in comparison to reactions run with ligand **1a** and enantiodiscrimination experienced an increase of 4% to give a maximum of 50% ee. In contrast, employment of the C_1-symmetrical ligand **1d** as a catalyst component had a deleterious impact on stereoselectivity. While the presence of only one trifluoromethyl group seemed sufficient to promote a comparably high reaction rate, the ee values dropped to 41%.

To investigate combined influences of substrate and ligand electronic effects on the hydroformylation outcome, we also performed reactions employing *p*-chloro- and *p*-methoxystyrene as substrates (Scheme 5). Since coordination of (substituted) alkenes presumably exerts a strong influence on charge distribution in catalytic species as compared to effects imposed by (electronically modified) phosphine ligation, different mechanistic pathways might apply for these substrates. A relation between, on one hand, reactivity and aldehyde selectivities and, on the other hand, Hammett σ_p constants or χ values is well-established, whereby electron-withdrawing groups in *para* positions of a styrene substrate were found to promote higher turnover frequencies and branched/linear ratios.[32] Thus, hydroformylation of 4-methoxystyrene employing ligands **1a**−**d** as catalyst modifiers necessitated increased reaction temperatures of 60 °C; results are included in Table 4.

The trend in turnover frequencies observed for styrene was, expectedly, continued in a pronounced fashion, with the less basic ligands promoting faster reaction rates. In contrast, optical inductions were affected in a dissimilar manner. While with respective complexes of diphosphines **1a**,**c**,**d** enantioselectivities for 2-(4-methoxyphenyl)propanal were found to be lower than in the case of the unsubstituted product, the catalyst comprising ligand **1b** effected a noteworthy increase to 51% ee in the hydroformylation of 4-methoxystyrene. Obviously, low reaction rates and a favorable combination of electronic parameters positively influenced enantiodiscrimination.

A different picture was obtained when utilizing 4-chlorostyrene as the substrate. As anticipated, branched/linear ratios were found to be higher than those for the other two substrates investigated, whereby reactivity and ligand basicity obeyed the correlation already described.[32] The low turnover frequencies obtained on employing dppf-modified complexes were surprising. Considering a combination of factors such as reduced σ-donor capacity of the alkene and sterical overcrowding of a possibly bridged dinuclear rhodium precursor, this result could point toward alkene coordination as the crucial step in the mechanism. Additionally, catalyst deactivation might occur. The overall higher reaction rates observed for catalysts of ligands **1a**−**d** were accompanied by a decrease in optical yields, if compared to the other substrates. The electronically unmodified **1a** complex seemed to be best suited for asymmetric conversion of the electron-poor substrate, whereas enantioselectivities effected by the other cata-

(32) Hayashi, T.; Tanaka, M.; Ogata, I. *J. Mol. Catal.* **1981**, *13*, 323.

Table 5. Hydroformylation of 1-Octene (R = $(CH_3(CH_2)_5)$ at 80 °C Using Different diphosphines/ $Rh(CO)_2$acac Species[a]

ligand	l:b ratio[b]	*n*-ald sel/%	TOF[d]
1a	7.3	86.9	370
1b	7.4	86.5	224
1c	7.3	86.7	606
1d	7.2	86.7	650
dppf	5.4	83.3	87

[a] Reaction conditions: $CO/H_2 = 1$; pressure = 20 bar, 4/1 ligand/rhodium, 637/1 1-octene/rhodium; [Rh] = 1.18 mM in toluene. [b] Linear/branched product ratio. [c] Selectivity toward 1-nonanal. Substrate isomerization was found to be <2%. [d] Turnover frequency = (mol of aldehyde) (mol of Rh)$^{-1}$ h^{-1}. Reactions were stopped at ~30% conversion.

lysts were rather low. Consequently, no clear trend could be deduced from the latter results.

However, the generally valid relation between reactivity, product selectivities, and Hammett σ_p constants in the hydroformylation of styrene derivatives might be rationalized by invoking an early transition state for the (presumably selectivity-determining) hydride migration.[33] Negative polarization of the hydride and higher positive partial charge distribution on the terminal alkene carbon in comparison to the internal one could promote faster conversion of electron-poor substrates to the branched alkyl rhodium species, herewith effectively counterbalancing a possibly slower alkene coordination.

To place this investigation and the obtained results in the context of regioselective aliphatic alkene hydroformylation, we also performed catalysis experiments using 1-octene as the model substrate (Scheme 5). The results of reactions conducted at 80 °C are displayed in Table 5. Interestingly, **1a**−**d**-modified rhodium complexes effected similar linear/branched ratios (~7), whereby the amounts of isomerized internal alkenes were found to be <2% for all four catalysts. These findings contrast with previous contributions, detailing a higher tendency toward isomerization with increasing ligand basicity.[7,8a] It might be reasoned, however, that in the present investigation electronic perturbations originating from phenyl ring substitution only were too weak to induce such effects. Virtually the same selectivities toward formation of the linear aldehyde product were observed, once again indicating that under the applied conditions electronic parameters might not affect the regioselectivity-determining step(s). The lower selectivity obtained using dppf-ligated catalysts could originate from a smaller bite angle displaying its influence during alkene coordination to a diphosphine monocarbonyl rhodium hydride intermediate.[7] Purely steric reasons might also be invoked, featuring the well-known argument of increased spatial congestion imposed by ligands **1a**−**d** favoring the formation of the linear alkyl rhodium species in comparison to the less bulky dppf chelate. In contrast, assumption of a RhL_2-LH species (with L_2 = chelating dppf and L = bridging dppf) as selectivity relevant intermediate[8a] seems unlikely, since for that case the argument of steric encumbrance would suggest a higher linear/branched ratio in comparison to results conferred by the CO-ligated **1a**−**d** rhodium hydrides.

An interesting feature of these catalytic results was found within the achieved turnover frequencies. While reactivities using the first three ligands as catalyst components expectedly correlated with phosphine donor capacities, the high activity of catalysts incorporating ligand **1d** represented an unanticipated performance. A possible explanation may be that the relatively large bite angles and steric demands of ligands **1a**−**d** promote faster CO dissociation from trigonal-bipyramidal dicarbonyl rhodium hydrides than small bite angle ligands exhibiting reduced spatial congestion.[34] Due to the rotational freedom around the Cp−Fe−Cp axis, a nearly *trans*-chelating stabilization of four-coordinate hydrido rhodium carbonyl species seems possible,[7] whereby a dissymmetric charge distribution imposed by ligand **1d** could prove advantageous in promoting hydride insertion.

Conclusions

Our investigation on rhodium-catalyzed hydroformylation using electronically perturbed phosphorus-chiral diphosphines revealed some interesting aspects. When 4-methoxystyrene, styrene, and 4-chlorostyrene were employed as substrates, reactivity and branched aldehyde selectivities were dominated by their correlation with Hammett σ_p constants, whereby ligand electronic variations affected the reaction outcome to a smaller extent. However, for a given styrene derivative, a clear trend in turnover frequencies was evidenced with electron-withdrawing ligands as catalyst modifiers promoting faster reaction rates. High-pressure NMR and IR measurements showed an inverse relation between ligand basicity and preference for the bis-equatorial coordination mode in diphosphine rhodium dicarbonyl hydride precursor complexes. Worthy of note is the fact that the observed *ee*:*ea* ratios correlated well with the enantiodiscriminating performance of the respective diphosphines in styrene hydroformylation, where the best π-acceptor ligand effected the highest ee values. As theoretically anticipated, these results indicate the relevance of diphosphine coordination modes in trigonal-bipyramidal alkene complexes for the enantioselectivity-determining step; however, the effects are small and could easily be overshadowed by more pronounced steric and electronic variations. Thus, for 4-methoxy- and 4-chlorostyrene substrates no such correlation was found; in the former case ee values rather (inversely) depended on reaction rates.

In the hydroformylation of 1-octene, ligand electronic perturbations influenced only the reactivity, whereas linear product selectivities and linear/branched ratios were left unaffected. Consequently, optimization of turnover frequencies is possible by means of electronic fine-tuning, but more drastic ligand variations by introduction of additional electronically perturbing groups,[7,8a] possibly in sterically relevant positions,[9,10] will inevitably alter catalytic pathways and change product distributions. To summarize, our results illustrate once more that regio- and enantiodiscriminating features in hydroformylation are governed by a subtle interplay of steric and electronic features linked

(33) Matsubara, T.; Koga, N.; Ding, Y.; Musaev, D. G.; Morokuma, K. *Organometallics* **1997**, *16*, 1065.

(34) van der Veen, L. A.; Keeven, P. H.; Schoemaker, G. C.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Lutz, M.; Spek, A. L. *Organometallics* **2000**, *19*, 872.

to substrate as well as ligand properties. To date, its origin and consequences appear, however, much too complex to be reliably predicted by quantum mechanical and/or molecular modeling treatments.[35]

Experimental Section

General Comments. If not stated otherwise, reactions were carried out under an atmosphere of argon using standard Schlenk techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl, CH_2Cl_2 and acetonitrile were distilled from CaH_2, and toluene and methanol from sodium wire under nitrogen. NMR spectra were recorded on 250, 300, and 400 MHz instruments; $CDCl_3$ was used as the solvent if not mentioned otherwise. Phosphorus−carbon coupling constants (J_{C-P}) were identified by comparison of *J*-modulated ^{13}C spectra measured at different magnetic field strengths. Phosphorus−boron coupling constants (J_{PB}) were determined between the central peaks of the nonbinomial quartets. Elemental analyses were obtained using an Elementar Vario EL apparatus. Mass spectra were recorded on a JEOL JMS SX/SX102A four-sector mass spectrometer; for FAB-MS 3-nitrobenzyl alcohol was used as matrix. Melting points are uncorrected. Optical rotations were measured in a thermostated polarimeter with $l = 1$ dm. With the exception of the compounds given below, all reagents were purchased from commercial suppliers and used without further purification. Bis(diethylamino)(4-methoxyphenyl)phosphine and bis(diethylamino)(4-(trifluoromethyl)phenyl)phosphine were prepared via reaction of the respective *para*-substituted phenyl Grignard reagents and phosphorus trichloride[36] and subsequent conversion of the aryldichlorophosphines in the presence of excess diethylamine.[37] The following compounds were synthesized according to published procedures: 1,1′-dilithioferrocene,[38] 1,1′-dibromoferrocene,[39] and (*S*,*S*)-1,1′-bis(1-naphthylphenylphosphino)ferrocene (**1a**).[14]

Synthesis of Oxaazaphospholidine−Boranes 2 (Typical Procedure). (1*R*,2*S*)-(−)-Ephedrine (0.1 mol) was dissolved in 500 mL of toluene and degassed by three freeze−pump−thaw cycles. Bis(diethylamino)(4-methoxyphenyl)phosphine or bis(diethylamino)(4-(trifluoromethyl)phenyl)phosphine (0.1 mol) was added, and the solution was heated at 105 °C for 15 h. During this period, the diethylamine produced was distilled off to drive the condensation toward completion. Afterward, the reaction mixture was cooled on ice and BH_3−dimethyl sulfide (0.11 mol) was added dropwise. The solution was stirred at room temperature overnight. The solvent was removed in vacuo, and the residue was subjected to column chromatography (SiO_2; 3/1 toluene/hexane for **2b**; 1/1 toluene/hexane for **2c**). Evaporation of the eluent left oxaazaphospholidine−boranes **2** as white solids.

(2R_P,4*S*,5*R*)-(−)-3,4-Dimethyl-2-(4-methoxyphenyl)-5-phenyl-1,3,2-oxaazaphospholidine−Borane (2b). Yield: 47%. Mp: 70−72 °C. ^1H NMR (400.13 MHz): δ 0.52−1.32 (m, br, 3H); 0.81 (d, 3H, $J = 6.5$ Hz); 2.63 (d, 3H, $J_{H-P} = 10.5$ Hz); 3.68 (m, 1H); 3.83 (s, 3H); 5.56 (dd, 1H, $J = 2.5$; 8.0 Hz); 6.97 (m, 2H); 7.28−7.40 (m, 5H); 7.75−7.79 (m, 2H) ppm. ^{13}C NMR (100.62 MHz); δ 13.42 (d, CH_3, $J_{C-P} = 2.3$ Hz); 28.44 (d, CH_3, $J_{C-P} = 8.4$ Hz); 55.38 (CH_3); 59.34 (d, CH, $J_{C-P} = 2.3$ Hz); 83.76 (d, CH, $J_{C-P} = 7.6$ Hz); 114.12 (d, CH, $J_{C-P} = 10.7$ Hz); 124.15 (d, C, $J_{C-P} = 49.8$ Hz); 126.54 (CH); 128.23 (CH); 128.33 (CH); 133.27 (d, CH, $J_{C-P} = 13.8$ Hz); 136.31 (d, C, $J_{C-P} = 6.1$ Hz); 163.05 (br, C) ppm. ^{31}P NMR (121.50 MHz): δ 132.95 (q, br, $J_{P-B} = 88$ Hz) ppm. $[\alpha]^{20}_D = -2.52°$ ($c = 0.60$; CH_2Cl_2). HRMS (EI^+): *m*/*z* calcd for $C_{17}H_{23}BNO_2P$, 315.1559; obsd, 315.1566. Anal. Calcd for $C_{17}H_{23}BNO_2P$: C, 64.79; H, 7.36; N, 4.44. Found: C, 64.49; H, 7.37; N, 4.52.

(2R_P,4*S*,5*R*)-(+)-3,4-Dimethyl-2-(4-(trifluoromethyl)-phenyl)-5-phenyl-1,3,2-oxaazaphospholidine−Borane (2c). Yield: 38%. Mp: 89 °C. ^1H NMR (400.13 MHz): δ 0.39-1.27 (m br, 3H); 0.70 (d, 3H, $J = 6.6$ Hz); 2.58 (d, 3H, $J_{H-P} = 11.1$ Hz); 3.54 (m 1H); 5.44 (dd, 1H, $J = 3.0$, 6.1 Hz); 7.19−7.26 (m, 5H); 7.61 (d, br, 2H, $J = 7.3$ Hz); 7.80 (tr, br, 2H, $J = 8.6$ Hz) ppm. ^{13}C NMR (100.62 MHz): δ 13.52 (d, CH_3, $J_{C-P} = 3.1$ Hz); 29.38 (d, CH_3, $J_{C-P} = 8.4$ Hz); 59.01 (d, CH, $J_{C-P} = 1.5$ Hz); 84.51 (d, CH, $J_{C-P} = 7.6$ Hz); 125.43 (m, CF_3); 125.43 (m, CH); 126.56 (CH); 128.43 (CH); 128.51 (CH); 131.20 (d, CH, $J_{C-P} = 12.1$ Hz); 133.92 (dd, C, $J = 2.3$; 32.9 Hz); 135.77 (d, C, $J_{C-P} = 5.4$ Hz); 137.48 (d, br, C, $J = 39.8$ Hz) ppm. ^{31}P NMR (161.98 MHz): δ 133.04 (q, br, $J_{P-B} = 80$ Hz) ppm. $[\alpha]^{20}_D = +9.87°$ ($c = 0.38$; CH_2Cl_2). HRMS (EI^+): *m*/*z* calcd for $C_{17}H_{20}BF_3NOP$, 353.1328; obsd, 353.1332. Anal. Calcd for $C_{17}H_{20}BF_3NOP$: C, 57.82; H, 5.71; N, 3.91. Found: C, 57.64; H, 5.82; N, 3.89.

Synthesis of Phosphine Amide−Boranes 3 (Typical Procedure). 1-Bromonaphthalene (21 mmol) was dissolved in 60 mL of Et_2O, and the solution was degassed and cooled to −78 °C. *n*-BuLi (22 mmol of a 2.5 M solution in hexane) was added slowly, and the suspension was warmed to −20 °C over a period of 2 h to ensure complete lithiation. Consecutively, it was transferred slowly via Teflon cannula into a Schlenk flask containing a precooled solution (−78 °C) of oxaazaphospholidine−borane **2** (20 mmol) in 20 mL of THF. The reaction mixture was warmed to room temperature overnight and then quenched with water. Extractive workup with CH_2Cl_2, filtration, and evaporation of solvent left the crude product, which was purified by column chromatography (SiO_2, 96/4 toluene/ethyl acetate for **3b**; 97.5/2.5 toluene/ethyl acetate for **3c**). The desired products were eluted first, followed by minor amounts (~5%) of phosphorus-epimeric byproducts.

(*S*$_P$,1*R*,2*S*)-(+)-*N*-Methyl-*N*-((1-hydroxy-1-phenyl)prop-2-yl)-*P*-(4-methoxyphenyl)-*P*-(1-naphthyl)phosphinamide−Borane (3b). Yield: 81%. Mp: 56−58 °C. ^1H NMR (400.13 MHz): δ 0.90−1.72 (m, br, 3H); 1.29 (d, 3H, $J = 6.8$ Hz); 1.86 (s, br, 1H); 2.62 (d, 3H, $J = 7.6$ Hz); 3.82 (s, 3H); 4.45 (m, 1H); 4.99 (d, 1H, $J = 4.0$ Hz); 6.90 (m, 2H); 7.14−7.19 (m, 1H); 7.23−7.56 (m, 10H); 7.85 (d, 1H; $J = 8.1$ Hz); 7.94 (d, 1H; $J = 8.1$ Hz); 8.22 (d, 1H, $J = 8.6$ Hz) ppm. ^{13}C NMR (100.62 MHz): δ 11.59 (d, CH_3, $J_{C-P} = 3.8$ Hz); 31.29 (d, CH_3, $J_{C-P} = 3.8$ Hz); 55.24 (CH_3); 58.00 (d, CH, $J_{C-P} = 10.7$ Hz); 79.06 (d, CH, $J_{C-P} = 2.3$ Hz); 114.06 (d, CH, $J_{C-P} = 11.5$ Hz); 123.27 (d, C, $J_{C-P} = 67.3$ Hz); 124.60 (d, CH, $J_{C-P} = 9.9$ Hz); 126.05 (CH); 126.12 (CH); 126.22 (CH); 127.34 (d, CH, $J_{C-P} = 4.6$ Hz); 127.40 (CH); 127.49 (d, C, $J_{C-P} = 61.9$ Hz); 128.29 (CH); 128.76 (d, CH, $J_{C-P} = 0.9$ Hz); 132.21 (d, CH, $J_{C-P} = 2.3$ Hz); 132.55 (d, CH, $J_{C-P} = 7.6$ Hz); 133.31 (d, C, $J_{C-P} = 11.5$ Hz); 134.01 (C); 134.04 (d, CH, $J_{C-P} = 11.5$ Hz); 142.61 (C); 161.63 (d, C, $J_{C-P} = 1.5$ Hz) ppm. ^{31}P NMR (121.50 MHz): δ 70.73 (q, br, $J_{PB} = 56$ Hz) ppm. $[\alpha]^{20}_D = +98.3°$ ($c = 0.12$; CH_2Cl_2). HRMS (EI^+): *m*/*z* calcd for $C_{27}H_{31}BNO_2P$, 443.2185; obsd, 443.2193. Anal. Calcd for $C_{27}H_{31}BNO_2P$: C, 73.15; H, 7.05; N, 3.16. Found: C, 72.80; H, 6.95; N, 3.17.

(*S*$_P$,1*R*,2*S*)-(+)-*N*-Methyl-*N*-((1-hydroxy-1-phenyl)prop-2-yl)-*P*-(1-naphthyl)-*P*-(4-(trifluoromethyl)phenyl)phosphinamide−Borane (3c). Yield: 72%. Mp: 74 °C. ^1H NMR (400.13 MHz): δ 0.70−1.75 (m, br, 3H); 1.33 (d, 3H, $J = 6.8$ Hz); 1.86 (s, br, 1H); 2.59 (d, 3H, $J_{H-P} = 7.3$ Hz); 4.50 (m, 1H); 4.91 (d, br, 1H, $J = 4.6$ Hz); 7.22−7.33 (m, 4H); 7.38−7.52 (m, 6H); 7.58−7.66 (m, 3H); 7.88 (d, br, 1H, $J = 8.1$ Hz); 7.96−8.01 (m, 1H); 8.22 (d, br, 1H, $J = 8.6$ Hz) ppm. ^{13}C NMR (100.62 MHz): δ 12.10 (d, CH_3, $J_{C-P} = 3.8$ Hz); 31.33 (d, CH_3, $J_{C-P} = 3.8$ Hz); 58.22 (d, CH, $J_{C-P} = 10.7$ Hz); 78.96 (d, CH,

(35) Casey, C. P.; Petrovich, L. M. *J. Am. Chem. Soc.* **1995**, *117*, 6007.
(36) Gilheany, D. G.; Mitchel, C. M. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: New York, 1990; Vol. 1, p 151.
(37) Schumann, H. *J. Organomet. Chem.* **1986**, *299*, 169.
(38) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.
(39) (a) Kovar, R. F.; Rausch, M. D.; Rosenberg, H. *Organomet. Chem. Synth.* **1970/1971**, *1*, 173. (b) Dong, T.-Y.; Lai, L.-L. *J. Organomet. Chem.* **1996**, *509*, 131.

J_{C-P} = 3.1 Hz); 124.63 (d, CH, J_{C-P} = 10.7 Hz); 125.20 (m, CF_3); 126.16 (d, C, J_{C-P} = 62.0 Hz); 126.22 (CH); 126.42 (CH); 126.62 (CH); 126.88 (d, CH, J_{C-P} = 6.1 Hz); 127.77 (CH); 128.45 (CH); 129.01 (d, CH, J_{C-P} = 1.5 Hz); 132.43 (d, CH, J_{C-P} = 9.9 Hz); 132.78 (d, CH, J_{C-P} = 2.3 Hz); 132.92 (d, CH, J_{C-P} = 6.9 Hz); 133.24 (d, C, J_{C-P} = 11.5 Hz); 134.05 (d, C, J_{C-P} = 7.6 Hz); 137.20 (d, C, J_{C-P} = 59.7 Hz); 142.28 (C) ppm. ^{31}P NMR (121.50 MHz): δ 72.38 (q, br, J_{PB} = 34 Hz) ppm. $[\alpha]^{20}_D$ = +77.6° (*c* = 0.30; CH_2Cl_2). HRMS (FAB$^+$): *m/z* calcd for $C_{27}H_{29}BF_3NOP$ (MH^+), 482.2032; obsd, 482.2038. Anal. Calcd for $C_{27}H_{28}BF_3NOP$: C, 67.38; H, 5.87; N, 2.91. Found: C, 67.04; H, 6.15; N, 2.73.

Synthesis of Methyl Phosphinite−Boranes 4 (Typical Procedure). Phosphine amide−borane **3** (10 mmol) was dissolved in 80 mL of methanol and cooled on ice. Concentrated sulfuric acid (10.5 mmol) was added dropwise, and the solution was stirred at room temperature for 15 h. Then the reaction mixture was concentrated and subjected to column chromatography (SiO_2, 9/1 hexane/ethyl acetate for **4b**, 95/5 hexane/ethyl acetate for **4c**) to afford the respective methyl phosphinite−boranes as a colorless oil (**4b**) and white crystals (**4c**).

***(R)*-(−)-Methyl (1-Naphthyl)(4-methoxyphenyl)phosphinite−Borane (4b).** Yield: 84%. Oil. ^{1}H NMR (400.13 MHz): δ 3.72 (s, 3H); 3.77 (d, 3H, J_{H-P} = 12.1 Hz); 6.90 (m, 2H); 7.40−7.49 (m 2H); 7.53−7.58 (m, 1H); 7.61−7.68 (m, 2H); 7.91 (d, br, 1H, *J* = 7.8 Hz); 8.06 (d, br, 1H, *J* = 8.1 Hz); 8.23−8.31 (m, 2H) ppm. ^{13}C NMR (100.62 MHz): δ 53.55 (d, CH_3, J_{C-P} = 3.1 Hz); 55.05 (CH_3); 114.11 (d, CH, J_{C-P} = 11.5 Hz); 122.57 (d, C, J_{C-P} = 70.4 Hz); 124.55 (d, CH, J_{C-P} = 13.0 Hz); 126.11 (CH); 126.22 (d, CH, J_{C-P} = 4.6 Hz); 126.79 (CH); 126.93 (d, C, J_{C-P} = 57.4 Hz); 128.87 (CH); 132.45 (d, C, J_{C-P} = 6.1 Hz); 132.94 (d, CH, J_{C-P} = 12.3 Hz); 133.24 (d, CH, J_{C-P} = 2.3 Hz); 133.56 (d, C, J_{C-P} = 6.9 Hz); 134.10 (d, CH, J_{C-P} = 14.5 Hz); 162.23 (d, C, J_{C-P} = 2.3 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 110.91 (q, br, J_{PB} = 78 Hz) ppm. $[\alpha]^{20}_D$ = −49.5° (*c* = 0.59; CH_2Cl_2). HRMS (EI$^+$): *m/z* calcd for $C_{18}H_{20}BO_2P$, 310.1294; obsd, 310.1294. Anal. Calcd for $C_{18}H_{20}BO_2P$: C, 69.71; H, 6.50. Found: C, 69.69; H, 6.60.

***(R)*-(−)-Methyl (1-Naphthyl)(4-(trifluoromethyl)phenyl)phosphinite−Borane (4c).** Yield: 75%. Mp: 92 °C. ^{1}H NMR (400.13 MHz): δ 0.62−1.55 (m, br, 3H); 3.82 (d, 3H, J_{H-P} = 12.1 Hz); 7.41−7.45 (m, 1H); 7.49−7.53 (m, 1H); 7.61−7.67 (m, 3H); 7.73−7.79 (m, 2H); 7.92 (d, br, 1H, *J* = 8.1 Hz); 8.06 (d, br, 1H, *J* = 8.3 Hz); 8.11 (d, br, 1H, *J* = 8.3 Hz); 8.36 (ddd, 1H, *J* = 1.0; 7.3; 15.9 Hz) ppm. ^{13}C NMR (100.62 MHz): δ 54.27 (d, CH_3, J_{C-P} = 1.5 Hz); 124.82 (d, CH, J_{C-P} = 15.3 Hz); 125.38 (m, CH); 125.51 (d, C, J_{C-P} = 53.5 Hz); 125.91 (d, CH, J_{C-P} = 5.4 Hz); 126.53 (CH); 127.51 (CH); 129.29 (CH); 131.07 (d, CH, J_{C-P} = 11.5 Hz); 132.44 (d, C, J_{C-P} = 3.8 Hz); 133.21 (dd, C, *J* = 2.3; 32.9 Hz); 133.77 (d, C, J_{C-P} = 6.1 Hz); 134.35 (d, CH, J_{C-P} = 2.3 Hz); 136.13 (d, CH, J_{C-P} = 19.9 Hz); 137.20 (d, C, J_{C-P} = 66.5 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 112.32 (q, br, J_{PB} = 74.2 Hz) ppm. $[\alpha]^{20}_D$ = −2.5° (*c* = 0.39; CH_2Cl_2). HRMS (EI$^+$): *m/z* calcd for $C_{18}H_{17}BF_3OP$, 348.1062; obsd, 348.1088. Anal. Calcd for $C_{18}H_{17}BF_3OP$: C, 62.10; H, 4.93. Found: C, 62.25; H, 5.23.

Synthesis of Ferrocenyldiphosphines 1b,c (Typical Procedure). Dilithioferrocene (5 mmol) was dissolved in a mixture of 40 mL of Et_2O and 10 mL of THF and cooled to −50 °C. The resulting suspension was added via a Teflon cannula to a precooled (−50 °C) solution of methyl phosphinite **4** (10 mmol) in 10 mL of THF. The reaction mixture was allowed to reach room temperature over a period of 15 h and was then quenched with water. The solvent was removed in vacuo, and the residue was extracted twice with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was evaporated. Purification by column chromatography removed monosubstituted byproducts (∼10%) and small amounts (<10%) of isomerized meso diphosphine diboranes; the desired C_2-symmetrical diborane complexes **5b**,**c** were eluted last and concentrated.

***(S,S)*-(+)-1,1′-Bis((4-methoxyphenyl)(1-naphthyl)phosphino)ferrocene (1b).** Acidic decomplexation was performed for intermediate **5b**; this compound (∼2.5 mmol) was dissolved in 15 mL of toluene, the solution was cooled on ice, and trifluoromethanesulfonic acid (12.5 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 30 min and then warmed to ambient temperature. After 2 h, the solvent was removed in vacuo and the residue treated with a degassed solution of KOH (25 mmol) in 8 mL of 10/1 EtOH/H_2O. The suspension was agitated for 30 min and then repeatedly extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Column chromatography (alumina, 1/1 CH_2Cl_2/hexane) yielded enantiopure product **1b** as a yellow powder. Yield: 51%. Mp: 110 °C. ^{1}H NMR (400.13 MHz): δ 3.57 (m, 2H); 3.70 (s, 6H); 4.22 (m, 2H); 4.31 (m, 2H); 4.34 (m, 2H); 6.76 (d, 4H, *J* = 8.1 Hz); 7.10 (ddd, 2H, *J* = 1.0, 4.8, 6.8 Hz); 7.29−7.41 (m, 10H); 7.74 (d, 2H, *J* = 8.4 Hz); 7.77 (d, 2H, *J* = 7.8 Hz); 8.29 (dd, br, 2H, *J* = 3.8, 7.8 Hz) ppm. ^{13}C NMR (100.62 MHz): δ 55.05 (CH_3); 72.51 (br, CH); 72.64 (CH); 72.97 (d, CH, J_{C-P} = 6.9 Hz); 75.57 (d, CH, J_{C-P} = 29.1 Hz); 77.06 (C); 113.77 (d, CH, J_{C-P} = 8.4 Hz); 125.20 (CH); 125.68 (CH); 125.87 (CH); 126.00 (d, CH, J_{C-P} = 24.8 Hz); 127.48 (d, C, J_{C-P} = 5.4 Hz); 128.47 (CH); 128.84 (CH); 130.80 (CH); 133.34 (d, C, J_{C-P} = 4.6 Hz); 134.45 (d, C, J_{C-P} = 21.4 Hz); 135.53 (d, CH, J_{C-P} = 21.4 Hz); 137.42 (d, C, J_{C-P} = 13.8 Hz); 160.30 (C) ppm. ^{31}P NMR (121.50 MHz): δ −26.80 (s) ppm. $[\alpha]^{20}_D$ = +262° (*c* = 0.45; CH_2Cl_2). HRMS (FAB$^+$): *m/z* calcd for $C_{44}H_{37}FeO_2P_2$ (MH^+), 715.1618; obsd, 715.1613. Anal. Calcd for $C_{44}H_{36}FeO_2P_2$: C, 73.96; H, 5.08. Found: C, 73.82; H, 5.38.

***(S,S)*-(+)-1,1′-Bis((1-naphthyl)(4-(trifluoromethyl)phenyl)phosphino)ferrocene (1c).** Diphosphine−diborane **5c** (∼2.5 mmol) was dissolved in 10 mL of degassed diethylamine and stirred overnight at room temperature. Afterward, the solvent was removed in vacuo and the residue purified by column chromatography (alumina, 1/1 CH_2Cl_2/hexane) to afford the enantiopure ligand **1c** as orange foam. Yield: 36%. Mp: 95−97 °C. ^{1}H NMR (400.13 MHz): δ 3.81 (m, 2H); 4.15 (m, 2H); 4.24 (m, 2H); 4.28 (m, 2H); 7.12 (t, br, 2H, *J* = 5.8 Hz); 7.34 (tr, 2H, *J* = 7.4 Hz); 7.39−7.50 (m, 12H); 7.81 (d, 4H, *J* = 7.9 Hz); 8.36 (m, 2H) ppm. ^{13}C NMR (100.62 MHz): δ 72.45 (br, CH); 72.90 (d, CH, J_{C-P} = 5.2 Hz); 73.63 (d, CH, J_{C-P} = 9.9 Hz); 74.65 (d, CH, J_{C-P} = 20.8 Hz); 75.73 (d, C, J_{C-P} = 6.1 Hz); 124.85 (m, CF_3); 125.31 (CH); 125.70 (CH); 126.01 (CH); 126.03 (CH); 126.25 (d, CH, J_{C-P} = 2.3 Hz); 128.71 (CH); 129.80 (CH); 130.50 (d, C, J_{C-P} = 32.1 Hz); 132.39 (d, CH, J_{C-P} = 2.3 Hz); 133.45 (d, C, J_{C-P} = 2.3 Hz); 133.50 (d, CH, J_{C-P} = 19.9 Hz); 134.99 (d, C, J_{C-P} = 22.2 Hz); 135.20 (d, C, J_{C-P} = 13.8 Hz); 143.27 (d, C, J_{C-P} = 12.2 Hz) ppm. ^{31}P NMR (121.50 MHz): δ −25.95 (s) ppm. $[\alpha]^{20}_D$ = +130° (*c* = 0.29, CH_2Cl_2). HRMS (FAB$^+$): *m/z* calcd for $C_{44}H_{31}F_6FeP_2$ (MH^+), 791.1155; obsd, 791.1169. Anal. Calcd for $C_{44}H_{30}F_6FeP_2$: C, 66.85; H, 3.83. Found: C, 66.97; H, 4.17.

Synthesis of *(S)*-(+)-Methyl (1′-Bromo-1-ferrocenyl)-phenylphosphinite−Borane (6). 1,1′-Dibromoferrocene (12 mmol) was dissolved in 50 mL of THF and cooled to −50 °C. *sec*-BuLi (11 mmol of a 1.3 M solution in cyclohexane) was added slowly via syringe, and the mixture was warmed to −30 °C over a period of 2 h. After this mixture was cooled again, a solution of methyl phosphinite−borane (*R*)-**4b** (10 mmol) in 10 mL of THF was added via Teflon cannula at −70 °C, and the mixture was allowed to reach ambient temperature overnight. Then, the reaction was quenched with water, the solvent was removed in vacuo, and the residue was extracted with CH_2Cl_2. Drying over $MgSO_4$, filtration, and evaporation afforded the crude product, which was purified by column chromatography (SiO_2, 1/3 CH_2Cl_2/hexane). The desired bromo-containing phosphine−borane (*S*)-**6** was eluted first, closely followed by ∼20% of monosubstituted byproduct. Yield: 41%. Mp: 149−151 °C. ^{1}H NMR (400.13 MHz): δ 0.56−1.78 (m, br, 3H); 3.82 (s, 3H); 4.03 (m, 1H); 4.15 (m, 1H); 4.22 (m, 2H);

4.44 (m, 1H); 4.54 (m, 1H); 4.59 (m, 1H); 4.75 (m, 1H); 6.93 (m, 2H); 7.28 (ddd, 1H, J = 1.2, 6.8, 8.6 Hz); 7.35−7.44 (m, 3H); 7.63 (ddt, 2H, J = 2.3, 8.8, 10.6 Hz); 7.80 (d, br, 1H, J = 8.1 Hz); 7.88−7.95 (m, 2H) ppm. ^{13}C NMR (100.62 MHz): δ 30.46 (C); 55.30 (s, CH_3); 69.59 (d, 2CH, J_{C-P} = 6.1 Hz); 71.68 (d, 2CH, J_{C-P} = 13.8 Hz); 74.44 (d, CH, J_{C-P} = 5.4 Hz); 75.48 (d, CH, J_{C-P} = 7.6 Hz); 75.62 (d, CH, J_{C-P} = 6.1 Hz); 76.06 (d, CH, J_{C-P} = 13.8 Hz); 77.74 (C); 114.43 (d, CH, J_{C-P} = 11.5 Hz); 121.27 (d, C, J_{C-P} = 63.5 Hz); 124.57 (d, CH, J_{C-P} = 10.7 Hz); 126.15 (d, CH, J_{C-P} = 22.9 Hz); 127.35 (d, CH, J_{C-P} = 6.1 Hz); 128.38 (d, C, J_{C-P} = 55.1 Hz); 128.80 (d, CH, J_{C-P} = 0.9 Hz); 132.21 (d, CH, J_{C-P} = 2.3 Hz); 132.74 (d, C, J_{C-P} = 9.2 Hz); 133.47 (d, CH, J_{C-P} = 8.4 Hz); 133.90 (d, C, J_{C-P} = 6.9 Hz); 134.10 (d, CH, J_{C-P} = 11.5 Hz); 161.93 (d, C, J_{C-P} = 2.3 Hz) ppm. ^{31}P NMR (121.50 MHz): δ 17.85 (q, br, J_{PB} = 45 Hz) ppm. $[\alpha]^{20}_D$ = +112.9° (c = 0.42; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{27}H_{22}BrFeOP$ ($M^+ - BH_3$), 527.9943; obsd, 527.9968. Anal. Calcd for $C_{27}H_{25}BBrFeOP$: C, 59.72; H, 4.64. Found: C, 59.98; H, 4.75.

Synthesis of (*S*,*S*)-(+)-1-[(1-Naphthyl)(4-methoxyphenyl)phosphino]-1′-[(1-naphthyl)((4-trifluoromethyl)phenyl)phosphino]ferrocene (1d). Methyl phosphinite−borane **6** (1.5 mmol) was dissolved in 3 mL of Et_2O and 3 mL of THF and cooled to −70 °C. *sec*-BuLi (1.65 mmol) was added via syringe after 1 h, followed by cannula transfer of a solution of methyl phosphinite−borane (*R*)-**4c** (1.65 mmol) in 2 mL of THF. The reaction mixture was warmed to ambient temperature over a period of 15 h, quenched with water, and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Column chromatography (SiO_2, 1/2 CH_2Cl_2/hexane) afforded the enantiopure diphosphine−diborane complex, which was subjected to deprotection as described for compound **5b**. Final column chromatographic purification (alumina, 1/1 CH_2Cl_2/hexane) yielded the desired diphosphine (*S*,*S*)-**1d** as yellow foam. Yield: 70%. Mp: 99 °C. ^{1}H NMR (400.13 MHz): δ 3.71 (m, 1H); 3.75 (s, 3H); 3.77 (m, 1H); 4.19 (m, 1H); 4.25−4.32 (m, 4H); 4.40 (m, 1H); 6.79 (m, 2H); 7.08 (ddd, 1H; J = 1.0, 4.8, 6.8 Hz); 7.18 (ddd, 1H, J = 1.0, 5.3, 6.6 Hz); 7.28−7.45 (m, 8H); 7.46 (d, 4H, J = 4.0 Hz); 7.74 (d, 1H, J = 8.1 Hz); 7.77 (d, 1H, J = 7.8 Hz); 7.81 (d, 2H, J = 7.8 Hz); 8.30 (m, 1H); 8.35 (m, 1H) ppm. ^{13}C NMR (100.62 MHz): δ 55.08 (CH_3); 72.15 (CH); 72.67 (d, CH, J_{C-P} = 2.3 Hz); 72.75 (d, CH, J_{C-P} = 7.5 Hz); 72.79 (CH); 73.13 (dd, CH J = 1.4; 5.5 Hz); 73.29 (d, CH, J_{C-P} = 7.6 Hz); 74.89 (d, CH, J_{C-P} = 22.9 Hz); 75.28 (d, C, J_{C-P} = 5.5 Hz); 75.43 (d, CH, J_{C-P} = 26.8 Hz); 77.54 (d, C, J_{C-P} = 5.4 Hz); 113.89 (d, CH, J_{C-P} = 8.4 Hz); 124.76 (m, CF_3); 125.20 (d, CH, J_{C-P} = 0.9 Hz); 125.33 (d, CH, J_{C-P} = 1.5 Hz); 125.72 (br, CH); 125.86 (d, CH, J_{C-P} = 26.8 Hz); 125.90 (d, CH, J_{C-P} = 2.3 Hz); 125.96 (d, CH, J_{C-P} = 26.0 Hz); 125.98 (d, CH, J_{C-P} = 1.5 Hz); 126.23 (d, CH, J_{C-P} = 2.3 Hz); 127.44 (d, C, J_{C-P} = 5.4 Hz); 128.50 (d, CH, J_{C-P} = 1.5 Hz); 128.68 (d, CH, J_{C-P} = 1.4 Hz); 128.94 (CH); 129.69 (CH); 130.42 (d, C, J_{C-P} = 32.1 Hz); 130.88 (CH); 132.24 (d, CH, J_{C-P} = 2.3 Hz); 133.35 (d, C, J_{C-P} = 3.8 Hz); 133.42 (d, C, J_{C-P} = 4.6 Hz); 133.59 (d, CH, J_{C-P} = 19.9 Hz); 134.51 (d, C, J_{C-P} = 21.4 Hz); 134.93 (d, C, J_{C-P} = 21.4 Hz); 135.50 (d, C, J_{C-P} = 13.8 Hz); 135.53 (d, CH, J_{C-P} = 21.4 Hz); 137.13 (d, C, J_{C-P} = 13.8 Hz); 143.29 (dd, C, J = 1.4; 12.9 Hz); 160.39 (C) ppm. ^{31}P NMR (121.50 MHz): δ −25.34 (s), −26.94 (s) ppm. $[\alpha]^{20}_D$ = +117.9° (c = 0.28; CH_2Cl_2). HRMS (FAB$^+$): m/z calcd for $C_{44}H_{34}F_3FeOP_2$ (MH^+), 753.1386; obsd, 753.1397. Anal. Calcd for $C_{44}H_{33}F_3FeOP_2$: C, 70.23; H, 4.42. Found: C, 70.07; H, 4.78.

High-Pressure NMR Experiments (Typical Procedure). $Rh(CO)_2$acac (0.012 mmol) and the respective ligand **1a**−**d** or dppf (0.026 mmol) were dissolved in 1.5 mL of toluene-d_8, and the solution was degassed and transferred into a 0.5 mL sapphire NMR tube. The tube was pressurized with 18 bar of syngas (1/1 CO/H_2) and heated to 40 °C in the spectrometer. The formation of diphosphine rhodium dicarbonyl hydrides was usually completed within 1.5 h. Low-temperature measurements were conducted employing 1/1 THF-d_4/acetone-d_6 as the solvent.

High-Pressure IR Experiments (Typical Procedure). $Rh(CO)_2$acac (0.012 mmol) and the respective diphosphine (0.026 mmol) were dissolved in 15 mL of cyclohexane, and the solution was degassed and introduced into the high-pressure IR autoclave. The mechanically stirred solution was pressurized to 18 bar and heated to 60 °C in order to hasten formation of diphosphine rhodium dicarbonyl hydrides at the solubility-limited low concentrations. The reaction was usually completed within 2−6 h.

(Asymmetric) Hydroformylation Reactions (Typical Procedure). $Rh(CO)_2$acac (0.015 mmol) and diphosphine ligand (0.033 mmol) were dissolved in 3.5 mL of toluene, and the solution was degassed by three freeze−pump−thaw cycles. The solution was transferred into a 100 mL stainless steel autoclave, equipped with glass insert, substrate inlet vessel, electronic heating mantle, and liquid sampling valve. The argon atmosphere was replaced by 18 bar of syngas (1/1 CO/H_2), and the magnetically stirred solution was heated to the given temperature. After 2 h of catalyst preparation, the degassed substrate solution (7.5 mmol of (substituted) styrene in 3 mL of toluene and 0.5 mL of decane as internal standard) was purged three times with 1/1 CO/H_2 and added under pressure. The progress of the reaction was monitored by subjecting samples to GC analysis. After the desired degree of conversion had been reached, catalysis was stopped by cooling the autoclave on ice and depressurizing. The crude product mixture was purified by fractional distillation. Subsequently, linear and branched aldehyde products (1.5 mmol) were subjected to reduction with $NaBH_4$ (1.5 mmol) by stirring in 10 mL of EtOH for 30 min. Quenching with water, extraction with a 1/1 solution of ethyl acetate/hexane, drying of organic layers, filtration, and removal of solvent gave the corresponding alcohols, for which the enantioselectivity of the branched derivative was determined by chiral GC (Cyclosil-B; isothermal; T = 140 °C for 2-phenylpropanol, $t_R(R)$ = 18.1 min, $t_R(S)$ = 18.8 min; T = 150 °C for 2-(4-methoxyphenyl)-propanol, $t_R(R)$ = 42.5 min, $t_R(S)$ = 43.4 min; T = 150 °C for 2-(4-chlorophenyl)propanol, $t_R(R)$ = 45.1 min, $t_R(S)$ = 46.3 min).

For 1-octene hydroformylation, catalyst precursor solutions were prepared from 0.01 mmol of $Rh(CO)_2$acac and 0.04 mmol of diphosphine in 5 mL of toluene. After 2 h of catalyst preparation at 80 °C and 18 bar of 1/1 CO/H_2, reaction was started by substrate addition (6.37 mmol of 1-octene in 3.5 mL of toluene and 0.5 mL of decane as internal standard). Samples were drawn from the reaction mixture, immediately cooled on ice, and analyzed by GC.

Acknowledgment. We appreciate financial support by the IOP Katalyse program of The Netherlands Ministry of Economic Affairs (Project IKA 94081) and are thankful for a special grant to U.N.

OM0004489