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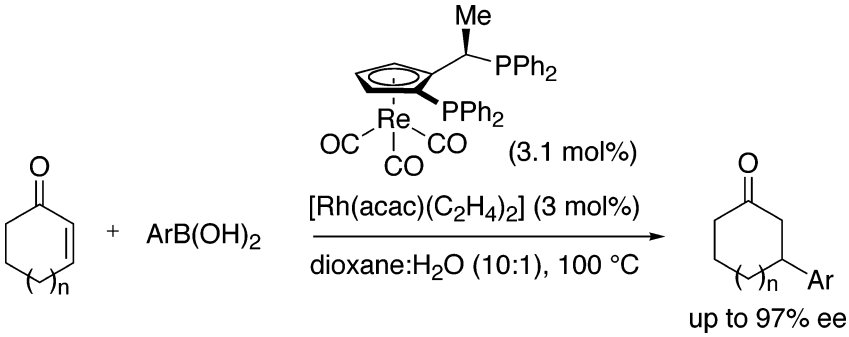
Planar-Chiral Cyrhetrenes for the Rhodium-Catalyzed Asymmetric 1,4-Addition and the Hydrogenation of Enamides

René T. Stemmler and Carsten Bolm*

Institut für Organische Chemie der RWTH Aachen, Landoltweg 1, D-52056 Aachen, Germany

Carsten.Bolm@oc.rwth-aachen.de

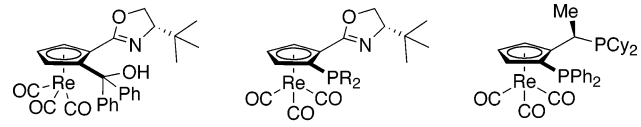
Received August 9, 2005



The syntheses of novel cyrhetrene**s 7a**−**c** and **8a**,**b** are described. These planar-chiral, mono- and diphosphines have been applied as ligands in the Rh-catalyzed 1,4-addition reaction to activated olefins and in the Rh-catalyzed hydrogenation of enamide **12**, giving the corresponding products with up to 97 and 93% ee, respectively.

Introduction

Asymmetric transition-metal-catalyzed reactions are of great importance, and continue to find widespread application. Some of these reactions are so well-developed that they are currently used for the industrial production of enantioenriched compounds.[1,2] Examples are the Monsanto L-dopa process, the metolachlor synthesis (Ciba-Geigy/Novartis), and the asymmetric sulfide oxidation in the industrial approach toward esomeprazole (Nexium, Astra Zeneca).[3] Chiral transition-metal-containing, nonmetallocene complexes are well-studied, and are used as ligands in asymmetric catalysis, including allylic alkylations,[4] alkylations and arylations of aldehydes,[5,6] and hydrogenations of dehydroamino acids,[7] to name just a few.[8] In 2001, we introduced cyrhetrene **1** as the first ligand bearing a cyrhetrene backbone to be applied in asymmetric catalysis.[6] With **1**, enantioselective phenyl−aldehyde transfer reactions were catalyzed very effectively, leading to products with up to 99% ee.



1 **2** **3** (AaPhos)

Recently, we demonstrated the applicability of cyrhetrene-based *P*,*N*- and *P*,*P*-ligands **2** and **3** in asymmetric

* To whom correspondence should be addressed. Phone +49 241 809 4675. Fax: +49 241 809 2391.

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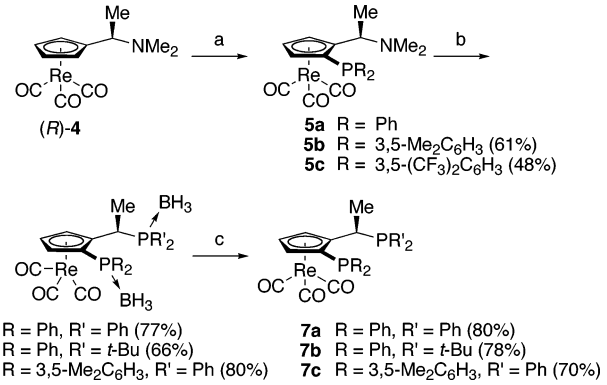
10.1021/jo051676l CCC: $30.25
Published on Web 10/13/2005

SCHEME 1[a]



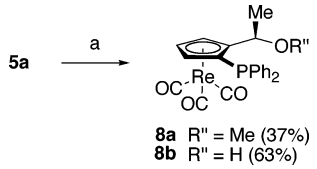
[a] Reagents and conditions: (a) *n*-BuLi, Et_2O, −20 °C, then $ClPR_2$; (b) (i) 1-chloroethyl chloroformate, THF, (ii) PR_2H, $TlPF_6$, (iii) BH_3·THF, (c) HBF_4·OMe_2, CH_2Cl_2.

catalysis.[9] In general, good to high enantiomeric excesses were achieved in various catalytic reactions. The electron-withdrawing rhenium(I) tricarbonyl fragment of these compounds reduces the electron density on the cyclopentadienyl-ring and attached donor atoms, thus influencing the outcome of the catalyzed reaction. In some instances, higher enantioselectivities compared to their ferrocene analogues have been observed. For example, **1** was generally more effective in the phenyl transfer to aldehydes,[6] and **2** (R = Ph) afforded (−)-(*R*)-(*E*)-*N*-benzyl-1,3-diphenylprop-2-en-1-amine in an allylic amination reaction with significantly higher enantiomeric excess than its ferrocene analogue (97% vs 77% ee).[9a] Furthermore, AaPhos (**3**) has shown great potential in the asymmetric hydrogenation of dimethyl itaconate and *N*-acetamidocinnamic acid derivatives,[9b] implying a broader applicability of this ligand and its derivatives. We herein report the synthesis of novel AaPhos derivatives **7a**−**c** and **8a**,**b** and their application in the Rh-catalyzed 1,4-addition and in the hydrogenation of enamides, respectively.

Results and Discussion

For the synthesis of the diphosphine derivatives of AaPhos **7a**−**c**, the route developed earlier in our group was employed with only minor modifications (Scheme 1).[9b] Starting from (*R*)-**4**,[10] which is accessible from acetylcyrhetrene in two steps, we introduced the first phosphine by diastereoselective ortho-lithiation at −20 °C and reaction with the corresponding chlorodiarylphosphine to give diarylphosphinocyrhetrenes **5a** (dr = 9:1),[9b] **5b** (dr = 5:1), and **5c** (dr = 9:1). Activation and displacement of the dimethylamine moiety with retention of configuration using the strategy developed by Salzer[11] and subsequent protection of both phosphines with borane afforded the bisborane adducts **6a**−**c**. Amine **5c** did not react with ethyl chloroformate or 1-chloroethyl chloroformate under these conditions, even after prolonged reaction time. This can be explained by the strong electron-withdrawing nature of the bis(3,5-bis(trifluoromethyl)phenyl)phosphino moiety connected to the cyrhetrene, which prevents the formation of a cationic intermediate in the S_N1-type substitution process. The protection of the phosphines was necessary to facilitate easy purification by flash chromatography without oxidation of the product. The free phosphines were then obtained by treatment of the bisborane adducts with HBF_4·OMe_2 in CH_2Cl_2. The least-oxidation-sensitive bisphosphine is AaPhos derivative **7a**. It is only sensitive to oxidation in solution, and can be handled in air in solid state.

SCHEME 2[a]



[a] Reagents and conditions: (a) (i) $ClCO_2Et$, THF, (ii) R″OH.

The corresponding *P*,*O*-derivatives **8a** and **8b** were obtained in a similar manner (Scheme 2). After treatment of **5a** with ethyl chloroformate, the intermediate reacted with MeOH or water to afford methyl ether **8a** (dr = 4:1) or the secondary alcohol **8b** (dr = 4:1), respectively.

The asymmetric conjugate addition to activated olefins is an important and widely used process for the generation of a stereogenic center at the β-carbon. Copper-,[12] rhodium-,[13] nickel-,[14] cobalt-,[15] alkalimetal-,[16] and other metal-catalyzed variants[17] of this reaction have been reported. In the case of the rhodium-catalyzed 1,4-addition to activated olefins, developed by Miyaura and Hayashi,[13a,b] aryl and alkenyl groups are introduced with excellent regio- and enantioselectivity. BINAP[13b,13e] and BINOL derivatives[18] are commonly used as chiral ligands in this reaction, giving the corresponding products with high enantiomeric excesses. There are only a few ex-

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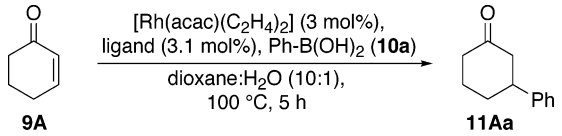
TABLE 1. Evaluation of the Cyrhetrene Derivatives in the Rh-Catalyzed 1,4-Addition of Phenylboronic Acid (10a) to Cyclohexenone (9A)[a]



9A 11Aa

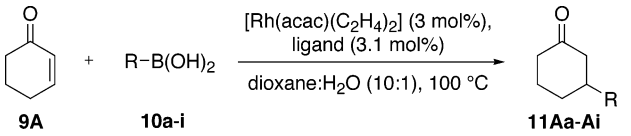
entry	ligand	yield (%)	ee (%)[b]
1	AaPhos (**3**)	81	88 (*R*)
2	**7a**	93	95 (*R*)
3	**7b**	<2	nd[c]
4	**7c**	99	91 (*R*)
5	**5a**	17	20 (*S*)
6	**8a**	25	52 (*S*)
7	**8b**	32	62 (*S*)

[a] Reaction conditions: [Rh(acac)(C_2H_2)$_2$] (12 μmol), ligand (12.4 μmol), **9A** (0.4 mmol), **10a** (2.0 mmol), dioxane/H_2O (10:1, 1.1 mL), 100 °C. [b] The enantiomer ratios were determined by HPLC using a chiral column (OD-H column); see Experimental Section for details. [c] Not determined.

amples of planar-chiral ligands that have been used in Rh-catalyzed 1,4-additons of arylboronic acids or organotrifluoroborates to activated olefins. These include (*S*)-(*R*)-bppfa,[19,20] Josiphos,[21] and (*R*)-(*S*)-ppf-P(*t*-Bu)$_2$.[20,22] The evaluation of AaPhos (**3**) and its derivatives in the Rh-catalyzed 1,4-addition of phenylboronic acid (**10a**) to cyclohexenone (**9A**) illustrates a general difference between diphosphines **7a**−**c** and *P*,*O*-derivatives **8a**,**b** (Table 1). Application of the diphosphines in this reaction generated (*R*)-3-phenylcyclohexanone (**11Aa**) as the major product enantiomer, with 88−95% ee (entries 1, 2, and 4), with cyrhetrene **7a** being the most effective ligand in this reaction. In contrast, *P*,*O*-derivatives **8a** and **8b**, as well as the *P*,*N*-chelate **5a**, resulted in the formation of the *S* isomer as the major product, with 20−62% ee (entries 5−7). This inversion of configuration suggests differences in the binding mode between the *P*,*O*- and *P*,*N*-ligands on one hand and the diphosphines on the other hand. Furthermore, the catalyst efficiency was significantly higher when bisphosphine ligands were used, resulting in higher chemical yields. This was also accompanied by higher enantioselectivities. Interestingly, the rhodium complex with cyrhetrene **7b** as ligand did not catalyze the reaction under these conditions at all (entry 3), which might be due to the increased steric hindrance of the *tert*-butyl substituents on the phosphine, preventing a chelate-type coordination of **7b** to the metal. With cyrhetrene **7c**, the reaction was significantly accelerated, giving the reaction product in almost quantitative yield, but (compared to reactions with **7a** as ligand) with a lower enantioselectivity of 91% ee (entry 4).

To evaluate the scope of the catalyst system, we have applied various arylboronic acids with electron-withdrawing as well as electron-donating groups to this reaction using cyrhetrene **7a** as the ligand (Table 2). Generally, high enantioselectivities of the corresponding products were obtained (90−97% ee; entries 1−4 and 6), with the exceptions of 3-(4-methoxyphenyl)cyclohexanone (**11Ag**) and 3-(1-naphthyl)cyclohexanone (**11Ah**), which were isolated with 82 and 85% ee, respectively (entries 7 and 8). Again, cyrhetrene **7c** formed a more-active but less-selective catalyst with Rh(I) than **7a** formed in the reaction of 2-tolylboronic acid (**10e**) with cyclohexenone (**9A**), giving the corresponding product **11Aa** within 5 h in 99% yield with 83% ee (vs 99% yield, 90% ee, entries 4 and 5). To summarize, we could obtain high yields of the reaction products using arylboronic acids with electron-withdrawing substituents (entries 9 and 10), and products stemming from arylboronic acids with electron-donating substituents were isolated in significantly lower yields (e.g., entries 1, 6, and 7). This can be explained by the Rh-catalyzed hydrolytic B−C bond cleavage of arylboronic acids. The side reaction competes under these reaction conditions, and is faster in the case of electron-donating substituents on the arylboronic acid, thereby diminishing the chemical yield. (*E*)-Phenylvinylboronic acid (**10i**) was also tested, but the enantomeric excess of the product **11Ai** was low (entry 9, 35% ee).

TABLE 2. Various Arylboronic Acids (10a−i) in the Rh-Catalyzed 1,4-Addition to Cyclohexenone (9A)[a]



9A 10a-i 11Aa-Ai

a: R = C_6H_5 **d**: R = 4-ClC_6H_4 **g**: R = 4-$MeOC_6H_4$
b: R = 4-MeC_6H_4 **e**: R = 2-MeC_6H_4 **h**: R = 1-Naphthyl
c: R = 4-$CF_3C_6H_4$ **f**: R = 3-$MeOC_6H_4$ **i**: R = 2-Phenylvinyl

entry	boronic acid	ligand	time (h)	product	yield (%)	ee (%)[b]
1	**10b**	**7a**	24	**11Ab**	67	92
2	**10c**	**7a**	15	**11Ac**	99	92
3	**10d**	**7a**	15	**11Ad**	99	97
4	**10e**	**7a**	16	**11Ae**	99	90
5	**10e**	**7c**	5	**11Ae**	99	83
6	**10f**	**7a**	17	**11Af**	71	93
7	**10g**	**7a**	17	**11Ag**	47	82
8	**10h**	**7a**	15	**11Ah**	51	85
9	**10i**	**7a**	17	**11Ai**	64	35

[a] Reaction conditions: [Rh(acac)(C_2H_2)$_2$] (12 μmol), ligand (12.4 μmol), **9** (0.4 mmol), **10** (2.0 mmol), dioxane/H_2O (10:1, 1.1 mL), 100 °C. [b] The enantiomer ratios were determined by chiral HPLC, see Experimental Section for details.

The reactions of other cyclic and acyclic enones with phenylboronic acid (**10a**) were also explored (Table 3). When 2-cyclopentenone (**9B**) reacted with PhB(OH)$_2$ (**10a**) using either AaPhos (**3**) or cyrhetrene **7a** as the chiral ligand, **11Ba** was isolated in both moderate yield and ee only (entries 1 and 2). 2-Cycloheptenone (**9C**) as a substrate was more reactive when using **7a** as the chiral ligand, but the corresponding product **11Ca** was isolated with a lower ee. In this case, the use of cyrhetrene **7c** not only furnished **11Ca** in quantitative yield but also produced a significantly higher ee of 76% (entries 3 and 4). The acyclic enone **9D** reacted well under the standard conditions, giving the reaction product **11Da** in high yield, but the enantioselectivity remained below 70% ee using either cyrhetrene AaPhos (**3**) or **7a** (entries

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(20) (*S*)-(*R*)-bppfa = (*S*)-*N*,*N*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine; Josiphos = (*R*)-(−)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl dicyclohexylphosphine; (*R*)-(*S*)-ppf-P(*t*-Bu)$_2$ = (*R*)-(−)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl di-*tert*-butylphosphine.
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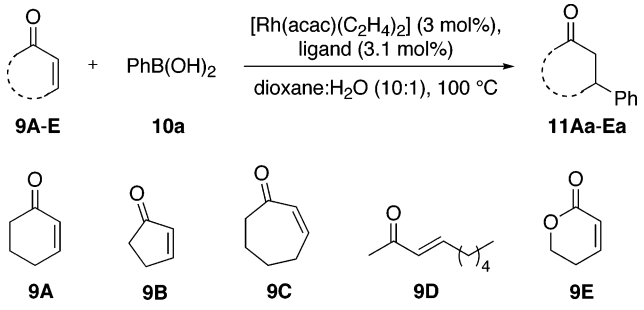
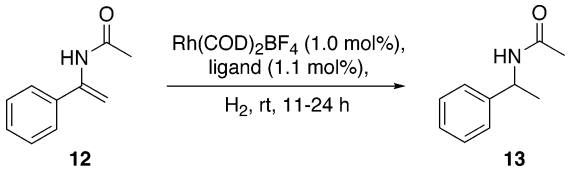
TABLE 3. Rh-Catalyzed Asymmetric 1,4-Addition of $PhB(OH)_2$ (10a) to α,β-Unsaturated Carbonyl Compounds 9B−E[a]



entry	substrate	ligand	time (h)	product	yield (%)	ee (%)[b]
1	**9B**	**3**	18	**11Ba**	52	73
2	**9B**	**7a**	6	**11Ba**	47	73
3	**9C**	**7a**	23	**11Ca**	92	35
4	**9C**	**7c**	21	**11Ca**	99	76
5	**9D**	**3**	18	**11Da**	76	62
6	**9D**	**7a**	6	**11Da**	97	69
7	**9E**	**7a**	23	**11Ea**	95	88
8	**9E**	**7c**	21	**11Ea**	98	88

[a] See footnote a of Table 2. [b] See footnote b of Table 2.

TABLE 4. Asymmetric Hydrogenation of Enamide 12[a]



entry	ligand	solvent	time (h)	conversion (%)	ee (%)[b]
1	**3**	CH_2Cl_2	19	100	87 (*R*)
2	**7a**	CH_2Cl_2	23	100	88
3[c]	**7a**	CH_2Cl_2	16	90	86
4	**7a**	toluene	22	40	82
5	**7a**	MeOH	24	100	89
6	**7a**	EtOAc	16	100	93
7	**7c**	EtOAc	11	100	77

[a] Reaction conditions: $[Rh(COD)_2]BF_4$ (5.0 μmol), ligand (5.5 μmol), enamide **12** (0.5 mmol), rt, 10 bar H_2. [b] The enantiomer ratios were determined by chiral GC (FS Cyclodex β); see Experimental Section for details. [c] Use of 5 bar H_2.

5 and 6). Finally, the unsaturated, cyclic ester **9E** was tested, using both cyrhetrenes **7a** and **7c** as ligands. In both cases the product was isolated in high yield with a promising 88% ee (entries 7 and 8).

The enantioselective hydrogenation of prochiral olefins plays an important role in the application of homogeneous catalysts, as it is one of the most practical methods in asymmetric synthesis.[1,2] Therefore, much effort has been devoted to the development of efficient synthetic methods for the preparation of enantioenriched hydrogenated compounds. As revealed by the data shown in Table 4, AaPhos ligands are also effective in the catalytic asymmetric hydrogenation of enamide **12**.

In the test reaction, *N*-(1-phenylvinyl)acetamide (**12**) was hydrogenated in CH_2Cl_2 at 10 bar H_2 using 1 mol % catalyst formed in situ from $Rh(COD)_2BF_4$ and AaPhos (**3**), which afforded (*R*)-acetylamine **13** with 87% ee (Table 4, entry 1). Neither the exchange of the chiral ligand to cyrhetrene **7a** nor the reduction of hydrogen pressure to 5 bar improved the enantioselectivity significantly (88 and 86% ee, respectively, entries 2 and 3). Since it is known that the solvent has some effect on the enantioselectivity of this reaction,[23] other solvents such as toluene, MeOH, and ethyl acetate were tested. When toluene was used, the conversion was incomplete, presumably because of the low solubility of both the substrate and the catalyst in toluene (entry 4). Also, the enantiomeric excess of **13** was lower. In MeOH (entry 5), the enantioselectivity was almost as high as in CH_2Cl_2, but ethyl acetate proved to be the most effective as a solvent, giving the product with 93% ee (entry 6). Application of cyrhetrene **7c** under these conditions furnished **13** with 77% ee only (entry 7).

Conclusion

We have introduced novel cyrhetrene derivatives and successfully applied them in both Rh-catalyzed asymmetric conjugate addition reactions and the enantioselective hydrogenation of enamide **12**. To the best of our knowledge, this is the first example of the use of a planar-chiral nonmetallocene ligand in the Rh-catalyzed 1,4-addition of arylboronic acids to enones and enoates leading to a high (>90%) ee.[24] Interestingly, cyrhetrene **7a**, which is easiest to purify and to handle, is also most effective in both catalyses, yielding the products with up to 97 and 93% ee, respectively. Further applications of the AaPhos derivatives in various asymmetric catalyses are currently the subject of ongoing studies in our laboratories.

Experimental Section

General Procedure (GP 1) for the Synthesis of Intermediates 5b and 5c. We have used a slight modification of a previously published procedure.[9b] *n*-BuLi (1.07 mL of a 1.6 M solution in hexanes, 1.71 mmol, 1.1 equiv) was added dropwise to a solution of (*R*)-1-dimethylaminoethylcyrhetrene [(*R*)-**4**] (634 mg, 1.56 mmol) in Et_2O (16 mL) at −20 °C. The yellow reaction mixture was stirred for 25 min, and the temperature was kept between −17 and −20 °C. A solution of bis(3,5-dimethylphenyl)chlorophosphine[25] (648 mg, 2.34 mmol, 1.5 equiv) in Et_2O (9 mL) was then added at −25 °C, and the reaction mixture was allowed to warm to room temperature over a period of 2 h. Saturated aqueous $NaHCO_3$ (15 mL) was added, and the aqueous layer was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. After removal of the solvent, the residue was subjected to column chromatography (neutral alumina, pentane/ether/Et_3N 100:3:1 → 100:7:1 → 100:17:1) affording the major diastereomer of **5b** as a colorless solid (617 mg, 61%).

(*R*,*S*$_p$)-2-(1′-*N*,*N*-Dimethylaminoethyl)-[bis(3″,5″-dimethylphenyl)phosphino]cyrhetrene [(*R*,*S*$_p$)-5b]: mp 128−130 °C; $[\alpha]^{22}_D$ −118 (*c* 0.65, $CHCl_3$); ^1H NMR (300 MHz, C_6D_6) δ 0.82 (d, *J* = 6.8 Hz, 3H), 1.72 (s, 6H), 2.07 (s, 6H), 2.12 (s, 6H), 4.20 (dq, *J* = 6.8, 3.1 Hz, 1H), 4.39 (t, *J* = 2.7 Hz, 1H), 4.85 (m_c, 1H), 5.04 (m_c, 1H), 6.72 (s, 1H), 6.76 (s, 1H), 7.04 (s, 1H), 7.07 (s, 1H), 7.35 (s, 1H), 7.38 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 8.3, 21.26, 21.31, 38.8 (4C), 55.7 (d, *J* = 7.0 Hz), 78.9,

(23) Zhu, G.; Zhang, X. *J. Org. Chem.* **1998**, *63*, 9590−9593.

(24) Actually, there is only one report of a planar-chiral ferrocene ligand, (*S*)-(*R*)-bppfa, which has been used in this reaction, giving the product in poor yield and with low enantioselectivity (5% yield, 3% ee; ref 19). Also noteworthy is that (*R*,*S*)-Josiphos has been successfully applied in the Rh-catalyzed 1,4-addition of phenyltrifluoroborate to cyclohexenone (**9A**), furnishing **11Aa** with 99% ee (ref 21).

(25) RajanBabu, T. V.; Ayers, T. A.; Halliday, G. A.; You, K. K.; Calabrese, J. C. *J. Org. Chem.* **1997**, *62*, 6012−6028.

85.8, 94.4 (d, J = 6.2 Hz), 98.9 (d, J = 24.7 Hz), 119.5 (d, J = 21.7 Hz), 130.0, 130.6 (d, J = 19.5 Hz, 2C), 131.3, 132.8 (d, J = 20.7 Hz, 2C), 137.15 (d, J = 7.2 Hz, 2C), 137.3 (d, J = 9.4 Hz), 138.2 (d, J = 7.6 Hz, 2C), 139.0 (d, J = 8.5 Hz), 194.5 (3C); ^{31}P NMR (121 MHz, C_6D_6) δ −24.8 (s); IR (KBr, cm^{-1}) ν 2972, 2939, 2778, 2361, 2341, 2017, 1919, 1583, 1457, 1263, 1036, 931, 848, 692, 601, 510; MS (EI) *m/z* (%) 647 (M^+, 100), 645 ((M − 2)$^+$, 57), 632 ((M − CH_3)$^+$, 28), 576 ((M − CH(Me)-(NCH_3)$_2$)$^+$, 85), 574 ((M − CH(Me)(NCH_3)$_2$ − 2)$^+$, 76), 518 (25). Anal. Calcd for $C_{28}H_{31}NO_3PRe$: C, 52.00; H, 4.83; N, 2.17. Found: C, 52.02; H, 4.50; N, 2.21.

(*R*,*S*$_p$)-2-(1′-*N*,*N*-Dimethylaminoethyl)-{bis[3″,5″-bis-(trifluoromethyl)phenyl]phosphino}cyrhetrene [(*R*,*S*$_p$)-5c]. Following GP 1 (1.48 mmol scale) using bis[3,5-bis-(trifluoromethyl)phenyl]chlorophosphine[26] (1.09 g, 2.21 mmol, 1.5 equiv) afforded the title compound as an off-white solid (614 mg, 48%) after purification of the crude reaction product by column chromatography (neutral alumina, pentane/Et_2O/Et_3N 90:10:1 → 80:20:1): mp 52−54 °C; $[\alpha]^{23}_D$ −100 (*c* 1.15, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (d, J = 6.7 Hz, 3H), 1.91 (s, 6H), 4.12 (qd, J = 6.7, 3.0 Hz, 1H), 5.09 (s, 1H), 5.27 (t, J = 2.5 Hz, 1H), 5.60 (s, 1H), 7.74 (s, 1H), 7.76 (s, 1H), 7.85−7.91 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.9, 38.5 (2C), 55.6 (d, J = 6.9 Hz), 80.9, 85.9 (d, J = 3.2 Hz), 91.5 (d, J = 19.0 Hz), 92.7 (d, J = 7.2 Hz), 120.7 (d, J = 23.9 Hz), 122.5, 122.9 (q, J = 273.2 Hz, 2C), 123.2 (q, J = 273.1 Hz, 2C), 124.0, 131.5 (qd, J = 33.4, 5.8 Hz, 2C), superimposed by 131.7 (d, J = 18.3 Hz, 2C), 132.3 (qd, J = 33.5, 7.4 Hz, 2C), 134.3 (d, J = 20.9 Hz, 2C), 139.7 (d, J = 14.9 Hz), 141.4 (d, J = 15.3 Hz), 192.3 (3C); ^{31}P NMR (121 MHz, $CDCl_3$) δ −23.8 (s); ^{19}F NMR (282 MHz, $CDCl_3$) δ −63.1 (s), −63.0 (s); IR ($CHCl_3$, cm^{-1}) ν 2975, 2940, 2869, 2830, 2787, 2029, 1936, 1356, 1280, 1185, 1135, 900, 762, 706, 683, 607, 510; MS (EI) *m/z* (%) 863 (M^+, 36), 861 ((M − 2)$^+$, 18), 848 ((M − CH_3)$^+$, 92), 846 ((M − CH_3 − 2)$^+$, 47), 792 ((M − CH_3 − 2CO)$^+$, 26), 790 ((M − CH_3 − 2CO − 2)$^+$, 16), 377 (49), 375 (36), 72 (100). Anal. Calcd for $C_{28}H_{19}NO_3PRe$: C, 38.99; H, 2.22; N, 1.62. Found: C, 39.16; H, 2.45; N, 1.62.

General Procedure (GP 2) for the Synthesis of the Bisborane Adducts 6a−c. 1-Chloroethyl chloroformate (137 mg, 128 μL, 0.960 mmol, 2.1 equiv) was added dropwise to a solution of (*R*,*S*$_p$)-2-(1-dimethylaminoethyl)diphenylphosphinocyrhetrene [(*R*,*S*$_p$)-**5a**] (270 mg, 0.457 mmol) in THF (13 mL) at −40 °C. The reaction mixture was allowed to reach rt, and was stirred for 2 h. The dark red solution was then treated with diphenylphosphine (213 mg, 0.200 mL, 1.14 mmol, 2.5 equiv) and $TlPF_6$ (400 mg, 1.14 mmol, 2.5 equiv), and was stirred for 3 h. Subsequently, BH_3·SMe_2 (5.7 mL of a 2 M solution in THF, 11.4 mmol, 25 equiv) was added via syringe, and stirring was continued overnight. The solvent was evaporated in vacuo, and the residue was suspended in Et_2O (20 mL). After filtration and removal of the solvent, the crude product was subjected to column chromatography (silica gel, pentane/ethyl acetate 4:1 → 3:1), affording the bisborane adduct **6a** as a colorless foam (268 mg, 77% yield).

(*R*,*S*$_p$)-2-(1′-Diphenylphosphinoethyl)diphenylphosphinocyrhetrene, Bisborane Adduct [(*R*,*S*$_p$)-6a]: mp 88−91 °C; $[\alpha]^{24}_D$ −3.7 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.40−1.90 (br s, 6H), 1.41 (dd, J = 14.9, 7.2 Hz, 3H), 4.91 (m_c, 1H), 5.21 (t, J = 2.9 Hz, 1H), 5.30 (m_c, 1H), 6.13 (m_c, 1H), 6.85 (m_c, 2H), 7.00 (m_c, 1H), 7.25−7.46 (m, 15H), 7.90 (m_c, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 26.6 (d, J = 4.3 Hz), 79.9 (d, J = 5.1 Hz), 87.7 (dd, J = 51.4, 2.8 Hz), 91.2 (dd, J = 7.1, 3.5 Hz), 94.0 (d, J = 1.5 Hz), 119.8 (dd, J = 15.6, 7.7 Hz), 127.1−129.0 (10C), 130.4−133.3 (14C), 191.4 (3C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.6 (br s), 29.8 (br s); IR ($CHCl_3$, cm^{-1}) ν 2962, 2397, 2028, 1936, 1484, 1437, 1105, 1066, 756, 697, 608, 506; MS (EI) *m/z* (%) 760 (M^+, 1), 745 ((M − CH_3)$^+$, 100), 743 ((M − CH_3 − 2)$^+$, 67), 704 ((M − 2CO)$^+$, 51), 702 ((M − 2CO − 2)$^+$, 27), 520 (43), 518 (43). Anal. Calcd for $C_{34}H_{33}B_2O_3P_2Re$: C, 53.77; H, 4.38. Found: C, 53.76; H, 4.68.

(*R*,*S*$_p$)-2-(1′-Di-*tert*-butylphosphinoethyl)diphenylphosphinocyrhetrene, Bisborane Adduct [(*R*,*S*$_p$)-6b]. Following GP 2 (0.34 mmol scale) using di-*tert*-butylphosphine (2.5 equiv) afforded the title compound as a colorless solid (161 mg, 66%) after purification by column chromatography (silica gel, pentane/ethyl acetate 9:1 → 4:1): mp 249−252 °C ; $[\alpha]^{24}_D$ −20.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.15−0.70 (br s, 3H), 0.93 (d, J = 12.8 Hz, 9H), 1.10−1.80 (br s, 3H), 1.41 (d, J = 12.7 Hz, 9H), 1.88 (dd, J = 9.0, 8.1 Hz, 3H), 3.73 (m_c, 1H), 5.01 (s, 1H) 5.16 (t, J = 2.9 Hz, 1H), 6.00 (s, 1H), 7.40−7.59 (m, 8H), 7.86 (m_c, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0 (d, J = 21.3 Hz), 27.7 (3C), 29.7 (3C), 30.8 (d, J = 3.7 Hz), 34.3 (d, J = 6.4 Hz), 34.6, 78.8 (d, J = 5.1 Hz), 89.2 (dd, J = 54.5, 5.8 Hz), 92.7, 94.7 (dd, J = 6.0, 3.1 Hz), 122.9 (dd, J = 13.3, 6.5 Hz), 126.6 (d, J = 57.0 Hz), 128.6 (d, J = 10.5 Hz, 2C), 128.8 (d, J = 10.4 Hz, 2C), 129.6 (d, J = 62.4 Hz), 131.5, 131.9, 132.9 (d, J = 9.7 Hz, 2C), 133.6 (d, J = 9.9 Hz, 2C), 192.1 (3C); ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.1 (br s), 58.2 (br s); IR (KBr, cm^{-1}) ν 2961, 2921, 2391, 2029, 1931, 1475, 1437, 1100, 1071, 810, 742, 696, 604, 504; MS (EI) *m/z* (%) 720 (M^+, 3), 718 ((M − 2)$^+$, 5), 705 ((M − CH_3)$^+$, 100), 703 ((M − CH_3 − 2)$^+$, 60), 664 ((M − 2CO)$^+$, 39), 662 ((M − 2CO − 2)$^+$, 22), 649 ((M − 2CO − CH_3)$^+$, 27), 647 ((M − 2CO − CH_3 − 2)$^+$, 25). Anal. Calcd for $C_{30}H_{41}B_2O_3P_2Re$: C, 50.08; H, 5.74. Found: C, 49.69; H, 6.07.

(*R*,*S*$_p$)-2-(1′-Diphenylphosphinoethyl)-[bis(3″,5″-dimethylphenyl)phosphino]cyrhetrene, Bisborane Adduct [(*R*,*S*$_p$)-6c]. Following GP 2 using **5b** (0.235 mmol scale) afforded the title compound as a colorless foam (153 mg, 80% yield) after purification of the crude product by column chromatography (silica gel, pentane/ethyl acetate 9:1 → 4:1): mp 58−61 °C; $[\alpha]^{23}_D$ −12.0 (*c* 0.88, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 1.10−2.80 (br s, 6H), 1.61 (dd, J = 14.4, 7.2 Hz, 3H), 1.95 (s, 6H), 1.99 (s, 6H), 4.36 (d, J = 2.9 Hz, 1H), 5.00 (m_c, 1H), 5.39 (m_c, 1H), 6.08 (m_c, 1H), 6.51 (m_c, 3H), 6.64 (s, 1H), 6.68 (s, 1H), 6.96 (m_c, 3H), 7.20 (s, 1H), 7.23 (s, 1H), 7.40 (s, 1H), 7.43 (s, 1H), 7.71 (m_c, 2H), 8.11 (m_c, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 14.0, 21.1 (2C), 21.3 (2C), 26.9 (dd, J = 17.1, 13.6 Hz), 79.7 (d, J = 4.8 Hz), 89.6 (d, J = 49.5 Hz), 91.6, 94.5, 120.7 (dd, J = 15.2, 8.1 Hz), 127.8−134.6 (20C), 138.4 (d, J = 11.1 Hz, 2C), 138.6 (d, J = 11.1 Hz, 2C), 192.5 (3C); ^{31}P NMR (121 MHz, C_6D_6) δ 9.2 (br s), 30.6 (br s); IR (KBr, cm^{-1}) ν 3407, 2926, 2854, 2361, 2343, 2026, 1931, 1597, 1488, 1441, 1378, 1265, 1106, 1061, 848, 750, 690, 606, 507; MS (EI) *m/z* (%) 816 (M^+, 1), 801 ((M − CH_3)$^+$, 100), 799 ((M − CH_3 − 2)$^+$, 53), 760 ((M − 2CO)$^+$, 45), 758 ((M − 2CO − 2)$^+$, 29), 576 (46), 574 (35). Anal. Calcd for $C_{38}H_{41}B_2O_3P_2Re$: C, 55.97; H, 5.07. Found: C, 56.00; H, 5.25.

General Procedure (GP 3) for the Deprotection of Bisborane Adducts Giving the Free Diphosphines 7a−c. Using a slightly modified literature procedure,[9b] we treated a solution of bisborane adduct (*R*,*S*$_p$)-**6a** (230 mg, 0.303 mmol) in CH_2Cl_2 (4 mL) with HBF_4·OMe_2 (0.780 mL, 1.01 g, 7.57 mmol, 25 equiv) at −40 °C, and then stirred it overnight at room temperature. Degassed, saturated aqueous $NaHCO_3$ (5 mL) was added, and the mixture was stirred vigorously for 1 h. Extraction of the aqueous layer with CH_2Cl_2 (2 × 8 mL), drying of the combined organic layers over $MgSO_4$, and evaporation of the solvent gave the crude product. Purification by column chromatography under N_2 (neutral alumina, pentane/ethyl acetate 9:1) afforded cyrhetrene **7a** as a colorless foam (177 mg, 80%).

(*R*,*S*$_p$)-2-(1′-Diphenylphosphinoethyl)diphenylphosphinocyrhetrene [(*R*,*S*$_p$)-7a]: mp 142−144 °C dec; $[\alpha]^{20}_D$ −171 (*c* 0.46, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (dd, J = 7.0, 5.4 Hz, 3H), 3.98 (m_c, 1H), 4.85 (br s, 1H), 5.03 (t, J = 2.7 Hz, 1H), 5.33 (m_c, 1H), 7.23−7.30 (m, 5H), 7.31−7.50 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.6, 29.4 (dd, J = 21.5, 11.1 Hz), 79.3, 86.7, 93.2 (d, J = 5.1 Hz), 96.2 (dd, J = 22.2, 19.6 Hz), 121.4 (dd, J = 25.3, 22.9 Hz), 127.7, 128.0, 128.1,

(26) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869−9882.

128.2, 128.3, 128.4, 128.5, 128.6, 129.6 (d, J = 26.7 Hz), 131.5 (d, J = 15.4 Hz), 133.1 (dd, J = 18.4, 2.1 Hz), 133.6 (d, J = 21.7 Hz), 134.4 (d, J = 21.2 Hz), 135.8 (d, J = 21.7 Hz), 136.9 (d, J = 18.6 Hz), 137.5 (d, J = 7.2 Hz), 138.2 (d, J = 7.4 Hz), 193.5 (3C); ^{31}P NMR (121 MHz, $CDCl_3$) δ −29.8 (d, J = 22.9 Hz), 10.5 (d, J = 23.0 Hz); IR (KBr, cm^{-1}) ν 3059, 2020, 1922, 1479, 1432, 1375, 1164, 1091, 1032, 743, 695, 602, 505, 466; MS (EI) *m/z* (%) 732 (M^+, 6), 730 ($(M - 2)^+$, 3), 704 ($(M - CO)^+$, 100), 702 ($(M - CO - 2)^+$, 57), 676 ($(M - 2CO)^+$, 19), 674 ($M - 2CO - 2)^+$, 15), 519 (38), 461 (24). Anal. Calcd for $C_{34}H_{27}O_3P_2Re$: C, 55.81; H, 3.72. Found: C, 55.55; H, 4.08.

(*R*,*S*$_p$)-2-(1′-Di-*tert*-butylphosphinoethyl)diphenylphosphinocyrhetrene [(*R*,*S*$_p$)-7b]. Following GP 3 using (*R*,*S*$_p$)-**6b** (80 mg, 0.11 mmol) afforded the title compound as a colorless foam (60 mg, 78%). In this case, all operations were conducted under argon: mp 145−147 °C dec; $[\alpha]^{24}_D$ −177 (*c* 0.28, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6) δ 0.96 (d, J = 10.7 Hz, 9H), 1.12 (d, J = 10.8 Hz, 9H), 1.41 (dd, J = 7.3, 2.6 Hz, 3H), 3.66 (br q, J = 7.2 Hz, 1H), 4.36 (td, J = 2.7, 0.9 Hz, 1H), 4.82 (m_c, 1H), 5.04 (dd, J = 2.9, 1.7 Hz, 1H), 7.02−7.13 (m, 6H), 7.35−7.41 (m, 2H), 7.51−7.57 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 17.8, 29.8 (dd, J = 36.4, 5.5 Hz), 31.5 (d, J = 13.5 Hz, 3C), 31.6 (d, J = 14.7 Hz, 3C), 34.3 (d, J = 5.3 Hz), 34.7 (d, J = 10.7 Hz), 78.9, 86.9, 94.8 (d, J = 6.3 Hz), 96.8 (d, J = 15.7 Hz), 121.1 (d, J = 19.2 Hz), 127.7−128.4 (3C), 128.8 (d, J = 7.7 Hz, 2C), 129.5, 133.4 (dd, J = 17.9, 3.2 Hz, 2C), 135.3 (d, J = 21.9 Hz, 2C), 139.3 (d, J = 8.5 Hz), 139.7 (d, J = 9.4 Hz), 194.5 (3C, CO); ^{31}P NMR (121 MHz, C_6D_6) δ −29.5 (d, J = 55.1 Hz), 51.6 (d, J = 55.0 Hz); IR (KBr, cm^{-1}) ν 2942, 2863, 2391, 2021, 1911, 1473, 1435, 1038, 810, 744, 697, 603, 506; MS (EI) *m/z* (%) 692 (M^+, 2), 690 ($(M - 2)^+$, 2), 635 ($(M - t\text{-Bu})^+$, 100), 633 ($(M - t\text{-Bu} - 2)^+$, 59), 579 ($(M - t\text{-Bu} - 2CO)^+$, 21), 577 ($(M - t\text{-Bu} - 2CO - 2)^+$, 12). Anal. Calcd for $C_{30}H_{35}O_3P_2Re$: C, 52.09; H, 5.10. Found: C, 52.36; H, 5.43.

(*R*,*S*$_p$)-2-(1′-Diphenylphosphinoethyl)-[bis(3″,5″-dimethylphenyl)phosphino]cyrhetrene [(*R*,*S*$_p$)-7c]. Following GP 3 using (*R*,*S*$_p$)-**6c** (125 mg, 0.153 mmol) afforded the title compound after purification by column chromatography (neutral alumina, pentane/Et_2O 9:1) under N_2 as colorless foam (84 mg, 70%): mp 76−79 °C dec; $[\alpha]^{22}_D$ −205 (*c* 0.25, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6) δ 1.19 (dd, J = 7.0, 5.1 Hz, 3H), 2.08 (s, 6H), 2.13 (s, 6H), 4.24 (m_c, 1H), 4.33 (t, J = 2.7 Hz, 1H), 4.50 (br s, 1H), 5.21 (m_c, 1H), 6.70 (s, 1H), 6.79 (s, 1H), 6.89−6.91 (m, 3H), 7.03−7.13 (m, 3H), 7.16−7.22 (m, 2H), 7.26 (s, 1H), 7.29 (s, 1H), 7.35−7.41 (m, 2H), 7.43 (s, 1H), 7.46 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6) δ 18.3, 21.3 (2C), 21.4 (2C), 29.8 (dd, J = 21.6, 9.8 Hz), 79.3, 86.6, 93.8 (d, J = 4.4 Hz), 97.6 (d, J = 25.0 Hz), 121.6 (d, J = 24.3 Hz), 128.6 (d, J = 4.2 Hz, 2C), 129.8 (2C), 130.6 (2C), 131.4 (2C), 131.5 (2C), 131.7 (2C), 132.7 (d, J = 21.2 Hz, 2C), 134.7 (d, J = 22.6 Hz, 2C), 136.2 (d, J = 22.0 Hz, 2C), 137.3 (d, J = 19.0 Hz, 2C), 137.6 (d, J = 6.9 Hz), 137.8 (d, J = 6.7 Hz), 138.4 (d, J = 8.3 Hz), 138.6 (d, J = 8.4 Hz), 194.4 (3C); ^{31}P NMR (121 MHz, C_6D_6) δ −28.7 (d, J = 25.3 Hz), 10.8 (d, J = 25.2 Hz); IR (KBr, cm^{-1}) ν 2020, 1921, 1584, 1435, 1163, 1124, 1038, 848, 743, 694, 599, 505; MS (EI) *m/z* (%) 788 (M^+, 11), 785 ($(M - 2)^+$, 6), 776 (36), 760 ($(M - CO)^+$, 100), 758 ($(M - CO - 2)^+$, 59), 732 ($(M - 2CO)^+$, 27), 730 ($(M - 2CO - 2)^+$, 17), 519 (46), 517 (38). Anal. Calcd for $C_{38}H_{35}O_3P_2Re$: C, 57.93; H, 4.48. Found: C, 57.92; H, 4.83.

General Procedure (GP 4) for the Synthesis of *P*,*O* Ligands 8a and 8b. Ethyl chloroformate (48.0 mg, 42.0 μL, 0.437 mmol, 2.0 equiv) was added dropwise to a solution of (*R*,*S*$_p$)-2-(1-dimethylaminoethyl)diphenylphosphinocyrhetrene [(*R*,*S*$_p$)-**5a**] (129 mg, 218 μmol) in THF (2 mL) at −40 °C. The reaction mixture was allowed to reach room temperature, and was stirred for 6.5 h. The red solution was then treated with degassed water (2.00 g, 2.00 mL, 111 mmol, 550 equiv), and was stirred for 1 h. The solution was diluted with water (4 mL), extracted with Et_2O (3 × 10 mL), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (deactivated silica gel (Et_3N), pentane/ethyl acetate 9:1), giving the major diasteromer of **8b** as a colorless solid (78 mg, 63% yield).

(*R*,*S*$_p$)-2-(1′-Hydroxyethyl)diphenylphosphinocyrhetrene [(*R*,*S*$_p$)-8b, Major Diastereomer]: mp 108−111 °C; $[\alpha]^{23}_D$ −129 (*c* 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 1.32 (d, J = 6.9 Hz, 3H), 1.39 (s, 1H), 4.24 (t, J = 2.7 Hz, 1H), 4.68 (dd, J = 2.7, 1.7 Hz, 1H), 4.92 (m_c, 1H), 5.21 (qd, J = 6.8, 4.1 Hz, 1H), 7.02−7.19 (m, 6H), 7.31 (m_c, 2H), 7.46 (m_c, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 25.1, 50.1 (d, J = 12.3 Hz), 80.5, 86.6 (d, J = 2.3 Hz), 93.9 (d, J = 5.3 Hz), 97.5 (d, J = 24.4 Hz), 116.0 (d, J = 23.6 Hz), 128.5 (d, J = 6.9 Hz, 2C), 128.89, 128.93 (d, J = 7.6 Hz, 2C), 129.9, 133.1 (d, J = 18.3 Hz, 2C), 134.8 (d, J = 21.4 Hz, 2C), 136.5 (d, J = 8.4 Hz), 137.5 (d, J = 8.6 Hz), 193.2 (3C, CO); ^{31}P NMR (162 MHz, C_6D_6) δ −27.4 (s); IR (KBr, cm^{-1}) ν 3675, 3445, 3390, 2931, 2026, 1922, 1430, 1230, 1166, 1091, 1035, 827, 742, 694, 595, 502; MS (EI) *m/z* (%) 546 ($(M - H_2O)^+$, 43), 544 ($(M - H_2O - 2)^+$, 29), 518 ($(M - H_2O - CO)^+$, 57), 516 ($(M - H_2O - CO - 2)^+$, 36), 462 ($(M - H_2O - 3CO)^+$, 100), 382 (36), 230 (43). Anal. Calcd for $C_{22}H_{18}O_4PRe$: C, 46.89; H, 3.22. Found: C, 46.59; H, 3.62.

(*R*,*S*$_p$)-2-(1′-Methoxyethyl)diphenylphosphinocyrhetrene [(*R*,*S*$_p$)-8a, Major Diastereomer]. Following GP 4 using (*R*,*S*$_p$)-**5a** (0.188 mmol scale) and MeOH (2 mL) afforded (*R*,*S*$_p$)-**8a** as a colorless solid (40 mg, 37% yield) after purification by column chromatography (silica gel, pentane/ethyl acetate 19:1 → 9:1): mp 114−117 °C; $[\alpha]^{23}_D$ −126 (*c* 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 1.13 (d, J = 6.4 Hz, 3H), 2.73 (s, 3H), 4.30 (t, J = 2.7 Hz, 1H), 4.43 (qd, J = 6.4, 3.0 Hz, 1H), 4.65 (m_c, 1H), 5.02 (m_c, 1H), 7.01−7.10 (m, 6H), 7.27−7.32 (m, 2H), 7.48−7.52 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 18.6, 56.0, 71.7 (d, J = 7.9 Hz), 80.3, 86.8 (d, J = 2.9 Hz), 93.3 (d, J = 5.9 Hz), 97.7 (d, J = 23.0 Hz), 116.9 (d, J = 22.9 Hz), 128.4 (d, J = 6.1 Hz, 2C), 128.6, 128.9 (d, J = 7.6 Hz, 2C), 129.8, 132.9 (d, J = 18.3 Hz, 2C), 135.0 (d, J = 20.8 Hz, 2C), 136.4 (d, J = 9.2 Hz), 138.5 (d, J = 9.9 Hz), 193.9 (3C); ^{31}P NMR (121 MHz, C_6D_6) δ −24.5 (s); IR (KBr, cm^{-1}) ν 3452, 3416, 3371, 2978, 2930, 2020, 1920, 1431, 1242, 1177, 1091, 749, 696, 597, 500; MS (EI) *m/z* (%) 578 (M^+, 51), 576 ($(M - 2)^+$, 33), 563 ($(M - CH_3)^+$, 100), 561 ($(M - CH_3 - 2)^+$, 60), 550 ($(M - CO)^+$, 55), 548 ($(M - CO - 2)^+$, 35), 520 (25), 518 (35), 462 (68). Anal. Calcd for $C_{23}H_{20}O_4PRe$: C, 47.83; H, 3.49. Found: C, 48.19; H, 3.60.

General Procedure for the Rh-Catalyzed, Asymmetric 1,4-Addition Reaction. Under argon, a Schlenk tube was filled with $Rh(acac)(C_2H_4)_2$ (3.10 mg, 12.0 μmol, 3 mol %), cyrhetrene **7a** (9.07 mg, 12.4 μmol, 3.1 mol %), and $PhB(OH)_2$ (**10a**, 244 mg, 2.00 mmol, 5.0 equiv). The mixture was dissolved in dioxane/water (10:1, 1.1 mL). After the addition of 2-cyclohexen-1-one (**9A**, 38.5 mg, 39.0 μL, 0.400 mmol), the solution was heated to 100 °C for 5 h. The solvent was removed in vacuo, and the brown residue was suspended in ethyl acetate (5 mL) and aqueous $NaHCO_3$ (5 mL). The aqueous layer was extracted with ethyl acetate (10 mL), and the combined organic layers were dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (silica gel, pentane/ethyl acetate 6:1) to afford 3-phenylcyclohexanone (**11Aa**) as a colorless oil (65 mg, 93%).

3-Phenylcyclohexanone (11Aa).[13b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73−1.91 (m, 2H), 2.08−2.17 (m, 2H), 2.34−2.63 (m, 4H), 3.01 (m_c, 1H), 7.22−7.26 (m, 3H), 7.31−7.36 (m, 2H). The enantiomer ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), heptane/2-propanol 99:1, 0.5 mL/min, 220 nm, 10 °C, 33.73 min (minor), 35.58 min (major).

Asymmetric Hydrogenation of Enamide 12. Under argon, $Rh(COD)_2BF_4$ (2.0 mg, 5.0 μmol, 1.0 mol %) and cyrhetrene **7a** (4.0 mg, 5.5 μmol, 1.1 mol %) were dissolved in EtOAc (0.4 mL), and the solution was stirred at room temperature for 20 min. A solution of *N*-(1-phenylvinyl)acetamide

(**12**,[27] 81 mg, 0.50 mmol) in EtOAc (0.4 mL) was added, and the vial was placed into an argon-filled 100 mL autoclave. The autoclave was sealed, and it was purged with H_2 (3 × 10 bar). It was then pressurized with H_2 (10 bar), and the reaction mixture was stirred for 16 h. TLC analysis (pentane/ethyl acetate 1:3) indicated complete conversion of the starting material. The solution was filtered through a short plug of silica gel (elution with EtOAc), and removal of the solvent afforded *N*-(1-phenylethyl)acetamide (**13**, 81 mg, 99%).

***N*-(1-Phenylethyl)acetamide (13):**[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49 (d, J = 6.9 Hz, 3H), 1.99 (s, 3H), 5.13 (dq, J = 7.4, 6.9 Hz, 1H), 5.64 (br s, 1H), 7.25−7.37 (m, 5H). The enantiomer ratio was determined by chiral GC using an FS Cyclodex β-I/P capillary column (25 m × 0.2 mm), with H_2 as the carrier gas; 49.35 min (minor), 50.66 min (major).

Acknowledgment. We gratefully acknowledge the Deutsche Forschungsgemeinschaft (SFB 380) and the Fonds der Chemischen Industrie for financial support. R.T.S. thanks the Graduiertenkolleg (GRK 440) for a predoctoral stipend.

Supporting Information Available: Analytical data for products **11**, and ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO051676L

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