Synthesis of Chiral Cyrhetrenes and Their Application in Asymmetric Catalysis

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Planar-chiral diphosphine (R,S_p)-**4**, having a η^5-cyclopentadienylrhenium(I) tricarbonyl backbone was prepared by a sequence involving an enantioselective (CBS) reduction of acetylcyrhetrene **5** to give alcohol (*R*)-**6**, several retentive S_N1-type substitution reactions, and a diastereoselective introduction of the phosphino substituent at the cyclopentadienyl ring through directed *ortho*-lithiation. The application of a palladium complex of (R,S_p)-**4** in allylic alkylation reactions afforded a product with up to 88% ee. Use of (R,S_p)-**4** in Rh-catalyzed hydrogenations of dimethyl itaconate and acetamidocinnamic acid gave enantioselectivities of up to 95 and 89% ee, respectively. Thus, in the catalyses cyrhetrenyl diphosphine (R,S_p)-**4** compares well with its ferrocene-based analogue, Josiphos **1a**. The ligand/metal binding mode of *P,N*-cyrhetrene (R,S_p)-**10** was revealed by the X-ray crystal structure analysis of complex [$PdCl_2$·(R,S_p)-**10**]. The results of this study confirmed the expected structural similarities between the planar-chiral cyrhetrene and the analogous ferrocene and suggested a lower basicity of the former due to the electron-withdrawing property of its $Re(CO)_3$ fragment. This structure-based analysis is in accord with the interpretation of the catalytic properties of metal complexes bearing cyrhetrenyl diphosphine (R,S_p)-**4**.

Introduction

Chiral 1,2-disubstituted ferrocenes having both central and planar chirality are among the most successful ligands in asymmetric catalysis.[1] Some of them have even reached the stage of industrial application. For example, in the synthesis of the herbicide (*S*)-Metolachlor developed by Novartis a ferrocenyl diphosphine of the Josiphos[2] (**1a**) type serves as ligand. In this particular process, which appears to be one of the largest applications of asymmetric catalysis so far, an iridium/xyliphos (**1b**) complex is employed to enantioselectively reduce a prochiral imine.[3] Rhodium and ruthenium hydrogenation catalysts bearing Josiphos-type ligands **1b** and **1c**, respectively, have been applied in other industrial processes such as the productions of (+)-biotine (vitamin H)[4] and (+)-*cis*-methyl dihydrojasmonate.[5,6]

With the goal of improving the performance of such ferrocene-based catalysts the ligand framework was varied to a large extent. Some of those modifications involved the metallocene unit, and as early as 1994, Togni and co-workers reported the syntheses of ruthenocene analogues of **1a**.[7] One year later, the use of tricarbonyl(η^6-benzene) chromium complexes **2** as ligands in palladium-catalyzed asymmetric allylic alkylations was described by Uemura and co-workers.[8a] Subsequently, Salzer et al. investigated applications of **2** in asymmetric hydrogenations, hydroaminations, and allylic sulfinations catalyzed by rhodium, iridium, and palladium complexes, respectively.[8b] The results of these catalyses compared rather well to those obtained with the corresponding Josiphos-type ferrocenes.

Recently, we introduced planar-chiral η^5-cyclopentadienylrhenium(I) tricarbonyl complexes **3** (cyrhetrenes) and demonstrated their applicability as ligands in asymmetric catalysis.[9−11] On the basis of these positive

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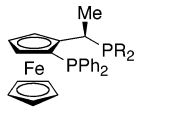
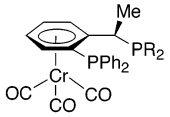
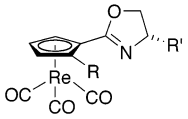
results we decided to extend our attention on the synthesis of Josiphos-type cyrhetrenyl diphosphine **4** (AaPhos).[12] Due to the electron-withdrawing property of the rhenium tricarbonyl fragment, the phosphorus atoms in **4** were expected to be less basic than those in ferrocene-based Josiphos. Consequently, the catalytic performance of metal complexes bearing such ligands should be altered, which we hoped could result in an increased efficiency in catalyzed asymmetric transformations.



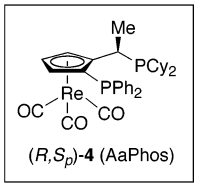
1a (Josiphos): R = Cy
1b (Xyliphos): R = Xyl
1c (PPF-P*t*-Bu$_2$): R = *t*-Bu



2: R = Ph, Cy



3a: R = CPh_2OH
3b: R = PR''_2



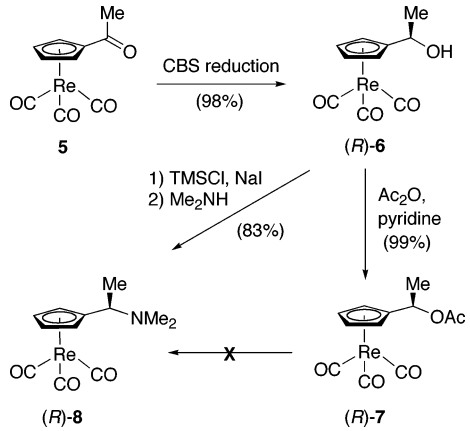
(*R*,*S*$_p$)-**4** (AaPhos)

Here, we report on the syntheses of a number of novel chiral cyrhetrenes bearing amino and phosphino groups, an X-ray structure of a palladium complex of an amino cyrhetrenyl phosphine, and the application of such compounds as ligands in asymmetric catalysis.

Results and Discussion

Ferrocenes **1** and arene-tricarbonyl chromium complexes **2** have been prepared by diastereoselective *ortho*-lithiations of enantiomerically enriched dimethylamine derivatives.[2a,8] This strategy proved highly flexible and appeared to be applicable for the synthesis of cyrhetrenyl diphosphine **4** as well. For that purpose, tertiary amine **8**, which can be considered as the Re(CO)$_3$ analogue of Ugi's amine,[13] became the prime target. As shown in Scheme 1, the reaction sequence for the preparation of **8** started from acetylcyrhetrene (**5**), which was prepared from Re(CO)$_5$Br and (acetylcyclopentadienyl)thallium in high yield.[14] Enantioselective CBS reduction of **5** [using a chiral (*S*)-proline-derived oxazoborolidine as catalyst and BH_3·SMe_2 as reductant][15] afforded alcohol (*R*)-**6** in both excellent yield (98%) and enantioselectivity (99% ee). The absolute configuration of (*R*)-**6** and those of all subsequent

Scheme 1



products were assigned as described below. Treatment of (*R*)-**6** with acetic anhydride in pyridine gave 1-acetoxyethyl cyrhetrene [(*R*)-**7**] in 99% yield. Unfortunately, all attempts to convert (*R*)-**7** into amine (*R*)-**8** led to hydrolysis and regenerated alcohol (*R*)-**6**.[16] Apparently, the oxygen carbon bond of **7** (with acetate as leaving group) is more difficult to cleave than in the analogous ferrocene derivative,[17] which can be explained by the lower stability of the resulting α-cyrhetrenylethyl carbocation due to the electron-withdrawing property of the Re(CO)$_3$ fragment. Finally, (*R*)-**8** was obtained by activation of alcohol (*R*)-**6** with NaI/TMSCl[18] and treatment of the mixture with 40% aqueous dimethylamine to give the product in 83% yield. Since this transformation was accompanied by a slight decrease of the enantiomeric excess (from 99 to 96% ee for the conversion of **6** into **8**), the product had to be recrystallized (once) to give (*R*)-**8** with >99% ee.

Directed lithiation of (*R*)-**8** with *n*-BuLi at −15 °C and subsequent reaction with benzophenone or chlorodiphenylphosphine afforded diphenylmethanol (*R*,*S*$_p$)-**9** (70%, dr = 11:1) and aminophosphine (*R*,*S*$_p$)-**10** (62%, dr = 9.2:1), respectively. (The stereochemical assignments will be discussed below.) A direct substitution of the dimethylamino group of (*R*,*S*$_p$)-**10** with dicyclohexylphosphine in acetic acid under the conditions used for the preparation of Josiphos-type diphosphines[2] failed. More successful for the conversion of (*R*,*S*$_p$)-**10** into (*R*,*S*$_p$)-**4** was the application of the unique strategy developed by Salzer and co-workers for the synthesis of chromium arene complexes **2** from their dimethylamino precursors.[19] Thus, treatment of (*R*,*S*$_p$)-**10** with ethyl chloroformate and subsequent nucleophilic displacement of the chloro substituent of the resulting intermediate upon addition of dicyclohexylphosphine and $TlPF_6$ afforded diphosphine (*R*,*S*$_p$)-**4** without any indication of epimerization. Unfortunately, however, even though according to TLC analysis the reaction appeared to be a "spot to spot" transformation, only 25%

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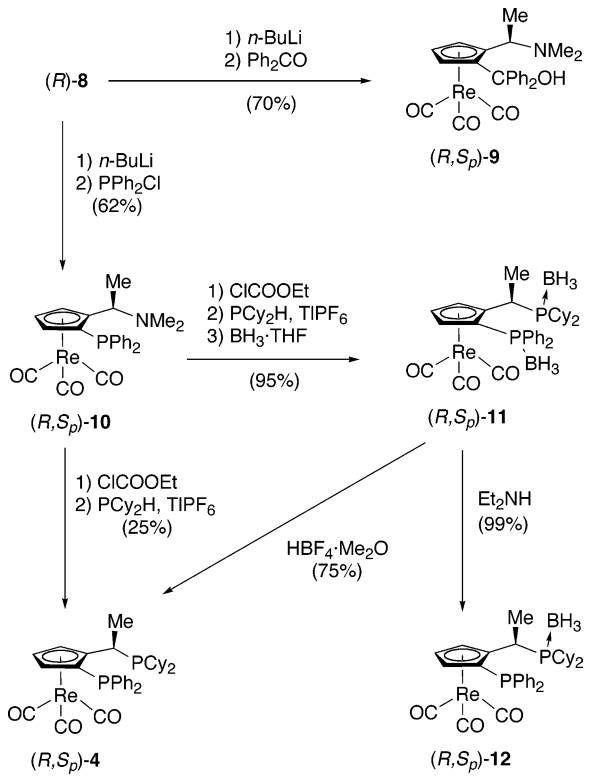
Scheme 2



of the product was obtained after chromatographic purification (over deactivated silica gel under argon). This observation indicated that diphosphine (R,S_p)-**4** was rather air and light sensitive as well as unstable in solution. To prepare larger quantities of it, the reaction mixture containing (R,S_p)-**4** was treated with a solution of borane in THF to give the air-stable diphosphine diborane adduct (R,S_p)-**11**.[20] Its deboranation with diethylamine[21] afforded monoprotected diphosphine (R,S_p)-**12**[22] in 99% yield. All attempts to remove both boranes of (R,S_p)-**11** with bases such as DABCO,[23] morpholine,[24] or other amines failed. Finally it was found that the desired full deprotection of (R,S_p)-**11** was readily achieved with HBF_4·OMe_2,[25] whereby AaPhos (R,S_p)-**4** was obtained in 75% yield (Scheme 2).

Various methods were used to determine and ensure the stereochemistry of the products. First, the *R*-configuration of alcohol **6** was deduced from the general rules of the well-studied enantioselective ketone reduction with *S*-configured oxazaborolidine as catalyst.[15] Furthermore, the comparison of the specific rotations of various ferrocenyl and (η^6-benzene) chromium tricarbonyl derivatives with the new cyrhetrenyl compounds (Table 1) gave additional evidence for the *R*-configuration of **6**. The same was suggested for tertiary amine **8**. Thus, in analogy with the related ferrocenyl-[26] and arene-chromium-tricarbonyl[27] chemistry, the transformation of **6** into **8** involves two retentive substitution reactions.

The overall retention in the conversion of **6** into **8** was further evidenced by chemical correlations. As depicted in Scheme 3, enantiomerically pure amine **8**, prepared from (*R*)-**6**, was treated with acetic anhydride to give (*R*)-**7**. The configuration of this product was first ensured by its identity (including optical rotation) to a sample of (*R*)-**7**, which was independently prepared by acetylation of (*R*)-**6** under basic conditions, and second, by the fact that its basic hydrolysis gave alcohol (*R*)-**6** (analyzed by chiral HPLC).

The assignments of the relative configurations of the planar-chiral cyrhetrenes follow from the X-ray crystal structure analysis of palladium dichloride complex (R,S_p)-**13** (vide infra). The Flack parameter of this analysis is in agreement with the proposed absolute configuration and proves the previous stereochemical assignments. It also shows that the diastereoselective lithiation of (*R*)-**8** proceeds similarly to that in the ferrocene chemistry, where R,S_p products are formed from *R*-amines.[13] Finally, the assignment of the R,S_p-configuration of diphosphine **4** is based on the observed retentive stereochemistry of the substitution reactions of (*R*)-**6** and (*R*)-**8** and on Salzer's results obtained in his substitutions.[19]

X-ray Crystal Structure of Palladium(II) Complex (R,S_p)-13

To investigate the structural characteristics of the new chelating cyrhetrenes and to compare them to those of the analogous ferrocenes, the molecular structure of palladium complex (R,S_p)-**13**, which was readily prepared by treatment of (R,S_p)-**10** with [$PdCl_2$(COD)] in dichloromethane (Scheme 4), was determined by X-ray crystal structure analysis.[32] The analogous ferrocene complex [$PdCl_2$·PPFA] [(R,S_p)-**14**] with amino phosphine PPFA as ligand is known and has structurally been characterized (as its $CDCl_3$-solvate) by van der Steen and Kanters.[35]

Both palladium complexes, cyrhetrene (R,S_p)-**13** and ferrocene (R,S_p)-**14**, adopt a square planar coordination geometry (Figure 1). The *P,N*-binding mode of the amino phosphine fragments to palladium results in six-membered chelate rings, forcing the chloro ligands into a *cis*-geometry. As a consequence of the largely identical atom connectivities in the upper parts of the molecules, the overall structures of both complexes are very similar.

The bond lengths for the Pd−Cl(1), Pd−Cl(2), Pd−N, and Pd−P bonds (for data see Figure 1) in cyrhetrene (R,S_p)-**13** and the respective ones in ferrocene (R,S_p)-**14** (with values of 2.283(7), 2.401(8), 2.12(2), and

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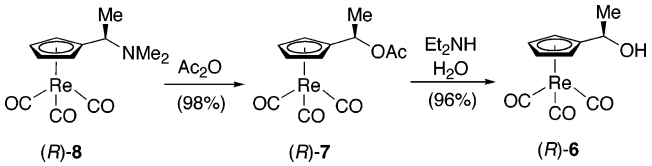
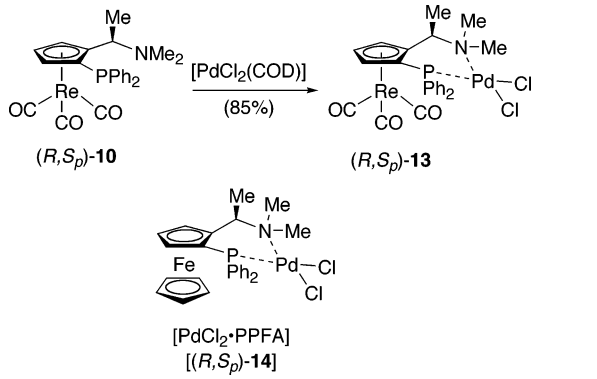
Table 1. Specific Rotations of Various Chiral Metallocenes

compound	$[\alpha]_D$
(*R*)-1-[CH(OH)Me)]C_5H_4FeCp	−30.5 (*c* = 1.1, benzene)[26]
(*S*)-1-[CH(OH)Me)]$C_6H_5Cr(CO)_3$	+18 (*c* = 2.1, $CHCl_3$) for 89% ee[28]
1-[CH(OH)Me)]$C_5H_4Re(CO)_3$ (**6**)	−3.4 (*c* = 0.65, $CHCl_3$)
(*R*)-[CH(Me)NMe_2]C_5H_4FeCp (Ugi-amine)	+14.9 (*c* = 0.99, $CHCl_3$)[13]
(*R*)-[CH(Me)NMe_2]$C_6H_5Cr(CO)_3$	+13.8 (*c* = 0.96, $CHCl_3$)[29]
[CH(Me)NMe_2]$C_5H_4Re(CO)_3$ (**8**)	+11.0 (*c* = 1.0, $CHCl_3$)
(R,S_p)-[2-(CH(Me)NMe_2)-PPh_2]C_5H_3FeCp (PPFA)	−361 (*c* = 0.6, ethanol)[30]
(R,S_p)-[2-(CH(Me)NMe_2)-PPh_2]$C_6H_4Cr(CO)_3$	−42 (*c* = 1.1, $CHCl_3$)[31]
[2-(CH(Me)NMe_2)-PPh_2]$C_5H_3Re(CO)_3$ (**10**)	−165 (*c* = 1.0, $CHCl_3$)
(R,S_p)-[2-(CH(Me)PCy_2)-PPh_2]C_5H_3FeCp (**1a**)	−346 (*c* = 0.6, $CHCl_3$)[2a]
(S,R_p)-[2-(CH(Me)PCy_2)-PPh_2]$C_6H_4Cr(CO)_3$	+31.5 (*c* = 3.25, $CHCl_3$)[8]
[2-(CH(Me)PCy_2)-PPh_2]$C_5H_3Re(CO)_3$ (**4**)	−162.2 (*c* = 0.18, $CHCl_3$)

Scheme 3



Scheme 4



2.231(6) Å) are similar. The largest difference is found for the Pd−Cl(2) bond *trans* to phosphorus, which reflects the lower *trans* influence of the less basic cyrhetrenyl phosphino group. The most significant difference between the two complexes is best described by the interplane angle between the cyclopentadienyl plane and the coordination plane defined by the P, Pd, and N atoms. In cyrhetrene (R,S_p)-**13** this angle is 22.8°, whereas in the analogous ferrocene (R,S_p)-**14** it is 32.5°. In other words, the palladium(II) fragment is bending away from the metallocene backbone, and this effect is more pronounced in the ferrocene than in the cyrhetrene complex. A simple explanation of this result is that the ferrocene backbone (lower FeCp-unit) is sterically more demanding than the cyrhetrene backbone ($Re(CO)_3$-unit) and that in the lowest energy conformation of the complex the down-pointing phenyl group is transmitting this steric bulk toward the palladium(II) fragment.

Catalyses with Phosphino Cyrhetrenes as Ligands

The well-studied enantioselective palladium(0)-catalyzed allylic alkylation[36] served as the first test reaction to evaluate the catalytic activity of the new cyrhetrene-based complexes. To our delight, we found that cyrhetrenyl phosphine (R,S_p)-**4** performed very well in this reaction (Table 2, entry 1). Thus, after 2 h the substitution product was obtained in excellent yield (99%) with

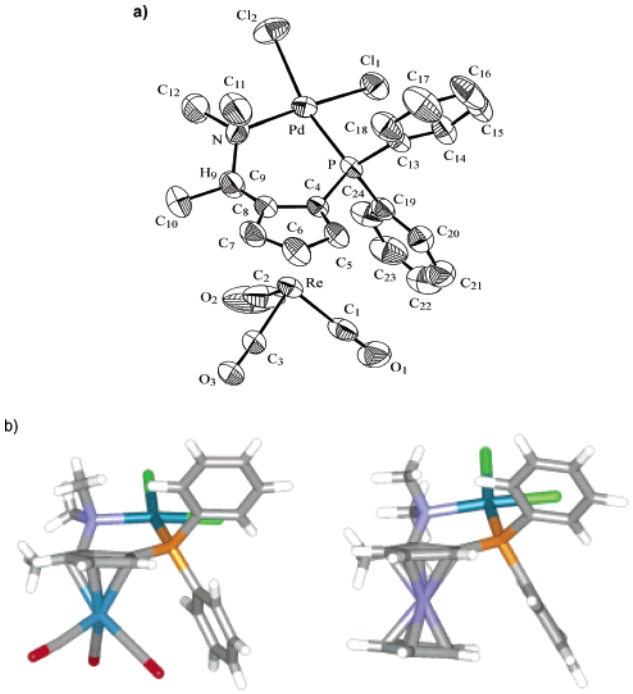
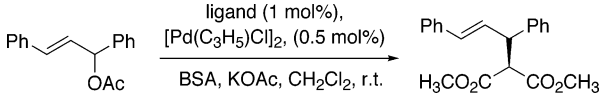


Figure 1. (a) ORTEP plot of complex (R,S_p)-**13**.[32] Selected bond lengths (Å) and angles (deg) for (R,S_p)-**13** as determined by X-ray crystal structure analysis: Pd−Cl(1): 2.288(1), Pd−Cl(2): 2.364(2), Pd−N: 2.136(4), Pd−P: 2.236(1). Cl(1)−Pd−Cl(2): 87.43(6), Cl(1)−Pd−P: 82.84(5), Cl(2)−Pd−N: 93.7(1), P−Pd−N: 97.0(1). (b) Side views of cyrhetrene (R,S_p)-**13** (left) and ferrocene (R,S_p)-**14** (right; data taken from ref 35).

Table 2. Asymmetric Allylic Alkylation Using Pd Catalysts with Planar-Chiral Ligands[a]



entry	ligand	reaction time (h)	yield (%)	ee (%)	abs config
1	(R,S_p)-**1a**	2	98	92	(−)-(*S*)
2	(R,S_p)-**4**	2	99	88	(−)-(*S*)
3	(R,S_p)-**12**	1.5	98	86	(−)-(*S*)

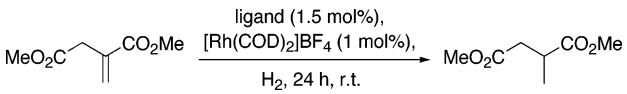
[a] For details see Experimental Section.

an ee of 88%. This value is almost the same as that achieved with Josiphos **1a** (92% ee). The *S*-enantiomer of the product was preferentially formed in both cases. In terms of the enantioselectivity, other chelating ferrocene-based ligands are known to perform equally well or even better.[1f,36] Recently, Blaser et al. stated that the utility of a ligand can be negatively affected if it is extremely air and/or moisture sensitive.[6] Therefore we

also tested the use of the monoborane adduct of AaPhos (R,S_p)-**12** as ligand in this catalysis.[37] Gratifyingly, both catalyst activity (2 h vs 1.5 h reaction time until complete substrate conversion) and enantioselectivity (88% ee vs 86% ee) were almost the same when either (R,S_p)-**4** or (R,S_p)-**12** was employed in the palladium catalysis. These results could be interpreted as an indication for the transformation of monoborane diphosphane (R,S_p)-**12** to a palladium complex of (R,S_p)-**4** under the conditions of the catalytic reaction.

Asymmetric hydrogenation is one of the most important catalytic methods in synthetic organic chemistry. It is widely employed on both laboratory and production scale and constitutes an ideal method for the synthesis of optically active compounds such as alkanes, alcohols, amines, and α-amino acids.[38,39] We therefore decided to include two types of rhodium-catalyzed hydrogenations in the evaluation of the catalytic profile of the cyrhetrene-based complexes. In the first, dimethyl itaconate served as starting material (Table 3); in the second, α-acetamidocinnamic acid and its methyl ester were test substrates (Table 4).

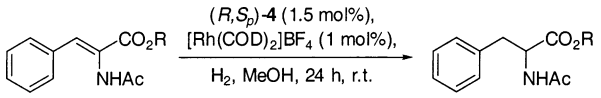
Table 3. Asymmetric Hydrogenation of Dimethyl Itaconate with Rh Complexes Bearing Planar-Chiral Cyrhetrenes[a]



entry	ligand	$p(H_2)$ (bar)	solvent	conversion (%)	ee (%), abs config
1	(R,S_p)-**4**	1	MeOH	35	n.d.
2	(R,S_p)-**4**	10	MeOH	100	92 (*S*)
3	(R,S_p)-**4**	10	CH_2Cl_2	100	91 (*S*)
4	(R,S_p)-**4**	50	CH_2Cl_2	100	95 (*S*)
5	(R,S_p)-**11**	5	CH_2Cl_2	100	43 (*R*)
6	(R,S_p)-**11**	5	MeOH	100	14 (*S*)
7	(R,S_p)-**11**	10	MeOH	100	9 (*S*)
8	(R,S_p)-**12**	5	CH_2Cl_2	5−8	n.d.[b]
9	(R,S_p)-**12**	5	MeOH	23−48	23 (*S*)

[a] For details see Experimental Section. [b] Not determined.

Table 4. Asymmetric Hydrogenation of (*Z*)-Acetamidocinnamic Acid (R = H) and Methyl (*Z*)-Acetamidocinnamate (R = Me) with a Rh Complex Bearing AaPhos (R,S_p)-4[a]



entry	R	$p(H_2)$ (bar)	conversion (%)	ee (%)
1	H	5	88	89 (*R*)
2	H	10	100	86 (*R*)
3	H	50	100	57 (*R*)
4	Me	5	27	71 (*R*)
5	Me	10	100	70 (*R*)
6	Me	50	100	39 (*R*)

[a] For details see Experimental Section.

Again, the complexes with the cyrhetrenes as ligands performed well, and with AaPhos (R,S_p)-**4** an enantioselectivity of 95% ee was achieved in the hydrogenation of dimethyl itaconate (Table 3, entry 4). This ee is only slightly lower that that achieved with the ferrocene analogue Josiphos **1a** (98−99% ee at 1 bar H_2).[2a] To reach full substrate conversion, a hydrogen pressure above 1 MPa (10 bar) was necessary. Variations of pressure and solvent had only a minor influence on the ee of the product (Table 3, entries 2−4). In all cases the major enantiomer had *S*-configuration. Even at 0.5 MPa (5 bar) of hydrogen pressure use of bisborane adduct (R,S_p)-**11** led to an active catalyst for the asymmetric hydrogenation of dimethyl itaconate, but in both dichloromethane and methanol solvents the enantioselectivity remained low or moderate at best (Table 3, entries 5−7). Interestingly, and in contrast to the results of the allylic alkylation, the monoborane adduct of AaPhos, (R,S_p)-**12**, gave only low conversions and enantioselectivities (at 5 bar of H_2 pressure).

Next, the applicability and efficiency of AaPhos (R,S_p)-**4** in rhodium-catalyzed asymmetric olefin hydrogenations to give optically active amino acid derivatives was investigated. As test reactions the conversions of (*Z*)-acetamidocinnamic acid and its methyl ester into the corresponding *N*-protected phenylalanine derivatives

(32) X-ray structure determination of (R,S_p)-**13**: A suitable crystal (0.18 × 0.20 × 0.71 mm) has been obtained by slow diffusion of hexanes into a CH_2Cl_2 solution of the complex at 4 °C. The compound ($C_{24}H_{23}Cl_2NO_3PPdRe$, M_r = 767.96) crystallizes in orthorhombic space group $P2_12_12_1$ (No. 19) with cell dimensions a = 9.8770(16) Å, b = 15.963(3) Å, and c = 16.074(3) Å. A cell volume of V = 2534.3(7) Å^3 and Z = 4 result in a calculated density of d_{calc} = 2.013 g cm^{-3}. 69 940 reflections have been collected in the ω mode at T = 298 K on a Bruker SMART APEX CCD diffractometer employing Mo Kα radiation (λ = 0.71073 Å). Data collection covered the range $-13 \le h \le 13$, $-21 \le k \le 21$, and $-21 \le l \le 21$ up to θ_{max} = 28.34°. Absorption correction with SADABS (μ = 5.782 mm^{-1}). The structure has been solved by direct methods as implemented in the Xtal3.7 suite of crystallographic routines[33] where GENSIN has been used to generate the structure-invariant relationships and GENTAN for the general tangent phasing procedure. 6144 observed reflections ($I > 2\sigma(I)$) have been included in the final full-matrix least-squares refinement on F involving 298 parameters and converging at $R(R_w)$ = 0.028 (0.033), $w = 1/[\sigma^2(F) + 0.0004F^2]$, S = 1.179, and a residual electron density of −0.54/1.91 e Å^{-3}. The absolute configuration has been determined using Flack's method. x_{abs} = −0.001(7)[34] for the structure shown in Figure 1a. The hydrogen positions have been calculated in idealized positions. Their U's have been fixed at 1.5 times U of the relevant heavy atom before the final refinement, and no hydrogen parameters have been refined. The crystal structure of (R,S_p)-**13** has been deposited as supplementary publication no. CCDC 229655 at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk, or http//www.ccdc.cam.ac.uk).

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were studied (Table 4). Most noteworthy is the fact that here the enantioselectivity achieved with the cyrhetrene-based complex in transformation of the free acrylic acid *exceeded* that obtained with the analogous complex bearing Josiphos **1a**. Whereas the former led to the product with 89% ee (Table 4, entry 1), the latter gave *N*-protected phenylalanine with an ee_{max} of 84% (at 1 bar of H_2 pressure).[2a] The performance of the catalyst was hydrogen pressure dependent, and although an increase in pressure led to a decrease in enantioselectivity, it was beneficial for the reaction rate (Table 4, entries 1−3). A marked difference between catalysts with either AaPhos (R,S_p)-**4** or Josiphos **1a** as ligand was finally seen in the catalytic hydrogenation of methyl acetamidocinnamate (Table 4, entries 4−6). Compared to reductions of the free acid, use of cyrhetrenyl diphosphine (R,S_p)-**4** as ligand led to the product with much lower enantioselectivity. The opposite was true for the catalysis with Josiphos **1a**. With this ferrocene-based ligand, enantioselectivities of up of 96% ee were achieved (at 1 bar of H_2 pressure), and thus here, the methyl ester reacted more selectively than the free acid.[2a] In all cases, the *R*-configured product was obtained in excess.

Overall, the catalytic behavior of complexes bearing AaPhos (R,S_p)-**4** as ligand reveals a close structural relationship between the cyrhetrenyl diphosphine and its widely and most successfully applied ferrocene-based analogue, Josiphos **1a**. The sense of asymmetric induction matches in all cases, and often the enantioselectivities come close in absolute values. We have previously shown that cyrhetrenyl phosphines are less basic than their ferrocene analogues, due to the electron-withdrawing properties of the $Re(CO)_3$ unit.[10] This decreased basicity explains the limited conversions in catalytic hydrogenations with complexes bearing (R,S_p)-**4** at low hydrogen pressure. Noteworthy is the fact that only in this reaction is the difference between the cyrethrene- and the ferrocene-based ligands apparent. In the allylic alkylation reaction, in contrast, where strongly basic phosphines are not a required, both ligands ferrocene **1a** and cyrhetrene (R,S_p)-**4** perform almost equally well.

Conclusions and Perspectives

We have designed and synthesized cyrhetrenyl diphosphine (R,S_p)-**4**, which can be considered as a structural analogue of Josiphos **1a**. The synthetic route is highly flexible and allows the steric and electronic variation on both phosphinyl substituents. The first results from applications of AaPhos (R,S_p)-**4** as ligand in asymmetric allylic alkylations and hydrogenations were very promising, yielding products with up to 95% ee. Additional modifications of the cyrhetrenyl backbone are the subject of ongoing studies. Furthermore, new catalytic applications of diphosphine (R,S_p)-**4**, amino alcohol (R,S_p)-**9**, and aminophosphine (R,S_p)-**10** are currently being explored.

Experimental Section

General Procedures. NMR spectra were recorded at 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR), and 162 MHz (^{31}P NMR) in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in ppm relative to the internal reference TMS (^{1}H NMR and ^{13}C NMR) and external 85% H_3PO_4 (^{31}P NMR). Mass spectra were measured using the EI ionization mode. IR spectra were measured as KBr pellets. Optical rotations were determined in $CHCl_3$ at ambient temperature. All manipulations except workup and purification were conducted under an Ar atmosphere using Schlenk techniques. Et_2O, toluene, and THF were distilled from sodium-benzophenone ketyl; CH_2Cl_2 and CH_3CN were dried over CaH_2 prior to use. Flash chromatography was conducted using either silica gel (40−63 μm) or alumina (activity II−III, 63−200 μm). Acetylcyrhetrene (**5**) was synthesized according to a literature procedure.[14] "Hexanes" denotes light petroleum ether (boiling range 30−60 °C), Et_2O is diethyl ether, and EtOAc is ethyl acetate. CC is column chromatography.

(*R*)-1-Hydroxyethylcyrhetrene [(*R*)-5]. (*S*)-Diphenylprolinol (2.35 g, 9.3 mmol) and methaneboronic acid (556 mg, 9.3 mmol) in toluene (20 mL) were heated to reflux for 5 h, while water was removed with a Dean-Stark trap. The solvent was then evaporated under vacuum to leave a white solid, which was directly used in the reduction. The resulting oxazaborolidine (2.56 g, 9.3 mmol) was dissolved in THF (90 mL) and cooled to 0 °C. From a syringe charged with $BH_3{\cdot}Me_2S$ (15 mL, 1 M in THF, 15 mmol), 20% of the total amount was added to the catalyst solution. After 5 min stirring, the remaining reagent and a solution of acetylcyrhetrene (**5**, 5.47 g, 14.5 mmol) in THF (50 mL) were added simultaneously over 20 min. After another 15 min at 0 °C, excess reagent was quenched by slow addition of MeOH (10 mL). After the gas evolution had ceased, the mixture was poured into saturated NH_4Cl and extracted with Et_2O. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated. The residue was purified by CC on silica gel. Elution with hexanes/Et_2O (1:1) yielded (*R*)-**6** as a colorless solid (5.44 g, 99%). The ee of the product was determined as 99.8% by chiral HPLC (Chiralcel OD, 250 × 4.6 mm^2, 0.5 mL/min, 2-propanol/*n*-heptane = 5:95, 20 °C, retention times (min) = 61.2 (*S*), 71.8 (*R*). A racemic reference sample was prepared by addition of $NaBH_4$ (2.3 mg, 0.06 mmol) to a solution of acetylcyrhetrene (76 mg, 0.2 mmol) in ethanol (5 mL), stirring 1 h at rt, quenching with water (1 mL), and the usual workup. The resulting solid (74 mg, 98%) was sufficiently pure for HPLC analysis. Analytical data for (*R*)-**6**: mp 48 °C; $[\alpha]_D$ −3.4 (*c* 0.65, $CHCl_3$). Anal. Calcd for $C_{10}H_9O_4Re$: C, 31.66; H, 2.39. Found: C, 32.03; H, 2.36. IR (KBr): $\tilde{\nu}$/cm^{-1} 3334, 2021, 1917. ^{1}H NMR: δ 1.38 (d, J = 6.3 Hz, 3H, CH_3), 1.47 (m, 1H, OH), 4.56 (q, J = 6.3 Hz, 1H, CH), 5.19 (m, 2H, Cp-H), 5.22 (m, 1H, Cp-H), 5.36 (m, 1H, Cp-H). ^{13}C NMR: δ 25.46 (CH_3), 64.16 (CH), 82.98 (Cp-CH), 83.16 (Cp-CH), 83.37 (Cp-CH), 83.90 (Cp-CH), 115.17 (Cp-C), 194.01 (CO). MS *m*/*z* (rel%): 380 (M^+, 90), 294 (100).

(*R*)-1-Dimethylaminoethylcyrhetrene [(*R*)-8]. Chlorotrimethylsilane (3.70 g, 4.36 mL, 34.1 mmol) was added dropwise to a solution of (*R*)-**6** (5.4 g, 14.2 mmol) and NaI (4.26 g, 28.4 mmol) in anhydrous MeCN (100 mL) at 0 °C. After 5 min, Me_2NH (6.4 mL, 40% in H_2O, 56.8 mmol) was added and the reaction mixture stirred for another 20 min at 0 °C. MeCN was removed under reduced pressure, then CH_2Cl_2 (100 mL) was added, and the organic layer was separated and washed with water and brine. After drying over $MgSO_4$ and removal of the solvents, the residue was purified by CC on alumina. Elution with hexanes/EtOAc (9:1) afforded (*R*)-**8** as a white solid (4.82 g, 83%, 96% ee). Crystallization from hot petroleum ether (25 mL) gave white crystals (4.09 g, 71%, >99% ee). HPLC: Chiralcel OD-H, 250 × 4.6 mm^2, 0.5 mL/min, Et_2NH/2-propanol/*n*-heptane = 0.25:0.5:99.25, 12 °C, retention times (min) = 67.3 (*R*), 73.9 (*S*). Mp: 79 °C; $[\alpha]_D$ +11.0 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{12}H_{14}NO_3Re$: C, 35.46; H, 3.47; N, 3.45. Found: C, 35.80; H, 3.52; N, 3.45. IR (KBr): $\tilde{\nu}$/cm^{-1} 3435, 2933, 2016, 1912. ^{1}H NMR: δ 1.21 (d, J = 6.9 Hz, 3H, CH_3), 2.13 (s, 6H, NCH_3), 3.46 (q, J = 6.9 Hz, 1H, CH), 5.18 (m, 1H, Cp-H), 5.26 (m, 1H, Cp-H), 5.28 (m, 1H, Cp-H), 5.32 (m, 1H, Cp-H). ^{13}C NMR: δ 16.79 (CH_3), 40.97 (NCH_3), 57.39 (CH), 81.88

(Cp-CH), 84.28 (Cp-CH), 84.64 (Cp-CH), 85.43 (Cp-CH), 108.41 (Cp-C), 194.41 (CO). MS *m*/*z* (rel%): 407 (M^+, 95), 392 (100), 363 (77).

(*R*)-1-Acetoxyethylcyrhetrene [(*R*)-7]. Acetic acid anhydride (1 mL) was added dropwise at 0 °C to a solution of (*R*)-**6** (190 mg, 0.5 mmol) in pyridine (3 mL). After stirring at rt for 16 h, the solvent was removed in a vacuum. The residue was dissolved in Et_2O and the solution washed with water and brine. After drying ($MgSO_4$) and evaporation, the residue was purified by CC on silica gel. Elution with hexanes/Et_2O (4:1) afforded (*R*)-**7** (208 mg, 99%) as a colorless liquid. $[\alpha]_D$ +47.0 (*c* 0.66, $CHCl_3$). Anal. Calcd for $C_{12}H_{11}O_5Re$: C, 34.20; H, 2.63. Found: C, 34.48; H, 2.81. IR (KBr): $\tilde{\nu}$/cm^{-1} 2022, 1917, 1740. ^{1}H NMR: δ 1.40 (d, J = 6.6 Hz, 3H, CH_3), 2.00 (s, 3H, CH_3), 5.18−5.22 (m, 2H, Cp-H), 5.38 (m, 1H, Cp-H), 5.42 (m, 1H, Cp-H), 5.60 (d, J = 6.6 Hz, 1H, CH). ^{13}C NMR: δ 21.33 (CH_3), 21.59 (CH_3), 65.63 (CH), 83.46 (Cp-CH), 83.48 (Cp-CH), 84.14 (Cp-CH), 85.33 (Cp-CH), 108.66 (Cp-C), 170.31 (CO), 193.84 (ReCO). MS *m*/*z* (rel%): 422 (M^+, 38), 365 (28), 338 (100).

Preparation of 1-Acetoxyethylcyrhetrene [(*R*)-7] from 1-Dimethylaminoethylcyrhetrene [(*R*)-8] and Subsequent Hydrolysis to 1-Hydroxyethylcyrhetrene [(*R*)-6]. Amine (*R*)-**8** (50 mg, 0.12 mmol, >99% ee) in degassed acetic anhydride (1 mL) was kept at 105 °C for 2 h. After removal of Ac_2O in a vacuum, CC as described above gave (*R*)-**7** (51 mg, 98%). The analytical data, including the value of the specific rotation, was in accordance with (*R*)-**7**, prepared as described above from (*R*)-**6**. 1-Acetoxyethyl cyrhetrene [(*R*)-**7**, 51 mg, 0.12 mmol] was dissolved in MeOH/H_2O (1:1, 5 mL), then Me_2NH (3 mL, 40% in H_2O) was added. After stirring at rt for 3 h, the reaction mixture was extracted with Et_2O (20 mL). Drying ($MgSO_4$), evaporation, and CC of the residue gave (*R*)-hydroxyethylcyrhetrene [(*R*)-**8**] as a white solid (44 mg, 96%, >99% ee by HPLC).

(*R*,*S*$_p$)-2-(1-Dimethylaminoethyl)(1-hydroxy-1,1-diphenyl)methylcyrhetrene [(*R*,*S*$_p$)-9]. The same procedure as described in the synthesis of (*R*,*S*$_p$)-**10** was used, except that benzophenone served as electrophile. After workup, the residue was purified by CC on silica gel. Elution with hexanes/EtOAc (9:1) afforded the major diastereoisomer (*R*,*S*$_p$)-**9** as a white solid (70%). Mp: 131 °C; $[\alpha]_D$ −42.7 (*c* 0.43, $CHCl_3$). Anal. Calcd for $C_{25}H_{24}NO_4Re$: C, 51.01; H, 4.11; N, 2.38. Found: C, 51.19; H, 4.39; N, 2.31. IR (KBr): $\tilde{\nu}$/cm^{-1} 3440, 2016, 1918. ^{1}H NMR: δ 0.93 (d, J = 6.6 Hz, 3H, CH_3), 1.86 (s, 6H, NCH_3), 3.73 (q, J = 6.9 Hz, 1H, CH), 4.97 (m, 2H, Cp-H), 5.17 (m, 1H, Cp-H), 7.13−7.32 (m, 6H, Ph-H), 7.43−7.45 (m, 2H, Ph-H), 7.67−7.70 (m, 2H, Ph-H), 8.46 (br s, 1H, OH). ^{13}C NMR: δ 7.80 (CH_3), 39.01 (NCH_3), 55.98 (CH), 76.52 (C), 78.30 (Cp-CH), 82.99 (Cp-CH), 91.43 (Cp-CH), 111.07 (Cp-C), 114.58 (Cp-C), 127.22 (Ph-CH), 127.30(Ph-CH), 127.45 (Ph-CH), 127.77 (Ph-CH), 127.99 (Ph-CH), 128.09 (Ph-CH), 146.66 (Ph-C), 146.71 (Ph-C), 194.30 (CO). MS *m*/*z* (rel%): 589 (M^+, 73), 574 (84), 467 (28), 286 (100).

(*R*,*S*$_p$)-2-(1-Dimethylaminoethyl)diphenylphosphinocyrhetrene [(*R*,*S*$_p$)-10]. To a degassed solution of (*R*)-**8** (4.09 g, 10.1 mmol) in Et_2O (150 mL) was added dropwise *n*-BuLi (7.6 mL of a 1.6 M solution in hexane, 12.1 mmol) at −15 °C. The reaction mixture was stirred at this temperature for 15 min, then Ph_2PCl (3.35 g, 2.72 mL, 15.2 mmol) was added. After 10 min at −15 °C the reaction was quenched with saturated $NaHCO_3$ solution (20 mL). The organic phase was washed with 10% NaOH, water, and brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by CC on alumina. Elution with hexanes/Et_2O (4:1) afforded the major diastereoisomer (*R*,*S*$_p$)-**10** as a white solid (3.67 g, 62%). Mp: 115 °C; $[\alpha]_D$ −165.0 (*c* 1.0, $CHCl_3$). Anal. Calcd for $C_{24}H_{23}NO_3PRe$: C, 48.81; H, 3.93; N, 2.37. Found: C, 48.95; H, 4.31; N, 2.31. IR (KBr): $\tilde{\nu}$/cm^{-1} 3425, 2016, 1632. ^{1}H NMR: δ 1.01 (d, J = 6.6 Hz, 3H, CH_3), 1.76 (s, 6H, NCH_3), 4.05 (dq, J = 6.6 and 2.8 Hz, 1H, CH), 5.04 (m, 1H, Cp-H), 5.07 (m, 1H, Cp-H), 5.43 (m, 1H, Cp-H), 7.19−7.41 (m, 10H, Ph-H). ^{13}C NMR: δ 8.86 (CH_3), 39.02 (NCH_3), 55.76 (d, J = 6.1 Hz, CH), 79.16 (Cp-CH), 86.17 (d, J = 2.3 Hz, Cp-CH), 94.26 (d, J = 6.8 Hz, Cp-CH), 97.92 (d, J = 22.2 Hz, Cp-C), 119.35 (d, J = 21.4 Hz, Cp-C), 127.99 (d, J = 7.7 Hz, Ph-CH), 128.24 (Ph-CH), 128.59 (d, J = 7.6 Hz, Ph-CH), 129.21 (Ph-CH), 132.58 (d, J = 19.9 Hz, Ph-CH), 134.68 (d, J = 20.6 Hz, Ph-CH), 137.15 (d, J = 9.2 Hz, Ph-C), 138.49 (d, J = 7.6 Hz, Ph-C), 193.89 (CO). ^{31}P NMR: δ −24.55. MS *m*/*z* (rel%) 591 (M^+, 98), 576 (57), 520 (100), 462 (54).

(*R*,*S*$_p$)-2-(1-Dicyclohexylphosphinoethyl)diphenylphosphinocyrhetrene, Bisborane Adduct [(*R*,*S*$_p$)-11]. Ethyl chloroformate (217 mg, 0.19 mL, 2.0 mmol) was added dropwise to a solution of (*R*,*S*$_p$)-**10** (590 mg, 1.0 mmol) in THF (25 mL) at −40 °C. The reaction mixture was allowed to warm to rt and stirred for 6 h. Dicyclohexylphosphine (496 mg, 0.5 mL, 2.5 mmol), followed by $TlPF_6$ (872 mg, 2.5 mmol), was added to the reaction mixture. After stirring overnight, BH_3·THF (25 mL of a 1 M solution in THF, 25 mmol) was added via syringe, and stirring was continued for 4 h until completion of the reaction. The solvent was evaporated, and the residue was purified by CC. Elution with hexanes/EtOAc (4:1) afforded the bisborane adduct (*R*,*S*$_p$)-**11** as a white solid (734 mg, 95% yield). Mp: 250 °C (dec); $[\alpha]_D$ −14.7 (*c* 0.58, $CHCl_3$). Anal. Calcd for $C_{34}H_{46}B_2O_3P_2Re$: C, 52.86; H, 6.00. Found: C, 52.87; H, 5.70. IR (KBr): $\tilde{\nu}$/cm^{-1} 3453, 2931, 2373, 2024, 1937, 1916. ^{1}H NMR (C_6D_6): δ 0.44−1.43 (m, 25 H, 10 × CH_2, 2 × CH and CH_3), 1.43−2.30 (br s, 6 H, 2 × BH_3), 3.65 (dq, J = 7.4 and 3.0 Hz, 1H, CH), 4.12 (m, 1H, Cp-H), 4.38 (m, 1H, Cp-H), 5.50 (m, 1H, Cp-H), 6.60−6.87 (m, 6H, Ph-H); 7.32−7.39 (m, 2H, Ph-H); 7.51−7.58 (m, 2H, Ph-H). ^{13}C NMR (C_6D_6): δ 23.29 (d, J = 23.6 Hz, CH), 25.82 (d, J = 9.1 Hz, CH_2), 26.12 (CH_2), 26.73 (d, J = 21.3 Hz, CH_2), 26.76 (d, J = 4.5 Hz, CH_2), 26.93 (d, J = 7.7 Hz, CH_2), 27.65 (CH_3), 28.74 (CH_2), 30.33 (d, J = 26.7 Hz, CH), 33.26 (d, J = 30.5 Hz, CH), 79.52 (d, J = 4.6 Hz, Cp-CH), 88.76 (d, J = 51.9 Hz, Cp-C), 92.77 (Cp-CH), 93.58 (Cp-CH), 122.91 (dd, J = 7.2 and 15.0 Hz, Cp-C), 128.52 (d, J = 9.9 Hz, Ph-CH), 128.72 (d, J = 9.1 Hz, Ph-CH), 130.31 (Ph-C), 130.92 (Ph-C), 131.28 (d, J = 2.2 Hz, Ph-CH), 131.33 (d, J = 2.2 Hz, Ph-CH), 132.89 (d, J = 9.9 Hz, Ph-CH), 133.41 (d, J = 9.2 Hz, Ph-CH), 192.28 (CO). ^{31}P NMR (C_6D_6): δ 10.81 (br s), 41.00 (br s). MS *m*/*z* (rel%): 759 (M^+ − BH_3, 6), 757 (100), 716 (22).

(*R*,*S*$_p$)-2-(*P*-Borane-1-dicyclohexylphosphinoethyl)-diphenylphosphinocyrhetrene [(*R*,*S*$_p$)-12]. Bisborane diphosphine (*R*,*S*$_p$)-**11** (155 mg, 0.2 mmol) was stirred in degassed Et_2NH (5 mL) at rt for 1 h. The reaction mixture was concentrated and redissolved in CH_2Cl_2 (10 mL). After washing with water (5 mL), drying ($MgSO_4$), and evaporation, (*R*,*S*$_p$)-**12** (151 mg, 99%) remained as white solid. Mp: 165 °C (dec); $[\alpha]_D$ −121.8 (*c* 0.65, $CHCl_3$). Anal. Calcd for $C_{34}H_{43}BO_3P_2Re$: C, 53.83; H, 5.71. Found: C, 53.72; H, 5.99. IR (KBr): $\tilde{\nu}$/cm^{-1} 3436, 2920, 2378, 2028, 1944, 1909. ^{1}H NMR (C_6D_6): δ 0.38−2.04 (m, 28 H, 10 × CH_2, 2 × CH, CH_3 and BH_3), 3.65 (dq, J = 7.4 and 3.0 Hz, 1H, CH), 4.12 (m, 1H, Cp-H), 4.38 (m, 1H, Cp-H), 5.50 (m, 1H, Cp-H), 6.60−6.87 (m, 6H, Ph-H), 7.32−7.39 (m, 2H, Ph-H), 7.51−7.58 (m, 2H, Ph-H). ^{13}C NMR (C_6D_6): δ 9.99 (CH_3), 22.19 (dd, J = 11.4 and 23.3 Hz, CH), 24.02 (CH), 24.70 (d, J = 10.2 Hz, CH_2), 25.07−25.91 (m, 4 × CH_2), 26.26 (CH_2), 26.47 (d, J = 10.2 Hz, CH_2), 27.07 (d, J = 10.2 Hz, CH_2), 30.94 (d, J = 23.3 Hz, CH), 78.18 (Cp-CH), 90.04 (Cp-CH), 91.77 (d, J = 5.9 Hz, Cp-CH), 96.29 (d, J = 21.5 Hz, Cp-C), 119.88 (d, J = 26.3 Hz, Cp-C), 127.45 (d, J = 6.6 Hz, Ph-CH), 127.49 (PH-CH), 127.64 (d, J = 4.8 Hz, Ph-CH), 128.78 (Ph-CH), 132.11 (d, J = 19.2 Hz, Ph-CH), 133.33 (d, J = 22.1 Hz, Ph-CH), 135.99 (d, J = 7.2 Hz, Ph-C), 138.06 (d, J = 7.2 Hz, Ph-C), 192.35 (CO). ^{31}P NMR (C_6D_6): δ −30.55, 39.88 (br s). MS (CI) *m*/*z* (rel%): 760 (M^+ + 1, 1), 757 (14), 549 (25), 79 (100).

(*R*,*S*$_p$)-2-(1-Dicyclohexylphosphinoethyl)diphenylphosphinocyrhetrene [(*R*,*S*$_p$)-4]. Method A, Direct Preparation. Starting from aminophosphine (*R*,*S*$_p$)-**10** (590 mg, 1

mmol), the procedure as described for the synthesis of (R,S_p)-**11** was followed, without addition of borane. The solvent was removed in high vacuum, and the residue purified by CC on deactivated silica gel under argon. Elution with degassed hexanes/Et_2O/NEt_3 (50:1:1 → 50:2.5:1) afforded (R,S_p)-**4** as a white solid (189 mg, 25%) after evaporation of the solvents. The low yield was caused by separation problems (unreacted PCy_2H) and product instability. As the product is rather air and light sensitive in solution, all manipulation should be conducted quickly under argon. After isolation, the diphosphine was kept at −20 °C.

Method B, Deprotection of Bisborane Adduct (R,S_p)-11. HBF_4·Me_2O (536 mg, 4.0 mmol) was added slowly to a degassed solution of bisborane adduct (R,S_p)-**11** (155 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) at −5 °C. After stirring at rt for 2 h, the mixture was diluted with degassed Et_2O (4 mL) and quenched with saturated aqueous $NaHCO_3$ (5 mL). The resulting biphasic mixture was stirred vigorously for 10 min and the upper organic phase transferred via cannula into a Schlenk tube containing $MgSO_4$. The dried solution was transferred into another Schlenk tube. Concentration in vacuo afforded the free diphosphine (R,S_p)-**4** as a white solid (112 mg, 75%). Mp: 111 °C (dec); $[\alpha]_D$ −162.2 (*c* 0.18, $CHCl_3$); HRMS calcd for $C_{34}H_{40}O_3P_2Re$ 745.2010, obsd 745.2012. IR (KBr): $\tilde{\nu}$/cm^{-1} 3437, 2928, 2020, 1926. ^{1}H NMR (C_6D_6): δ 0.76−1.88 (m, 25 H, 10 × CH_2, 2 × CH, CH_3), 3.32 (m, 1H, CH), 4.12 (m, 1H, Cp-H), 4.56 (m, 1H, Cp-H), 4.75 (m, 1H, Cp-H), 6.72−6.88 (m, 6H, Ph-H); 7.10−7.14 (m, 2H, Ph-H); 7.24−7.27 (m, 2H, Ph-H). ^{13}C NMR (C_6D_6): δ 15.70 (CH_3), 25.22 (d, J = 16.8 Hz, CH_2), 25.60 (d, J = 8.4 Hz, CH), 25.71−26.45 (4 × CH_2), 28.20 (d, J = 6.9 Hz, CH_2), 28.70 (d, J = 6.9 Hz, CH_2), 30.04 (d, J = 15.3 Hz, CH_2), 30.24 (d, J = 23.6 Hz, CH), 31.88 (d, J = 22.1 Hz, CH_2), 32.10 (d, J = 19.8 Hz, CH), 78.14 (Cp-CH), 84.05 (Cp-CH), 92.58 (d, J = 6.1 Hz, Cp-CH), 94.08 (d, J = 16.0 Hz, Cp-C), 123.99 (d, J = 24.4 Hz, Cp-C), 125.99 (Ph-CH), 126.53 (d, J = 8.4 Hz, Ph-CH), 127.31 (d, J = 8.4 Hz, Ph-CH), 128.17 (Ph-CH), 131.81 (dd, J = 3.1 and 17.6 Hz, Ph-CH), 133.55 (d, J = 22.1 Hz, Ph-CH), 13762. (d, J = 9.2 Hz, Ph-C), 137.84 (d, J = 11.4 Hz, Ph-C), 192.65 (CO). ^{31}P NMR (C_6D_6): δ −29.78 (d, J = 39.7 Hz), 17.89 (d, J = 39.7 Hz). MS *m*/*z* (rel%): 745 (M^+, 4), 716 (100), 661 (91).

Dichloro-[(R,S_p)-2-(1-dimethylaminoethyl)diphenylphosphinocyrhetrene]palladium(II) [(R,S_p)-13]. A solution of (R,S_p)-**10** (118 mg, 0.2 mmol) and [$PdCl_2$(COD)] (57.1 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) was stirred 2 h at rt. The solvent was removed in a vacuum and the residue recrystallized from $CHCl_3$ to afford yellow crystals of (R,S_p)-**13** (130 mg, 85%). Mp: 191 °C (dec); $[\alpha]_D$ +277.5 (*c* 0.28, $CHCl_3$). Anal. Calcd for $C_{24}H_{23}Cl_2NO_3PPdRe$: C, 37.54; H, 3.02; N, 1.82. Found: C, 37.45; H, 3.34; N, 1.74. IR (KBr): $\tilde{\nu}$/cm^{-1} 3441, 2027, 1927. ^{1}H NMR: δ 1.18 (d, J = 6.4 Hz, 3H, CH_3), 2.73 (s, 3H, NCH_3), 3.32 (s, 3H, NCH_3), 3.50 (q, J = 6.4 Hz, 1H, CH), 5.24 (m, 1H, Cp-H), 5.31 (m, 1H, Cp-H), 5.57 (m, 1H, Cp-H), 7.34−7.61 (m, 8H, Ph-H), 8.40−8.47 (m, 2H, Ph-H). ^{13}C NMR: δ 9.84 (CH_3), 41.02 (NCH_3), 50.28 (NCH_3), 61.12 (d, J = 6.6 Hz, CH), 81.24 (d, J = 6.0 Hz, Cp-CH), 85.32 (d, J = 7.2 Hz, Cp-CH), 87.64 (d, J = 37.1 Hz, Cp-C), 93.56 (Cp-CH), 115.15 (d, J = 17.4 Hz, Cp-C), 125.76 (d, J = 73.0 Hz, Ph-C), 126.59 (d, J = 52.0 Hz, Ph-C), 127.62 (d, J = 12.6 Hz, Ph-CH), 128.27 (d, J = 11.9 Hz, Ph-CH), 130.74 (Ph-CH), 132.41 (Ph-CH), 132.56 (d, J = 10.8 Hz, Ph-CH), 135.28 (d, J = 13.7 Hz, Ph-CH), 190.22 (CO). ^{31}P NMR: δ 13.67. MS *m*/*z* (rel%): 591 (M^+ − $PdCl_2$, 71), 262 (100).

General Procedure for the Asymmetric Pd-Catalyzed Allylic Alkylation Reaction. The ligand (0.01 mmol, 1 mol %) and [Pd(η^3-C_3H_5)Cl]$_2$ (1.8 mg, 0.005 mmol, 1 mol % Pd) were stirred in degassed CH_2Cl_2 (1 mL) to give a pale yellow solution. Subsequently, (*E*)-1,3-diphenylprop-2-ene-1-yl acetate (252 mg, 1 mmol), dimethyl malonate (390 mg, 0.34 mL, 3 mmol), BSA (610 mg, 0.74 mL, 3 mmol), and a few milligrams of KOAc were added. The reaction mixture was degassed and then stirred at rt. When the reaction was complete (TLC monitoring), Et_2O (15 mL) was added and the organic layer washed twice with saturated NH_4Cl solution and dried over $MgSO_4$. After removal of the solvent, the residue was purified by CC on silica gel. Elution with hexanes/EtOAc (9:1) afforded the product as an oil. The enantiomer ratio was determined by HPLC (Chiralcel AD, 250 × 4.6 mm^2, 0.5 mL min^{-1}, 2-propanol/*n*-heptane = 5:95, 20 °C, retention times (min) = 26.9 (*R*), 37.4 (*S*)).

General Procedure for the Rh-Catalyzed Asymmetric Hydrogenation. Under argon, a small tube was charged with 4.5 mg (0.006 mmol) of diphosphine (R,S_p)-**4** and 1.6 mg of [Rh(COD)$_2$]BF_4 (0.004 mmol) and sealed with a rubber septum. Dry MeOH (1 mL) was added and the resulting orange solution stirred for 30 min. The substrate was added as a 0.4 M solution (1 mL, 0.4 mmol) and the tube placed into an argon-filled 100 mL autoclave. The septum was removed, and the autoclave was sealed, filled with hydrogen, and vented three times before pressurizing to 5−50 bar of hydrogen. The reaction mixture was stirred for 24 h at rt. Reaction times were not optimized. After evaporation of the solvent, the residue was passed through a short silica gel plug using hexane/EtOAc (3:1) as eluent (Et_2O in the case of acetamidocinnamates). Acids were converted to their methyl esters with etheral CH_2N_2 prior to filtration. The conversion was determined by ^{1}H NMR or GC, and the enantiomer ratio by HPLC using a chiral column. Conditions for the HPLC analysis: 2-methylsuccinic acid dimethyl ester: Daicel Chiralcel OD-H column, 215 nm, 20 °C, 0.5 mL·min^{-1}, *n*-heptane/2-propanol, 96:4, retention times (min) = 13.7 (*R*), 21.6 (*S*);[40] *N*-acetyl phenylalanine methyl ester: Daicel Chiralcel OD-H column, 254 nm, 20 °C, 0.6 mL·min^{-1}, *n*-heptane/2-propanol, 90:10, retention times (min) = 17.1 (*R*), 23.8 (*S*).[40]

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Supporting Information Available: Experimental details for the X-ray crystal structure determination (crystal data, data collection, solution, refinement, definitions), atomic positional and isotropic displacement parameters, atomic displacement parameters, bond distances, bond angles, and dihedral angles for (R,S_p)-**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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