Novel Chiral Bidentate η^5-Cyclopentadienylphosphine Ligands: Their Asymmetric Induction at the Ruthenium(II) Center and Application in Catalysis

Barry M. Trost,* Bernat Vidal, and Marc Thommen[a]

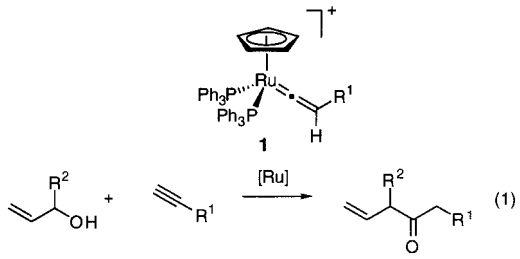
Abstract: The syntheses of four classes of novel ruthenium(II) complexes with chiral bidentate cyclopentadienylphosphine ligands and their application in asymmetric catalysis are described. This approach to an enantioselective reconstitutive condensation was assisted by molecular modeling to deal with the question of asymmetric induction at the metal center and lead to a more precise understanding of the enantiodiscriminating step. The catalysts were routinely tested towards the enantioselective reconstitutive condensation of ethyl undecynoate and cyclohexyl-2-propen-1-ol to provide ethyl 12-cyclohexyl-11-oxo-13-tetradecenoate.

Keywords: atom economy · enantioselective catalysis · homogeneous catalysis · ruthenium · transition metals

Introduction

Apart from catalytic hydrogenation,[1] asymmetric reactions catalyzed by ruthenium are almost unknown.[2] Thus, little impetus existed for developing chiral, enantiomerically pure ruthenium complexes. Nevertheless, the metal as a stereogenic center in cyclopentadienylruthenium complexes has been studied to some extent.[3] These studies also reveal some of the anticipated problems for designing such asymmetric ruthenium complexes in terms of the interconversion of diastereomers by loss of stereochemistry at the metal center.

Our interest in the organic processes catalyzed by ruthenium complexes led to a need for optically active chiral cyclopentadienyl complexes.[2a] While chiral cyclopentadienyl complexes of many metals have been made, complexes of ruthenium that possess chiral pockets were virtually unknown at the initiation of our study.[3–5] We considered this question in the context of vinylidene ruthenium complexes such as **1**, which are intermediates in what we have termed a reconstitutive addition reaction as outlined in Equation (1).[6] Influencing the enantiodiscriminating step in order to achieve asymmetric induction requires control of three stereogenic centers during the catalytic cycle (Scheme 1), the ruthenium, the metalla-allene, and the π-allyl unit, or at least of the rate at which reactions proceed through the manifold set of possible diastereomeric transition states. Obviously, the large number of variables make such a task quite daunting. Nevertheless,



the novelty of the process wherein an α-alkylated-β,γ-unsaturated ketone is formed solely by the addition of a terminal alkyne and an allyl alcohol make this goal quite significant. Access to these systems asymmetrically in such a simple fashion does not exist, yet the juxtaposition of functionalities thus created imparts versatility to these compounds as intermediates in synthetic strategies.

Exploration of several types of asymmetric cyclopentadienyl complexes (**2**–**4**) has begun contemporaneously with our work.[5] In relation to our reaction [Eq. (1)], complex **3** is reported to be ineffective for performing the reaction[5b] and complex **2** is stated to give an optically active product but of indeterminate enantiomeric excess.[5c] The very recently reported study of complex **4** emphasizes the difficulty of the task as stated above.[5a] In a catalytic reaction, a low yield of the product of reconstitutive addition of only 25% *ee* forms. On the other hand, by stoichiometrically preforming a single diastereomeric vinylidene complex and then treating it with an allyl alcohol, up to 65% *ee* could be obtained. Clearly, the multiple and variable stereogenic centers involved in the catalytic cycle have major ramifications for asymmetric induction in this ruthenium-catalyzed reaction.

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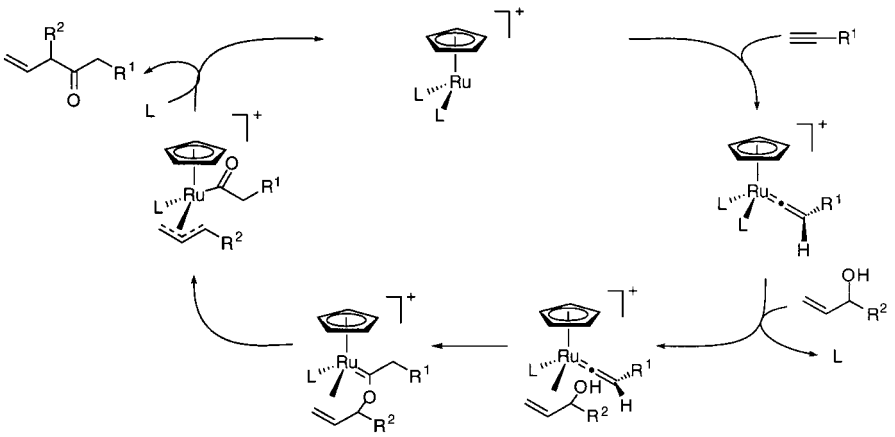
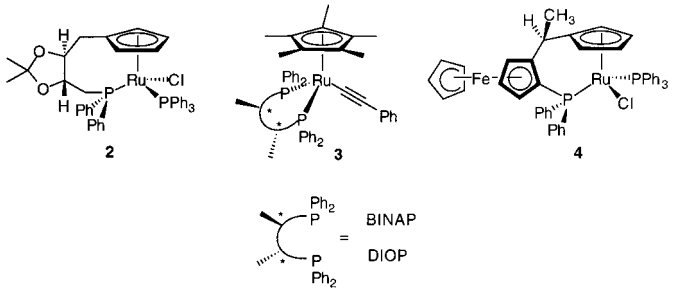


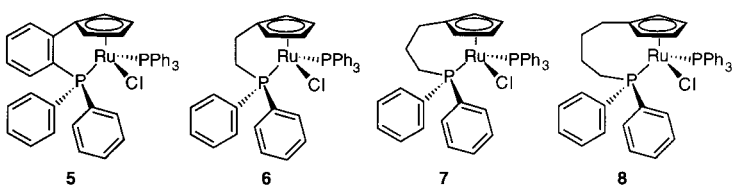
Scheme 1. Catalytic cycle of reconstitutive addition.



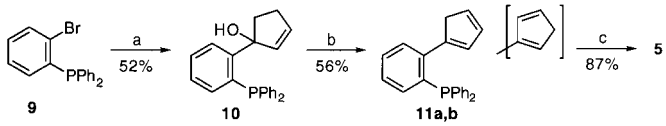
The design of chiral ligands for ruthenium in these reactions could not employ bisphosphine ligands like **3** since, as our initial studies revealed, bidentate phosphines shut down the reaction.[6] Examination of the catalytic cycle (Scheme 1) suggests the reason: loss of one of the phosphines, which is inhibited by the bidentate coordination, must occur during the process. In fact, the proposed catalytic cycle suggests that retaining one phosphine on ruthenium throughout the cycle is desirable. Tethering it to the cyclopentadienyl unit might be a good way to rigidify the system and thereby limit some of the degrees of freedom. In a systematic approach, we first determined the tether length of the ligand that leads to maximum yield for the reconstitutive addition reaction of terminal alkynes and allyl alcohols. On the basis of that information and supported by molecular modeling, we then designed, prepared, and tested four different classes of chiral ligands. The synthesis and characterization of these novel complexes, the extent of chiral induction at the ruthenium(II) center, and their preliminary application as catalysts for the asymmetric reconstitutive condensation are described herein.

Results and Discussion

Effect of tether length: In order to first study and optimize the yield as a function of the tether length we prepared the complexes **5**–**8** according to published or new procedures.



The ligand syntheses were known in the cases of **6** and **7**.[7, 8] The preparation of complex **5** (Scheme 2) began with (2-bromophenyl)diphenylphosphine (**9**), which was prepared from 1,2-dibromobenzene in 71% yield following a known protocol.[9] Dehydration of the addition product with 2-cyclopentenone **10** led to the desired ligand **11a,b** as a mixture of double-bond isomers.[4a] To obtain complex **5** we heated a 1:1 mixture of **11a,b** with $[(Ph_3P)_3RuCl_2]$ at 90 °C in 1,2-

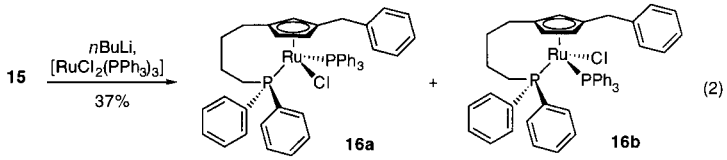


Scheme 2. Preparation of benzo linker complex **5**: a) *n*BuLi, 2-cyclopentenone; b) cat. *p*-TsOH acid, CH_2Cl_2; c) $(Ph_3P)_3RuCl_2$, DCE, 90 °C.

dichloroethane (DCE) as described by Slawin and Williams.[10]

The preparation of complex **8**, began with iodosilyl ether **12** (Scheme 3) prepared from THF as previously described.[11] In order to obtain good yields of **14a,b** we introduced the diphenylphosphino moiety before the thermally labile cyclopentadiene unit. However, the diarylphosphine substituent required a borane protection – deprotection sequence in order to deal with its high air-sensitivity.[12] The intermediate **13** could then be prepared, purified, and handled without extra caution. Alkylation of sodium cyclopentadienide proceeded satisfactorily after liberation of the diphenylphosphino unit to give **14a,b**. In contrast to the other complexes, **8** was only obtained in a reasonable yield when the cyclopentadienide salt of **14a,b** was formed with *n*-butyllithium in toluene at low temperature prior to the addition of $[(PPh_3)_3RuCl_2]$ at room temperature and followed by heating to 90 °C for 1 h to give complex **8** in 38% overall yield.

The preparation of a tethered phosphine ligand possessing a substituted cyclopentadienyl complex was also pursued as shown in Scheme 3 and Equation (2). Alkylation of lithium



benzylcyclopentadienide with mesylate **13** gave the 1,3-disubstituted cyclopentadienes as a mixture of three isomers **15a,b,c**. Following the protocol outlined for **8**, the ruthenium complex was obtained as a 1:1 mixture of two diastereomers **16a** and **16b** that could be separated by flash chromatography.

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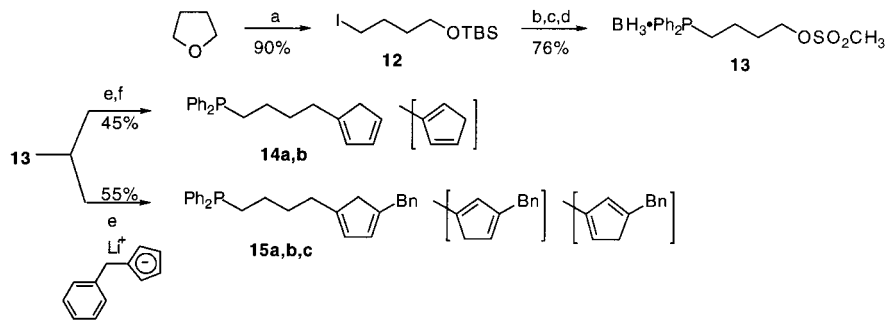
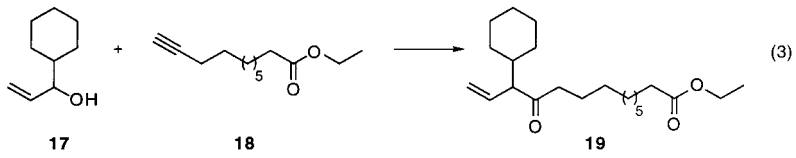


Scheme 3. Preparation of butano linker ligands: a) NaI, TBSCl, CH_3CN; b) $LiPPh_2$, THF, then $BH_3 \cdot THF$; c) TBAF, THF; d) methanesulfonyl chloride, CH_2Cl_2, NEt_3; e) $HBF_4 \cdot (CH_3)_2O$, CH_2Cl_2; f) NaCp, THF.

The assignment of the relative stereochemistry derived from the upfield ^{13}C shifts for the benzylic carbon and C-1 of the cyclopentadiene ring due to the proximity to the coordinated triphenylphosphine unit in diastereomer **16a** ($\delta = 24.6$ and 100.6) compared to **16b** ($\delta = 22.6$ and 88.8). Furthermore, the signal for C-1 in the ^{13}C NMR spectrum of **16a** showed coupling to phosphorus (11.7 Hz), which was absent in the spectrum of **16b**.

These complexes were tested for their reactivity for the reconstitutive addition using allyl alcohol **17** and alkyne **18**, as shown in Equation (3). The reaction was performed under a new set of conditions by heating a toluene solution of the reactants with 10% of the Ru complex and 15% indium triflate in toluene at 90 °C for 6 h. The results are summarized



(3)

in Table 1 and compared to the standard catalyst (entry 1). All of the tethered complexes effected reaction more slowly than the standard complex; however, the effects were much more dramatic for the two- (entries 2 and 3) and three- (entry 4) carbon linkers. Comparison of entries 2 and 3 suggest that some part of the effect was due to electronic effects of switching from a triarylphosphine to an alkyldiaryl phosphine (entry 2 vs. 3). The GC analyses of entries 2–4 indicated a number of additional side products, whereas the same analyses of the reactions of entries 1, 5, and 6 indicate clean formation of ketone **19**. Thus, the four-carbon tether is a significantly better linker than either a two- or three-carbon tether. Improvement in the reactivity of a four-carbon tether would undoubtedly derive from conversion of the diarylalkylphosphine to a triarylphosphine moiety by analogy to the differential reactivity of **6** vs. **5**. Additional steric hindrance created by substitution on the cyclopentadienyl ring as in **16a** and **16b** led to a significant loss of reactivity (entry 6) although the reaction remained selective for formation of the β,γ-unsaturated ketone.

Table 1. Effect of tether on reconstitutive addition.[a]

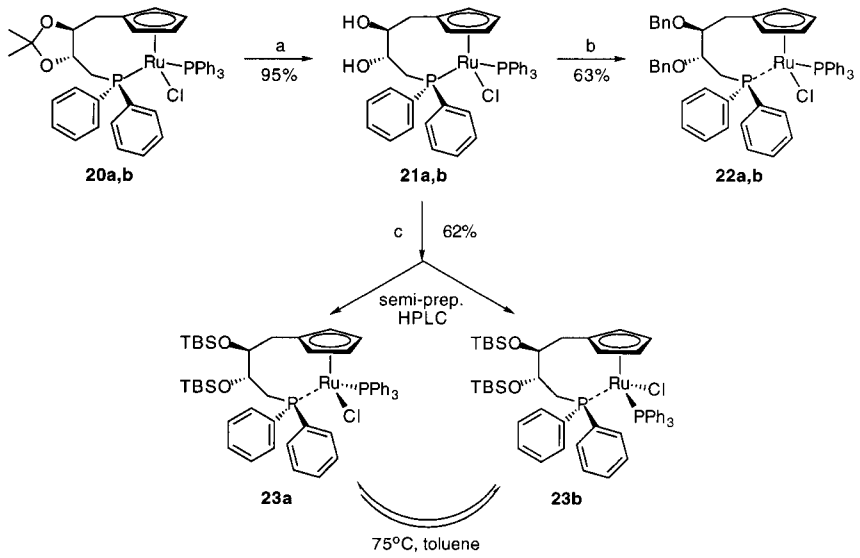
Entry	Catalyst	% Consumption alkyne	% Yield **19**[c]
1	$[CpRu(PPh_3)_2Cl]$	100	78
2	C-2 linker **5**	41	(26) [63]
3	C-2 linker **6**	23	(11) [48]
4	C-3 linker **7**	56	(30) [54]
5	C-4 linker **8**	95	59 [62]
6	C-4 linker **16**	33	20 [61]

[a] All reactions performed with a 4:1 ratio of **17:18** with 10 mol% Ru complex and 15 mol% indium triflate in toluene at 90 °C for 6 h. [b] Determined by GC. [c] Simply stated numbers are yields for isolated pure products; numbers in parentheses are yields determined by GC; numbers in brackets are yields based upon recovered starting materials.

Chiral ruthenium complexes: Given that a four-carbon tether resulted in the best reactivity of the tethered phosphines, we focused our efforts on the synthesis of chiral ruthenium complexes rigidified by a four-carbon tether. We initiated our studies with the complex derived from the readily available tartrate-derived linker shown in Scheme 4. The initial complex **20** forms as a 1.5:1.0 diastereomeric mixture at ruthenium.

Since the degree of stereochemical bias at the metal center may influence the enantioselectivity, we wanted to ascertain whether modification of the diol-protecting groups might influence this ratio. The simplest protocol proved to be direct modification at the complex, since attempts to modify the uncomplexed ligand were fruitless. Cleavage of the acetonide with aqueous hydrochloric acid required use of ethanol rather than methanol because decomposition only occurred in the latter case. The dibenzyl ether complex **22a,b** was prepared by a typical Williamson ether synthesis with potassium hydride as base. The complex still existed as a 1.5:1 ratio of diastereomers. Derivatization with *tert*-butyldimethylsilyl triflate gave a 2.5:1 ratio of the diastereomeric complexes **23a** and **23b**. In this case, the two diastereomeric complexes could be separated by preparative HPLC. While they are reasonably stable at room temperature, heating either one in toluene at 80 °C restores the 2.5:1 ratio, thereby suggesting it is the thermodynamic ratio. This demonstrated equilibration at a lower temperature than is typical for the reconstitutive addition suggests that Curtin–Hammett conditions will prevail with respect to the diastereochemical issues at the metal center. Nevertheless, those stereochemical issues will contribute differently to the transition state for the desired reaction. Thus, we wanted to design a ligand which would generate a complex with a higher thermodynamic bias for one of the two diastereomers.

Given that the syntheses of chiral ligands were multistep processes, we decided to aid our process by using molecular modeling with SPARTAN/SYBIL software. To test the approach, we examined the conformational minima for complexes **20a** and **20b**. Figure 1 depicts the calculated



Scheme 4. Tartrate-derived complexes: a) HCl(aq), EtOH; b) BnBr, KH, DME; c) TBSOTf, di-*tert*-butylpyridine, CH_2Cl_2.

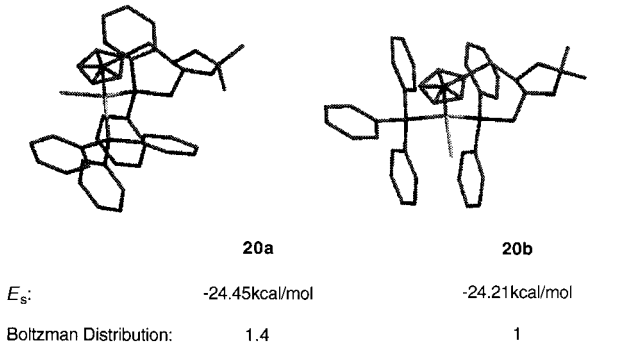


Figure 1. Molecular modeling of CpRu complexes **20a,b** derived from tartrate distereomeric ligands.

lowest energy conformations for the two diastereomeric complexes. The calculated energy difference of 0.24 kcal mol^{-1} corresponds to a 1.4:1 ratio which nicely reproduces the experimentally observed 1.5:1 ratio. The dibenzobicyclo[2.2.2]octyl scaffold in ligand **24a,b** introduces the dihydroanthranceno moiety as a steric barrier which should enhance the steric bias. Figure 2 depicts the calculated lowest energy conformations for the two diastereomeric Cp ruthenium chloride complexes **25a** and **25b**. The energy difference of 2.91 kcal mol^{-1} suggests a 50:1 ratio.

Scheme 5 depicts the synthesis of the ligand. The Diels–Alder adduct **26** between maleic anhydride and anthracene was reduced to the lactone **27** with sodium borohydride. Treatment with lithium diphenylphosphide[13] led to the product of ring opening, **28**, which was subjected directly to excess borane[14] in THF which simultaneously protected the phosphine and reduced the carboxylic acid to the alcohol **29**. Since deprotection of the phosphine after alkylation with cyclopentadiene led to decomposition, the deprotection was performed prior to the alkylation. Deprotection of the tosylate **30** proceeded best with fluoroboric acid–dimethyl ether complex.[12a] Normally, the resulting crude tosylate, which can potentially self-alkylate at phosphorus, was directly reacted with sodium cyclopentadienide or lithium benzylcyclopentadienide to give **24a,b** or **31a,b,c** as mixtures of double-bond isomers. Because of the complications of characterization of such mixtures, the corresponding

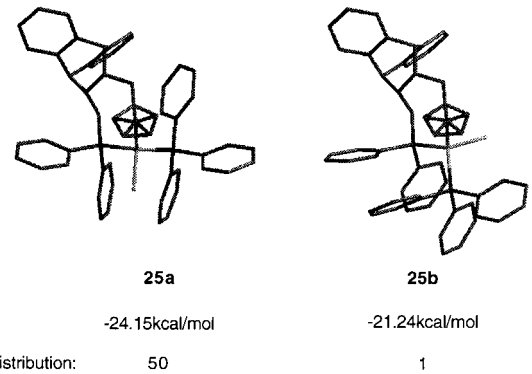
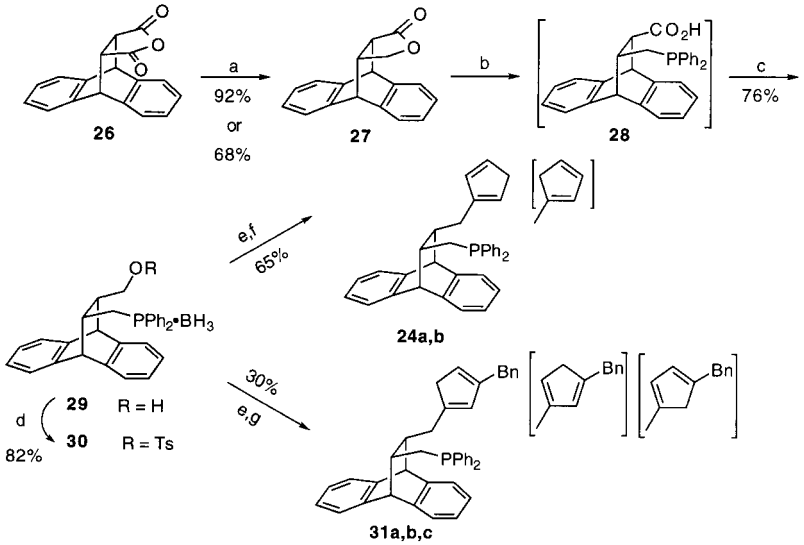


Figure 2. Molecular modeling of CpRu complexes **25a,b** from anthracene-derived distereomeric ligands.



Scheme 5. Synthesis of anthracene-derived distereomeric ligands: a) $NaBH_4$, THF; or $LiAlH_4$, (*R*)-(+)-BINOL, EtOH, THF; b) $LiPPh_2$, THF; c) $BH_3 \cdot THF$, THF; d) *p*-tosyl chloride, pyridine, CH_2Cl_2; e) $HBF_4 \cdot (CH_3)_2O$, CH_2Cl_2; f) NaCp, THF.

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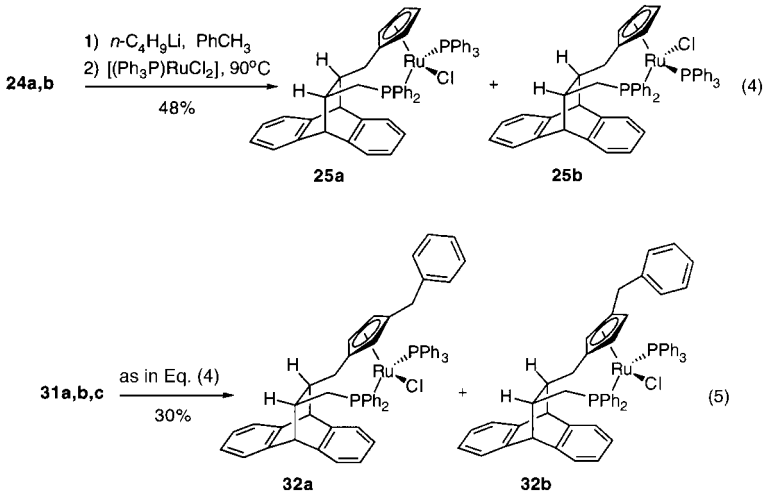


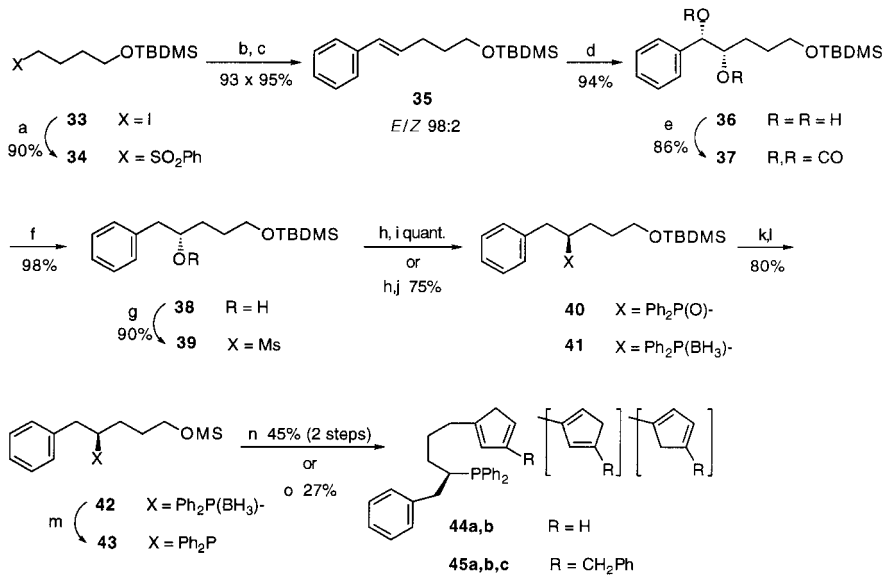
ruthenium complexes **25** and **32** were prepared as shown in Equations (4) and (5).

To obtain the optically active ligands, the anhydride was asymmetrically reduced with Noyori's BINOL-modified LAH.[15] After a single recrystallization from ethyl acetate, the lactone **27** was isolated in 68% yield; it had an *ee* of 91%. In agreement with the results of molecular modeling, formation of the ruthenium complex from **24a,b** gave a significantly enhanced diastereomeric ratio of 11:1 for the two diastereomeric complexes **25a,b**.

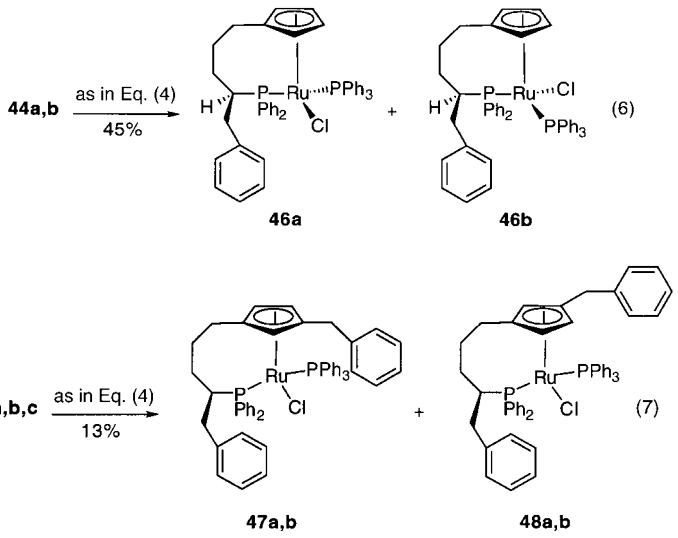
Formation of the Ru complex with the benzyl-substituted ligand **31a,b,c** gave only two out of the four possible complexes in a 1.6:1 ratio. The presence of two complexes could not be discerned by ^{31}P NMR spectroscopy, which detected only one pair of doublets. On the other hand, the ^{1}H NMR spectrum clearly revealed the presence of two diastereomers. Combined with observations of good diastereoselectivity at the Ru center in Equation (4), the presence of only one set of ^{31}P signals leads us to conclude that the stereochemistry at ruthenium is the same in both complexes. Thus, the two diastereomers differ from each other in terms of the coordination with the two enantiotopic faces of the cyclopentadienyl rings which leads to the structural assignments as **32a** and **32b**.

In a third class of chiral, enantiomerically enriched ligands we sought to place the chirality of the scaffold closer to the phosphorus and thus the ruthenium. Whereas the tartrate-derived ligands placed the stereogenic centers at the middle two carbons of the four-carbon tether, we wanted to place the stereogenic center on the phosphine-bearing carbon of the four-carbon tether. Scheme 6 outlines the ligand syntheses. Julia olefination[16] provided **35** with good (*E*)-olefin geometry (*E*:*Z* 98:2) setting the stage for an excellent asymmetric dihydroxylation[17] (97% *ee* by chiral HPLC) to form diol **36**. To minimize complications due to the presence of a diol, we chose to remove the benzylic hydroxyl group by hydrogenolysis. Direct hydrogenolysis of the diol failed[18] but the cyclic carbonate **37** smoothly hydrogenolyzed to form the monoalcohol **38**. The corresponding mesylate **39** underwent smooth displacement with lithium diphenylphosphide to give an unstable phosphine. The corresponding phosphine oxide **40** was easily isolated upon workup and analyzed by chiral HPLC to verify that the *ee* remained 97%. On the other hand, workup of the phosphine substitution with borane gave the stable complex **41**. Following the previous protocols, the mesylate **42** was deprotected to the free phosphine **43** prior to reaction with sodium cyclopentadienide to give **44** or lithium benzylcyclopentadienide to give **45**.

Coordination of these ligands with ruthenium followed the same protocol as before and gave the asymmetric ruthenium complexes **46** and **47**, as shown in Equations (6) and (7). The advantage of placing the stereogenic center closer to the phosphine metal-binding site is immediately obvious as the diastereomeric ratio of the complexes increased to 5:1, compared with the poor results for the various tartrate-

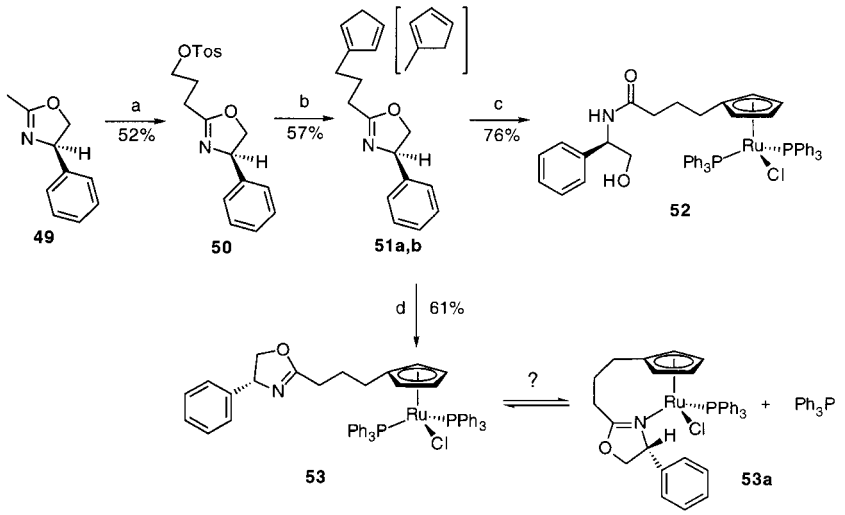


Scheme 6. Synthesis of 2-benzyl-substituted C-4 tethered ligand: a) $PhSO_2Na$, DMF; b) *n*BuLi, THF, $-78\,^{\circ}C$, then PhCHO folllowed by PhCOCl; c) 5% Na(Hg), NaH_2PO_4, THF; d) $(DHQD)_2PHAL$, $K_3Fe(CN)_6$, OsO_4, 1:1 *t*BuOH:H_2O; e) $(imidazole)_2CO$, PhH; f) H_2, 10% Pd/C, C_2H_5OAc; g) CH_3SO_2Cl, $(C_2H_5)_2N$, CH_2Cl_2; h) Ph_2PLi, THF, $-50\,^{\circ}C$ to RT; i) air, THF; j) $BH_3\cdot$THF, THF; k) TBAF, THF; l) CH_3SO_2Cl, $(C_2H_5)_3N$, CH_2Cl_2; m) $HBF_4\cdot O(CH_3)_2$, CH_2Cl_2; n) CPNa, THF; o) $PhCH_2CpLi$, THF.



derived ligands. On the basis of steric considerations, the major diastereomer is tentatively assigned as **46a**. The benzylcyclopentadiene ligand gave a complex mixture of all four diastereomeric complexes **47a,b** and **48a,b**. The complexity of the spectra made the determination of the exact ratio impossible.

For a final class of chiral complexes, we envisioned the prospect of replacing phosphorus complexation by nitrogen during a catalytic cycle. Maintaining the concept of a four-carbon tether, we designed complex **53a**. The cyclopentadienyl oxazoline is easily available as shown in Scheme 7.



Scheme 7. Oxazoline-based complex: a) *n*BuLi, ethylene oxide, THF; then *p*-TsCl, pyridine, CH_2Cl_2; b) NaCp, THF; c) $[RuCl_2(PPh_3)_3]$, CH_2ClCH_2Cl; d) *n*BuLi, toluene, $[RuCl_2(PPh_3)_3]$.

Starting from (*R*)-(−)-phenylglycinol and triethylorthoacetate, the corresponding oxazoline **49** was obtained in 73% yield.[19] The two-carbon chain extension was achieved with ethylene oxide, and the resulting alkoxide trapped with tosyl chloride in situ to give tosylate **50**.[20] The lability of the oxazoline ring is evident in its ease of hydrolysis to the hydroxyamide **52** during complexation without preformation of a cyclopentadienide anion. On the other hand, preformation of the lithium salt as usual does give the desired complex **53**. No evidence for nitrogen coordination in the neutral complex exists. For example, the ^{31}P NMR spectrum in toluene at 100 °C shows no dissociated triphenylphosphine.

Catalytic reconstitutive addition: With a range of chiral ruthenium complexes now available, we began a preliminary examination of their effectiveness as catalysts for the reconstitutive addition and the degree of chiral recognition. While the complex **2** has been claimed to effect the reconstitutive addition, no *ee* was recorded. We examined the reaction illustrated in Equation (3) as a test case using a new set of conditions recently developed in these laboratories. Using racemic chiral allyl alcohol **17**, terminal alkyne **18**, and 15 mol% indium triflate as a cocatalyst, we obtained a 72% yield of the desired product **19**. Increasing the amount of indium cocatalyst to 20 mol% decreased the yield to 55%. In both cases, however, the *ee* was 10–11%. Replacing indium triflate with silver triflate gave similar results. Replacing the acetonide by the benzyl groups as in complex **22** still gave good yields (56%) but low *ee*, 14%. Curiously, the major enantiomer in this case was the mirror image of that obtained in the acetonide case! On the other hand, the silyl ether complex **23** was virtually unreactive.

Surprisingly, the dihydroanthracenyl complex **25** gave good yields (61%) but low *ee*, 11%, quite the same as the simple series. The more bulky benzylcyclopentadiene complex **32** saw the conversion drop so that a 45% yield [but 80% based upon recovered starting material (brsm)] was obtained. Gratifyingly, the *ee* jumped to 30%. Similar results were obtained with complex **46** as catalyst: 45% yield and 25% *ee*. The benzyl analogues of this complex **47** and **48**, as well as the oxazoline complex **53** and its hydrolysis product **52**, gave both low reactivity and *ee*.

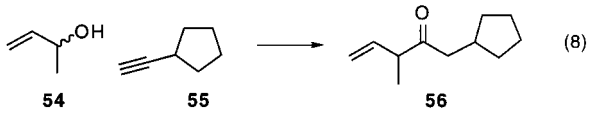
To probe whether anything unusual was happening with the chosen test reaction, we also examined the reaction summarized in Equation (8). The same general conditions as above with chiral ligand **25** gave a fine yield (74%) of β,γ-unsaturated ketone (**56**). The *ee* of 20% approximately doubled that seen for the reaction of Equation (3).

Because the product is a β,γ-unsaturated ketone, the possibility that the low *ee* stemmed from racemization was considered. Including ketone **19** of 46% *ee* in a reaction between phenylacetylene and racemic alcohol **17** gave the expected reconstitutive addition product as well as a 91% recovery of ketone **19**. Importantly, the recovered **19** retained an enantiomeric excess of 46%, a fact which indicates product racemization is not significant under the reaction conditions.

Since racemic alcohol is being used as substrate, the initial π-allyl complex may also not discriminate between the diastereotopic (enantiotopic) faces of the allyl fragment. To

0947-6539/99/0503-1060 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 3

get a good *ee*, scrambling between these two faces must be fast relative to the reductive elimination. We therefore tested this issue in order to determine whether this factor may be the source of the low *ee*. By means of kinetic resolution, the enantiomerically pure alcohols **17R** and **17S** were obtained and established to have >98% *ee*. The reaction of Equation (3) with **17R** gave the

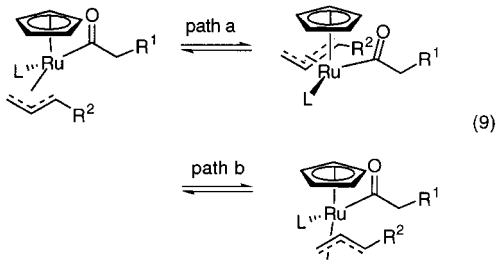


(8)

ketone **19** in 80% yield but only with 21% *ee*. The major enantiomer had an absolute configuration *opposite* to that obtained using racemic alcohol. On the other hand, the reaction with **17S** gave ketone **19** in 76% yield with an *ee* of 47%. In this case, the absolute configuration of **19** was the same as that obtained from the reaction with racemic **17**. Thus, clearly, facial equilibration of the π-allylruthenium intermediate occurs, but it is competitive with but not faster than the reductive elimination. Therefore, there is a matched and mismatched case.

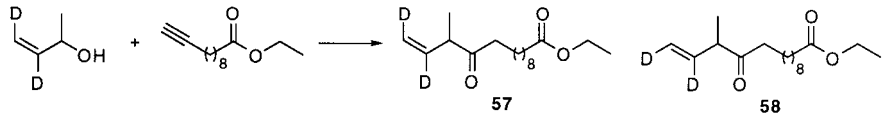
Performing the same experiment with the dihydroanthracenyl complex **25** gave a much different result. In this case, **17R** gave ketone **19** in 75% yield and with 6% *ee*, but the absolute configuration of the major enantiomer was the same as that obtained from racemic alcohol. The alcohol **17S** gave almost the same result, a 72% yield of **19** of 8% *ee* and possessing the same absolute configuration. With this more sterically demanding ligand, we are almost at the stage where facial equilibration is faster than reductive elimination. On the other hand, chiral complex **46** gave 49% *ee* with **17R** and 18% *ee* with **17S**, both in 45% yield.

Facial equilibration may be coupled with inversion at the metal center [Eq. (9), path a] or with *syn*/*anti* isomerization [Eq. (9), path b]. A most likely mechanism for the latter

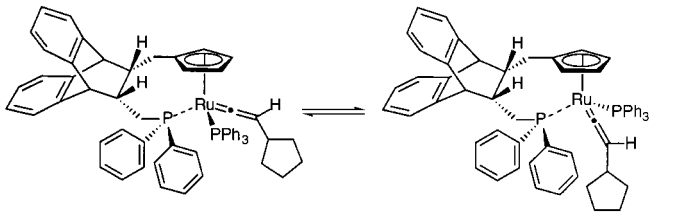


(9)

invokes a π–σ–π interconversion. To pursue this question, we examined the use of *trans*-3,4-dideutero-3-buten-2-ol as the alcohol substrate. When the dihydroanthracenyl complex was used, a 68:32 mixture of the *trans* and *cis* dideutero ketone products **57** and **58** were obtained [Eq. (10)]. Thus, in contrast to the reaction with $[CpRu(PPh_3)_2Cl]$ as catalyst wherein complete scrambling occurred, significant retention of the alkene geometry is observed. Thus, facial equilibration occurs by at least two pathways with this ligand, paths a and b of Equation (9).



The vinylidene complex offers another opportunity for stereochemical issues that can influence *ee*. The vinylidene complex between cyclopentylacetylene and ruthenium complex **25** was formed in $[D_8]$toluene in a NMR tube. The initial vinylidene complex showed two sets of AB patterns in the ^{31}P NMR spectrum at $\delta = 43.7$ (d, $J = 27.5$ Hz), 43.0 (d, $J = 42.9$ Hz), and $\delta = 42.2$ (d, $J = 27.5$ Hz), 39.2 (d, $J = 42.9$ Hz) in the same 11:1 ratio as starting complex. On the other hand, heating this mixture to 100° equilibrates this mixture to nearly 1:1. Thus, the equilibrium depicted in Equation (11) appears



(11)

to be fast under the conditions of the reconstitutive addition. Such an equilibration offers an alternative explanation for the formation of the two diastereomeric complexes of Equation (9), path a. Thus, a direct equilibration as depicted in Equation (9) may not be occurring.

Discussion and Conclusions

As the use of ruthenium for catalysis beyond asymmetric hydrogenation expands, the need for chiral enantiomerically pure ruthenium complexes increases. In creating such complexes, inducing the stereochemistry at the metal too is significant. This goal has been achieved with several novel enantiomerically enriched complexes described herein. Structural features whereby ligand stereochemistry may induce stereochemistry at ruthenium have been illustrated. Furthermore, molecular modeling has proven useful in designing a ligand in which such stereochemical induction occurs to a high degree and thereby encourages its more extensive use in ligand design.

These studies have also been quite illuminating with respect to the reconstitutive addition of alkynes and allyl alcohols. Tethering one phosphine to the cyclopentadienyl unit is permissible, depending upon tether length. This result is consistent with one phosphine remaining in the coordination sphere of the ruthenium throughout the catalytic cycle. The stereochemical biases of the starting ruthenium complexes appear to be decoupled from the asymmetric induction in the reaction. On the other hand, creation of an enhanced chiral pocket by placing a second substituent on the cyclopentadienyl ring does have a beneficial effect on the chiral recognition.

The results clearly show that the stereochemical issues associated with this reaction are complex. Stereomutation at

ruthenium[21] as well as with respect to the axial chirality of the vinylidene ligand[22] both appear to be fast. Thus, with respect to these two stereochemical issues, it appears we will be operating under Curtin–Hammett conditions. Clearly, the facial discrimination in the formation of the π-allylruthenium complexes and their rates of interconversion will undoubtedly be issues to resolve. The results reported herein clearly indicate that the rates of these processes are competitive with the stereochemical determining step and the ligand has a significant effect on these rates as well. Thus, control of chiral space around the ruthenium while maintaining catalytic activity that would control the formation and the subsequent reductive elimination of the π-allyl intermediate would appear to be the key for good enantioselectivity. We are continuing to pursue such designs.

Experimental Section

General comments: All reactions were performed in oven-dried glassware, under an atmosphere of dry nitrogen if not stated otherwise. Commercially available chemicals and solvents were purified by standard methods prior to use. For reactions involving transition metals, the solutions were deoxygenated by bubbling a stream of dry nitrogen through them for 10 to 20 min prior to syringe transfer into the reaction container. Organic solutions were routinely dried with anhydrous magnesium sulfate, unless otherwise noted.

NMR spectra were recorded at room temperature in $CDCl_3$ unless otherwise stated, using either the Varian Gemini-300, Varian Gemini-200 or EM-400 instruments as stated (δ). For new ligands and their ruthenium complexes ^{31}P NMR spectra were recorded on EM-400 using 85% H_3PO_4 as the external standard with downfield values taken as positive (δ, couplings in Hz). IR spectra were recorded on a Perkin Elmer FT-IR as neat films on NaCl plates or as KBr pellets for solid products (μ, cm^{-1}). Elemental analyses were performed by M-H-W Laboratories (USA). HRMS (EI) *m/z* and as well as MS (EI, FAB) *m/z* spectra were recorded by the Mass Spectrometer Facility of the School of Pharmacy, University of California, San Francisco (USA) (mass, % of most intense fragment). Optical rotations were measured with a Jasco DIP-360 digital polarimeter, in 5 cm cells, in the solvent specified. Melting points were determined with a Thomas Hoover capillary apparatus and are uncorrected. The melting points of the organometallic complexes were determined by means of tubes that were sealed under nitrogen. TLC was performed on glass plates precoated with Merck F_{254} silica gel 60. Flash column chromatography was performed with Merck silica gel 60 or Fluka neutral aluminum oxide with the solvents indicated. For analytical HPLC a Microsorb Silica Si-80-125-C5 (Rainin Instruments) column, 4.6 mm diameter, spherical 10^{-8} m pore size, was used. For semipreparative HPLC a Microsorb Silica Si-80-199-C5 column (Rainin Instruments), 10.0 mm diameter, spherical 10^{-8} m pore size, was used with UV detection at 254 nm unless otherwise stated. Solvent mixtures, flow rates, pressure, sample concentration, mL per injection, and retention times are given. For analytical chiral HPLC chiral pack AD or chiral cell OD colums were used as stated. UV detection at the wavelength specified. Solvent mixtures, flow rates, and retention times are given.

$[(C_5H_5)(PPh_3)_2RuCl_3]$ was prepared from $[RuCl_3 \cdot (H_2O)_x]$ $(1 < x < 3)$, PPh_3 and freshly distilled cyclopentadiene according to a described procedure, on a 7 g scale.[23] $[(PPh_3)_3RuCl_2]$ was conveniently prepared on a 4.5 g scale from $[RuCl_3 \cdot (H_2O)_x]$ $(1 < x < 3)$ and PPh_3 in methanol following a known procedure.[24] The filtration was carried out under N_2. When dry, the complex could be handled in air without significant decomposition.

Lithium benzylcyclopentadienide: Benzyl bromide (2 g, 11.7 mmol) was dissolved in THF (13 mL) and cooled to 0 °C. Then CpNa (6.43 mL, 2 M in THF, 12.86 mmol) was slowly added and the mixture was stirred at room temperature for 1.5 h. Water (20 mL) was added and, after extraction (3 × 100 mL ether) and concentration of the dry (Na_2SO_4) extracts, the residue was chromatographed (silica gel, petroleum ether) to give 800 mg (45%) of benzyl cyclopentadiene as a mixture of two double-bond isomers at the Cp ring. R_f: 0.5 (pentane); IR: $\tilde{\nu} = 1601, 1494, 1452, 1365\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.22$ (m, 5H), 6.40 (s, Cp), 6.25 (m, Cp), 6.15 (m, Cp), 6.00 (m, Cp), 3.73 (s, 0.8H), 3.70 (s, 1.2H), 2.97 (s, 1.2H), 2.85 (s, 0.8H).

n-Butyllithium (3.85 mL, 1.6 M in hexanes, 6.15 mmol) was added to a solution of benzyl cyclopentadiene (800 mg, 5.13 mmol) in THF (10 mL) at 0 °C. The resulting yellow mixture was allowed to warm to room temperature and was further stirred for 30 min until a deep red solution is formed.

Ligand syntheses:

1-[(2-Diphenylphosphino)phenyl]-2-cyclopenten-1-ol (10):[9] Compound **9** (200 mg, 0.59 mmol) dissolved in diethyl ether (2 mL) at room temperature was slowly added to a solution of *n*-butyllithium in hexane (1.6 M, 0.37 mL, 0.59 mmol). After an additional 10 min of stirring at room temperature, the mixture was cooled to −10 °C, at which point 2-cyclopentenone (48.4 mg, 0.59 mmol) was added dropwise. After 90 min at −5 to 0 °C, the cooling bath was removed and the solution stirred for another 2 h at room temperature. Prior to the quenching of the reaction mixture with aqueous hydrochloric acid (1 M, 1 mL), the flask was again cooled to 0 °C. The mixture was neutralized by addition of aqueous sodium hydroxide (1 M, 1 mL). Extraction with diethyl ether, drying, evaporation of the solvent, and subsequent flash chromatography (silica gel, 2:5 diethyl ether/hexane) led to 105 mg (52%) of **10** as a white foam that proved to be rather unstable and sensitive to air and moisture and therefore was used directly. R_f 0.15 (2:5 diethyl ether/hexane); ^1H NMR (300 MHz): $\delta = 7.38–7.17$ (m, 13H), 7.16–7.10 (m, 2H), 6.09–5.97 (m, 2H), 3.97(m, 1H, OH), 2.62–2.39 (m, 2H), 2.38–2.26 (m, 1H), 2.25–2.14 (m, 1H).

(2-Cyclopentadienylphenyl)diphenylphosphine (11a,b): *p*-Toluenesulfonic acid monohydrate (88 mg, 0.463 mmol) was added at room temperature to **10** (1.387 g, 4.03 mmol), dissolved in dry methylene chloride (40 mL). The reaction mixture was worked up immediately upon complete consumption of starting material as indicated by tlc by filtering through a plug of silica gel using 4:1 pentane/ether mixture (30 mL) as the solvent. Evaporation of the solvent provided 740 mg (56%) of **11a,b** as a clear colorless oil, which upon standing at room temperature slowly turned reddish under a nitrogen atmosphere. R_f 0.60 (1:2 diethyl ether/hexane); ^1H NMR (300 MHz, 2 double-bond isomers): $\delta = 7.42–7.10$ (m, 14.73H), 7.01–6.92 (m, 0.73H), 6.66–6.62 (m, 0.54H), 6.43–6.37 (m, 0.73H), 6.16–6.10 (m, 0.54H), 3.31 (s, 0.27H), 3.06–3.02 (m, 1.46H).

[4-(Methanesulfonyl)-1-butyl]diphenylphosphine–borane (13): Diphenylphosphine (5.5 g, 29.57 mmol) was added to degassed THF (150 mL). At −35 °C, a 1.6 M solution of *n*-butyllithium in THF (18.48 mL, 29.57 mmol) was added with exclusion of light. After the addition was complete, the orange-red solution was allowed to warm to room temperature and stirred for 2 h at which time **12** (6.20 g, 19.7 mmol) was added by syringe at room temperature over 10 min.[11] The mixture was stirred for 1 h before it was carefully quenched with degassed ice-water and extracted with degassed diethyl ether. After drying and evaporation (under Ar), 7.3 g of a semisolid crude product was obtained. This crude material was dissolved in THF (150 mL, degassed with Ar) and treated with borane/dimethyl sulfide (5.10 g, 68 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h. The quenching was most efficiently done by cannula transfer into a separating funnel filled with water (50 mL), ice (50 g), and diethyl ether (50 mL). The extraction was carried out with three portions of diethyl ether (30 mL). After drying and evaporation, the desired, now air-stable, crude semisolid white material (7.50 g, 98%) was obtained and used for the following step without further purification.

A solution of TBAF (1 M, 60 mL, 60 mmol) in THF was added to the crude silyl ether (7.50 g, 19 mmol) dissolved in THF (150 mL) at 0 °C. The mixture was then allowed to warm to room temperature and stirred for 12 h. After evaporation of the solvent, the crude oil was directly chromatographed on silica gel (1:1 pet. ether/diethyl ether, then pure diethyl ether) to give 4.80 g (89% from **12**) of alcohol as a clear colorless oil. $R_f = 0.40$ (diethyl ether); IR: $\tilde{\nu} = 3379, 2382, 1899, 1813, 1436\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.70–7.40$ (m, 10H), 3.62 (t, $J = 6.0$, 2H), 2.25 (m, 2H), 1.63 (m, 4H), 1.42 (br s, 1H), 1.40–0.50 (br m, 3H); ^{13}C NMR (75 MHz): $\delta = 132.2$ ($J_{PC} = 9.0$), 131.2, 129.5 ($J_{PC} = 60.0$), 128.9 ($J_{PC} = 10.0$), 62.1, 33.7 ($J_{PC} = 14.0$), 25.4 ($J_{PC} = 37.0$), 19.5; ^{31}P NMR (161.903 MHz): $\delta = 18.77$ (br); HRMS: calcd for $C_{16}H_{19}OP$ $[M^+ - BH_3]$: 258.1173; found: 258.1157.

To the primary alcohol (1.0 g, 3.68 mmol) dissolved in methylene chloride (40 mL) cooled to 0 °C was added triethyl amine (2.03 g, 20.1 mmol, 2.8 mL) followed by methanesulfonyl chloride (1.27 g, 11.1 mmol,

0947-6539/99/0503-1062 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 3

0.85 mL). After 30 min at 0 °C and 45 min at room temperature, the reaction was recooled to 0 °C, poured into aqueous hydrochloric acid (1N, 50 mL) and extracted three times with methylene chloride (50 mL). After washing with satd aqueous sodium bicarbonate and drying, the solvents were evaporated and the resulting crude oil was chromatographed on silica gel (CH_2Cl_2) to give 1.10 g (86% yield) of the mesylate **13** as a clear, colorless, viscous oil. $R_f = 0.65$ (CH_2Cl_2); IR: $\tilde{\nu} = 3058$, 2939, 2381, 1968, 1899, 1820, 1437, 1353 cm^{-1}; ^1H NMR (400 MHz): $\delta = 7.75 - 7.62$ (m, 4H), 7.53 – 7.41 (m, 6H), 4.19 (t, $J = 6.3$, 2H), 2.96 (s, 3H), 2.30 – 2.20 (m, 2H), 1.90 – 1.81 (m, 2H), 1.72 – 1.63 (m, 2H), 1.41 – 0.55 (br m, 3H); ^{13}C NMR (100 MHz): $\delta = 132.1$ ($J_{PC} = 8.9$), 131.3, 129.3 ($J_{PC} = 60.0$), 128.9 ($J_{PC} = 9.7$), 68.8, 37.4 30.1 ($J_{PC} = 13.4$), 25.0 ($J_{PC} = 37.5$), 19.3; ^{31}P NMR (161.903 MHz): $\delta = 16.6$ and 16.2 (br); HRMS: calcd for $C_{17}H_{24}BO_3PS$ [M^+]: 349.1199; found: 349.1187.

(4-Cyclopentadienyl-1-butyl)diphenylphosphine (**14a,b**): Fluoroboric acid dimethyl ether complex (2.96 g, 22.1 mmol, 2.69 mL) was added to **13** (1.1 g, 3.15 mmol) dissolved in methylene chloride (30 mL, degassed, Ar) at −15 °C. Stirring was continued overnight with slow warming to room temperature. The mixture was diluted with degassed methylene chloride (30 mL) and degassed satd aqueous sodium bicarbonate (80 mL). After stirring the mixture vigorously for 20 min, the aqueous phase was extracted three times with degassed methylene chloride. After washing with degassed brine and drying, the solvents were evaporated (under Ar) to give 890 mg (84% yield) of the rather air-sensitive phosphine intermediate as a colorless oil, which was not further characterized.

After suspension of the liberated phosphine (890 mg, 2.65 mmol) in degassed (Ar) THF (50 mL) at 0 °C, was added a solution of sodium cyclopentadienide, 2M in THF (10 mL, 20 mmol). After warming to room temperature and stirring for 45 min, the reaction was quenched with degassed aqueous sodium bicarbonate and extracted with degassed methylene chloride followed by drying, evaporation (under Ar), and chromatography (silica gel, 1:1 degassed pet. ether/diethyl ether) to give 435 mg (45% yield) of the desired heat- and air-sensitive ligand **14a,b** as a yellowish oil. $R_f = 0.85$ (7:3 pet. ether/diethyl ether); IR: $\tilde{\nu} = 1951$, 1879, 1813, 1586, 1481, 1433, 1366, 898, 738 cm^{-1}; ^1H NMR (400 MHz): $\delta = 7.45 - 7.21$ (m, 10H), 6.49 (s, Cp), 6.25 – 6.21 (m, Cp), 6.10 (s, Cp), 5.95 (s, Cp), 2.92 (s, Cp), 2.83 (s, Cp), 2.43 – 2.32 (m, 2H), 2.06 (t, $J = 8.1$, 2H), 1.73 – 1.57 (m, 2H), 1.53 – 1.43 (m, 2H); ^{13}C NMR (100 MHz) (both double-bond isomers are present; J_{PC} could not be properly assigned for all the carbon signals): $\delta = 146.8$, 138.9, 138.8, 134.6, 133.7, 132.2 ($J_{PC} = 18.2$), 132.4, 130.5, 128.4, 128.3, 128.3, 126.3, 125.9, 43.2, 41.2, 31.1 ($J_{PC} = 12.8$), 30.3, 30.2 ($J_{PC} = 8.9$), 29.4, 27.9 ($J_{PC} = 11.1$), 25.8 ($J_{PC} = 10.9$), 25.6 ($J_{PC} = 10.5$); ^{31}P NMR (161.903 MHz): δ −15.5 and −15.6 (two double-bond isomers); HRMS: calcd for $C_{21}H_{23}P$ [M^+]: 306.1537; found: 306.1540.

2,3-(9,10-Dihydro-9,10-anthracenediyl)-γ-butyrolactone (**27**): *Racemic*: A solution of the anhydride **26** (1.00 g, 3.62 mmol) in THF (15 mL) was added to a suspension of sodium borohydride (138 mg, 3.62 mmol) in THF (1 mL) at 0 °C over 10 min. Removal of the ice bath followed by stirring at room temperature for 1 h led to complete conversion of the starting material. The reaction mixture was quenched with aqueous hydrochloric acid (6M, 1.5 mL) at 0 °C followed by water (10 mL) and ether (20 mL). Extraction with ether, drying, and evaporation provided 1.1 g of a crude white solid that was recrystallized from ethyl acetate to give 680 mg in a first and 220 mg in a second crop for a total yield of 880 mg (92%). M.p. 225 °C (ref. [25] 226 °C).

2R,3S**: A solution of abs. ethanol (800 mg,17.4 mmol) in THF (24 mL) was added to a 0 °C suspension of 95% LAH (700 mg, 17.5 mmol) in THF (24 mL) followed by (*R*)-(+)-BINOL (5.00 g, 17.5 mmol) in THF (70 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 h before it was cooled to −78 °C, at which point the anhydride **26** (1.05 g, 3.80 mmol) in THF (24 mL) was slowly added to the white cloudy mixture. After 6 h at −78 °C, the mixture was allowed to reach room temperature overnight, quenched at 0 °C with 10% aqueous hydrochloric acid (10 mL), and poured onto methylene chloride (250 mL). This mixture was washed three times with brine, dried and evaporated to give 5.76 g of a white powder. The crude solid was dissolved in a minimum volume of methylene chloride and transferred onto a silica gel flash column. Elution with 1:4 ethyl acetate/pet. ether afforded 4.95 g (99% recovery) of BINOL (same 99% *ee* as before the reaction, checked by chiral HPLC) and 645 mg (68%) of the enantiomerically enriched lactone **27** (81% *ee* by chiral HPLC), m.p. 231 °C, $[\alpha]_D = +58.4(16)$ ($c = 2.1$, $CHCl_3$), that could be recrystallized from ethyl acetate in the fridge (91% *ee*, 1 recrystallization with 69% recovery). $R_f = 0.30$ (1:4 ethyl acetate/pet. ether). For the subsequent transformations, the 81% *ee* material was used. IR: $\tilde{\nu} = 1764$, 1458, 1379 cm^{-1}; ^1H NMR (300 MHz): $\delta = 7.40 - 7.28$ (m, 4H), 7.23 – 7.11 (m, 4H), 4.71 (d, $J = 3.3$, 1H), 4.35 (t, $J = 9.2$, 1H), 4.28 (d, $J = 3.2$, 1H), 3.79 (dd, $J = 9.5$, 4.0, 1H), 3.19 (dd, $J = 10.5$, 3.5, 1H), 3.12 – 3.03 (m, 1H); ^{13}C NMR (100 MHz): $\delta = 176.3$, 142.3, 141.6, 139.9, 138.7, 127.1, 126.8, 126.5, 126.5, 125.6, 125.1, 124.1, 123.9, 70.0, 47.5, 47.2, 45.7, 40.3; chiral HPLC: AD column, 1.0 mL flow, detection 254 nm, 9/1 *n*-heptane/isopropanol, retention times: major isomer 13.5 min, minor isomer 12.24 min.

[(2*R,3*S**)-2,3-(9,10-Dihydro-9,10-anthracenediyl)-4-(*p*-toluenesulfonyloxy)-1-butyl]diphenylphosphine – borane** (**30**): Diphenylphosphine (437 mg, 2.35 mmol) and a solution of *n*-butyllithium (1.5M, 1.64 mL, 2.464 mmol) in hexanes at 0 °C was added to degassed (Ar) THF (20 mL). After warming to room temperature and stirring for 2 h, the orange-red solution was treated with the solid lactone **27** (410 mg, 1.56 mmol) at room temperature, whereupon the color slowly started to fade and the lactone gradually dissolved. After stirring overnight, the solution was quenched with degassed ice-water and extracted twice with degassed methylene chloride. The aqueous phase was then acidified with degassed aqueous hydrochloric acid (2M) and extracted twice more with degassed methylene chloride. Drying and evaporation provided 680 mg of the crude diphenylphosphinocarboxylic acid derivative **28**, which was taken on directly to the reduction – protection step with $THF \cdot BH_3$. After dissolution of the acid in degassed (Ar) THF (10 mL) at −10 °C, a solution of $THF \cdot BH_3$ (1M, 40 mL, 40 mmol) was added by syringe over 10 min. After the addition was complete, the cooling bath was removed and the reaction stirred overnight at room temperature, and then carefully transferred by cannula into a beaker containing ice-water. When all the excess BH_3 was quenched, the mixture was diluted with ethyl acetate and satd aqueous sodium chloride solution. Upon stirring, the white suspension gradually disappeared and a clear phase separation was apparent. Extraction with ethyl acetate (4 × 45 mL), drying, evaporation, and flash chromatography (silica gel, 1:4 ethyl acetate/pet. ether) gave 551 mg (76%, 2 steps) of the desired borane-protected diphenylphosphino alcohol **29** as a white foam. M.p. 57 – 58 °C; $[\alpha]_D = -30.5(8)$ ($c = 3.3$, $CHCl_3$); $R_f = 0.59$ (1:2 ethyl acetate/pet. ether); IR: $\tilde{\nu} = 3418$, 1469, 1456, 1436 cm^{-1}; ^1H NMR (300 MHz): $\delta = 7.81 - 7.63$ (m, 4H), 7.54 – 7.37 (m, 6H), 7.24 – 7.16 (m, 3H), 7.11 – 7.02 (m, 5H), 4.43 (d, $J = 1.9$, 1H), 4.23 (s, 1H), 3.50 – 3.40 (m, 1H), 3.31 – 3.20 (m, 1H), 2.68 (t, $J = 15.3$, 1H), 2.54 – 2.36 (m, 1H), 2.28 – 2.17 (m, 1H), 1.85 – 0.70 (br m BH_3, 3H), 1.78 – 1.65 (m, 1H), 1.31 (t, $J = 4.9$, 1H); ^{13}C NMR (100 MHz) (aromatic signals show J_{PC}'s, couplings could not be determined for all peaks): $\delta = 143.3$, 142.9, 141.3, 140.3, 132.3 ($J_{PC} = 9.1$), 132.2 ($J_{PC} = 9.1$), 131.2 ($J_{PC} = 7.7$), 128.9, 128.8, 128.8, 126.3, 125.9, 125.7, 124.6, 123.8, 123.2, 64.5, 48.3, 47.2, 44.1 ($J_{PC} = 9.1$), 35.9, 24.5 ($J_{PC} = 35.6$); ^{31}P NMR (161.9 MHz): $\delta = 17.0$ (very br); HRMS: calcd for $C_{30}H_{27}OP$ [$M^+ - BH_3$]: 434.1799; found: 434.1781; chiral HPLC OD column, 1.0 mL flow, detection 254 nm, 9/1 *n*-heptane/isopropanol, retention times, major isomer 8.0 min, minor isomer 10.6 min; 81% ee according to chiral HPLC.

Pyridine (450 mg, 5.69 mmol) followed by *p*-toluenesulfonyl chloride (682 mg, 3.58 mmol) were added to a solution of **29** (551 mg, 1.23 mmol) dissolved in methylene chloride (13 mL) at 0 °C. The reaction mixture was allowed to reach room temperature and stirred for 48 h, then poured onto ice-water and extracted three times with methylene chloride. After drying, evaporation, and flash chromatography (silica gel 1:4 ethyl acetate/pet. ether), 596 mg (82%) of a white foam were obtained. M.p. 69 – 72 °C; $[\alpha]_D = -4.9(7)$ ($c = 8.3$, $CHCl_3$); $R_f = 0.49$ (1:2 ethyl acetate/pet. ether); IR: $\tilde{\nu} = 1598$, 1368 cm^{-1}; ^1H NMR (400 MHz): $\delta = 7.73 - 7.64$ (m, 4H), 7.75 (d, $J = 8.2$, 2H), 7.55 – 7.37 (m, 6H), 7.33 (d, $J = 8.2$, 2H), 7.21 – 7.15 (m, 2H), 7.09 – 6.96 (m, 5H), 6.90 (d, $J = 7.0$, 1H), 4.42 (s, 1H), 4.17 (s, 1H), 3.77 – 3.67 (m, 2H), 2.51 – 2.34 (m, 2H), 2.46 (s, 3H), 2.27 (t, $J = 14.6$, 1H), 1.73 – 1.62 (m, 1H), 1.70 – 0.80 (br m, BH_3, 3H); ^{13}C NMR (100 MHz) (aromatic signals show J_{PC}'s, couplings could not be determined for all peaks): $\delta = 151.0$, 145.1, 143.0, 141.8, 140.1, 139.9, 132.3 ($J_{PC} = 6.5$), 132.2 ($J_{PC} = 8.5$), 131.4, 130.0, 129.0, 129.0, 128.9, 127.8, 126.3, 126.2, 126.2, 126.1, 125.9, 124.8, 123.8, 123.4, 71.0, 47.8, 46.5, 40.7 ($J_{PC} = 10.3$), 36.0, 25.0 ($J_{PC} = 35.6$), 21.7; ^{31}P NMR (161.9 MHz): $\delta = 16.5$ (very br); HRMS: calcd for $C_{37}H_{33}O_3PS$ [$M^+ - BH_3$]: 588.1888; found: 588.1889.

[(2*R,3*R**)-4-Cyclopentadienyl-2,3-(9,10-dihydro-9,10-anthracenediyl)-1-butyl]diphenylphosphine** (**24a,b**): Fluoroboric acid/dimethyl ether complex (613 mg, 4.65 mmol, 0.557 mL) was added to a solution of **30** (400 mg,

0.664 mmol) dissolved in degassed (Ar) methylene chloride (9 mL) at −15 °C. Stirring was continued overnight with slow warming to room temperature. Then the mixture was diluted with degassed methylene chloride (12 mL) and degassed satd aqueous sodium bicarbonate (32 mL). After vigorous stirring of the mixture for 20 min at room temperature, the aqueous phase was extracted three times with degassed methylene chloride. After washing with degassed brine and drying, the solvents were evaporated (under Ar) to give 348 mg (89 % yield) of the deprotected diphenylphosphine tosylate as a white foam. M.p. 68–70 °C; $R_f = 0.49$ (1:4 ethyl acetate/pet. ether); IR: $\tilde{\nu} = 1468$, 1435, 1363 cm^{-1}; ^1H NMR (300 MHz): $\delta = 7.78$ (d, $J = 8.3$, 2H), 7.48–7.15 (m, 14H), 7.12–7.01 (m, 4H), 7.00–6.88 (m, 2H), 4.68 (s, 1H), 4.24 (s, 1H), 4.04 (dd, $J = 9.0$, 5.8, 1H), 3.47 (t, $J = 9.8$, 1H), 2.46 (s, 3H), 2.39–2.28 (m, 1H), 2.18–2.02 (m, 1H), 1.95 (dt, $J = 13.8$, 3.8, 1H), 1.31–1.18 (m, 1H); ^{13}C NMR (100 MHz) (J_{PC} couplings were only assigned when they could be clearly determined): $\delta = 144.8$, 143.3, 142.4, 140.6 139.8, 135.0, 133.1 ($J_{PC} = 19.8$), 132.9 ($J_{PC} = 5.2$), 132.3 ($J_{PC} = 18.5$), 131.8, 129.9, 129.1, 128.6 ($J_{PC} = 6.9$), 128.5, 128.4 ($J_{PC} = 6.4$), 127.9, 127.0, 126.6, 126.0, 125.9, 125.9, 125.7, 125.3, 124.2, 123.5 ($J_{PC} = 5.7$), 70.8, 48.1, 48.0, 45.8, 40.3 ($J_{PC} = 6.1$), 37.5 ($J_{PC} = 15.6$), 28.4 ($J_{PC} = 13.2$), 21.6; ^{31}P NMR (161.9 MHz): $\delta = -19.16$; HRMS: calcd for $C_{37}H_{33}O_3PS$ [M^+]: 588.1888; found: 588.1888.

A solution of sodium cyclopentadienide (2.3 mL, 2 M solution in THF, 4.6 mmol) was added to the crude deprotected diphenylphosphine tosylate (348 mg, ≈0.6 mmol) dissolved in degassed (Ar) THF (9 mL) at room temperature. After 24 h at room temperature, the cloudy greyish-red solution was poured into degassed ice-water (20 mL) and satd aqueous sodium bicarbonate, and extracted three times with degassed methylene chloride. After drying, evaporation (under Ar), and flash chromatography (silica gel, 1:12 diethyl ether/pet. ether), 210 mg (73 %) of a white foam, m.p. 56 °C, were obtained. $R_f = 0.45$ (1:10 diethyl ether/pet. ether); IR: $\tilde{\nu} =$ 1481, 1468, 1433, 1366 cm^{-1}; ^1H NMR (400 MHz) (both double-bond isomers): $\delta = 7.45–7.00$ (m, 18H), 6.52–6.46 (m, Cp), 6.45–6.39 (m, Cp), 6.33–6.29 (m, Cp), 6.16 (s, Cp), 6.00 (s, Cp), 4.73 (s, 1H), 4.09–4.07 (m, 1H), 3.10–2.75 (m, 1H), 2.40–2.23 (m, 2H), 2.22–1.93 (m, 3H), 1.40–1.29 (m, 1H); ^{13}C NMR (100 MHz) (J_{PC} couplings were only assigned when they could be clearly determined; both double-bond isomers present): $\delta = 148.3$, 145.9, 144.2, 143.7, 141.1, 141.0, 134.1 ($J_{PC} = 15.2$), 133.3 ($J_{PC} = 18.9$), 133.2 ($J_{PC} = 19.0$), 132.4 ($J_{PC} = 17.2$), 132.3 ($J_{PC} = 14.8$), 130.8, 128.9, 128.8, 128.6–128.1 (7 lines), 127.4, 125.7, 125.6, 123.5 ($J_{PC} = 4.8$), 123.0 ($J_{PC} = 7.7$), 48.7, 48.6, 48.4, 48.3 43.1, 41.4, 41.0 ($J_{PC} = 7.1$), 40.2 ($J_{PC} = 6.7$), 37.7 ($J_{PC} = 14.4$), 32.2, 31.2, 29.4, 29.34, 29.32, 29.2, 28.4 ($J_{PC} = 13.2$), 21.6; ^{31}P NMR (161.9 MHz): $\delta = -18.78$, −18.83 (both double-bond isomers); HRMS: calcd for $C_{35}H_{31}P$ [M^+]: 482.2163; found: 482.2166.

[(2*R,3*R**)-4-(3-Benzylcyclopentadienyl)-2,3-(9,10-dihydro-9,10-anthracenediyl)-1-butyl]diphenylphosphine** (**31a,b,c**): A dark red solution of lithium benzylcyclopentadienide (344.4 mg, 2.126 mmol) in THF (4 mL) was added to a solution of the deprotected phosphine–borane **30** (500 mg, 0.85 mmol) in degassed THF (10 mL), and the mixture was stirred at room temperature for 45 h and at 60 °C for 1 h. The solution was concentrated and the residue purified by flash chromatography (silica gel, gradient degassed pet. ether to 98:2 pet. ether/ether) give 120 mg (30 %) of air-sensitive compound **31a,b,c**, which was obtained as a mixture of three double-bond isomers at the Cp ring. $R_f = 0.4$ (9:1 pet. ether/ether); ^1H NMR (300 MHz): $\delta = 7.40–7.03$ (m, 23H), 6.50–5.81 (m, Cp), 4.74–4.65 (m, Cp), 4.11–3.90 (m, Cp), 3.72 (m, 1H), 3.51 (m, 1H), 2.87 (m, 2H), 2.40–1.85 (m, 4H), 1.45–1.11 (m, 2H); ^{13}C NMR (75 MHz) (not all the J_{PC} could be assigned): $\delta = 146.0$ ($J_{PC} = 11.1$ Hz), 142.4, 141.3, 141.2 ($J_{PC} = 7.5$ Hz), 133.4 ($J_{PC} = 19.5$ Hz), 132.4 ($J_{PC} = 18.2$ Hz), 130.2, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.5, 126.1, 126.0, 125.9, 125.7, 125.6, 125.5, 123.6, 123.0, 60.8, 51.1, 49.3, 48.8, 48.7 ($J_{PC} = 8.3$ Hz), 48.3 ($J_{PC} = 4.9$ Hz), 42.8 ($J_{PC} = 8.8$ Hz), 40.7 ($J_{PC} = 6.3$ Hz), 38.3, 37.7, 37.6, 37.5, 33.7.

(2*R)-5-(*tert*-Butyldimethylsilyloxy)-1-phenyl-2-pentanol** (**38**): Sodium benzenesulfinate (5.40 g, 30.4 mmol) was added to a solution of iodide **12** (7.34 g, 23.4 mmol) in anhydrous DMF (88 mL). After the resulting mixture had been stirred for 16 h at room temperature, an aqueous saturated solution of ammonium chloride (60 mL) was added and the mixture was extracted with ethyl acetate. The extracts were dried (Na_2SO_4) and the residue was chromatographed (silica 3:2 pet. ether/ethyl acetate) to give 6.0 g (80 %) of sulfone **34**. IR: $\tilde{\nu} = 1447$, 1307 cm^{-1}; ^1H NMR (300 MHz): $\delta = 7.5–7.9$ (m, 5H), 3.56 (t, $J = 5.9$ Hz, 2H), 3.10 (m, 2H), 1.76 (m, 2H), 1.54 (m, 2H), 0.81 (s, 9H), −0.03 (s, 6H).

A solution of *n*-butyllithium (1.6 M, 1.05 mL, 1.68 mmol) in hexanes under Ar was added to a cooled (−78 °C) solution of sulfone **34** (500 mg, 1.52 mmol) in THF (14 mL). The resulting bright yellow solution was stirred at −78 °C for 30 min and then benzaldehyde (169.8 mg, 1.6 mmol) was slowly added. After 3 h of stirring at −78 °C, benzoyl chloride (428.7 mg, 3.05 mmol) was added and the mixture was allowed to warm to room temperature overnight. Saturated aqueous ammonium chloride was added and the mixture was extracted with ethyl ether. After drying and concentrating, flash chromatography of the residue (silica gel, 3:2 pet. ether/ether) provided 760 mg (93 %) of a 4:1 diastereomeric mixture of benzoyloxysulfones. $R_f = (7:3$ pet. ether/ether); IR: $\tilde{\nu} = 1728$, 1307 cm^{-1}; ^1H NMR (300 MHz): δ(major) = 7.2–7.9 (m, 15H), 6.68 (s, 1H), 3.47 (m, 1H), 3.48 (t, $J = 6$ Hz, 2H), 1.2–2.2 (m, 4H), 0.84 (s, 9H), 0.02 (2 s, 6H) (minor) 7.2–7.9 (m, 15H), 6.36 (d, $J = 6$ Hz, 1H), 3.9 (m, 1H), 3.43 (m, 2H), 1.2–2.2 (m, 4H), 0.81 (s, 9H), −0.05 (s, 6H).

Sodium amalgam (5 %, 150 mg, 0.326 g atom) was added to a mixture of the above benzoyloxysulfones (70 mg, 0.13 mmol) and disodium hydrogenphosphate (88 mg, 0.65 mmol) in THF (0.9 mL), and methanol (0.3 mL) at −20 °C. After 3 h at −20 °C, the solution was decanted from the mercury and filtered through a pad of silica gel, then rinsed with ethyl acetate. After flash chromatography (silica gel, 9:1 pet. ether/ether) of the resulting crude material, 32 mg (94 %) of the alkene **35** (*E*/*Z* ratio 98:2) were obtained. $R_f = 0.8$ (7:3 pet. ether/ether) were isolated; IR: $\tilde{\nu} = 1471$, 1255, 1102 cm^{-1}; ^1H NMR (300 MHz): $\delta = 7.18–7.38$ (m, 5H), 6.40 (d, $J = 15.8$ Hz, 1H), 6.23 (dt, $J = 15.8$, 6.8 Hz, 1H), 3.67 (t, $J = 6.6$ Hz, 2H), 2.27 (q, $J = 7.5$ Hz, 2H), 1.70 (quint, $J = 6.9$ Hz, 2H), 0.92 (s, 9H); 0.07 (s, 6H); ^{13}C NMR (75 MHz): $\delta = 130.6$, 130.2, 128.6, 126.9, 126.0, 62.5, 32.4, 29.3, 25.9, 18.1, −5.4.

A mixture of potassium ferricyanide (644 mg, 1.95 mmol), potassium carbonate (269 mg, 1.95 mmol), $(DHQD)_2PHAL$ (10 mg, 0.0128 mmol), potassium osmate dihydrate (2.4 mg, 0.00652 mmol), methanesulfonamide (62 mg, 0.65 mmol), and the alkene **35** (180 mg, 0.65 mmol) in 1:1 *tert*-butyl alcohol/water (6.8 mL) were vigorously stirred at 4 °C for 24 h. The reaction was quenched with sodium sulfite (900 mg) and the solution was extracted with ethyl acetate. After drying (Na_2SO_4) and evaporating, the residue was chromatographed (silica gel, 1:1 pet. ether/ethyl acetate to give 190 mg (94 %) of diol **36**, $[\alpha]_D = -16.12$ ($c = 1.0$, $CHCl_3$), $R_f = 0.5$ (1:1 pet. ether/ethyl acetate); IR: $\tilde{\nu} = 3387$, 1472 cm^{-1}; ^1H NMR (300 MHz): $\delta = 7.32$ (m, 5H), 4.39 (dd, $J = 7.4$, 2.7 Hz, 1H), 3.79 (d, $J = 3.3$ Hz, 1H), 3.60 (m, 3H), 3.25 (d, $J = 2.2$ Hz, 1H), 1.62 (m, 2H), 0.87 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (75 MHz): $\delta = 141.3$, 128.5, 128.0, 127.2, 78.1, 75.8, 63.4, 30.1, 28.8, 25.8, 18.1, −5.6; HRMS: calcd for $C_{13}H_{20}O_2Si$ [$M^+ - t$BuOH] 236.1201; found: 236.1182; chiral HPLC: OD column, 1 mL flow heptane/isopropanol 98/2, 23.4 min and 27.3 min; 97 % *ee*.

A solution of diol (200 mg, 0.65 mmol) and 1,1′-carbonyldiimidazole (125 mg, 0.77 mmol) in anhydrous benzene (5 mL) was heated under reflux for 3 h. Then ether (30 mL) was added and the mixture was evaporated. Flash column chromatography of the crude (silica gel, 3:2 pet. ether/ether) provided 180 mg (86 %) of carbonate **37**: $R_f = 0.7$ (1:1 pet. ether/ether); IR: $\tilde{\nu} = 1809$, 1472, 1390 cm^{-1}; ^1H NMR (300 MHz): $\delta = 7.36$ (m, 5H), 5.16 (d, $J = 7.5$ Hz, 1H), 4.52 (q, $J = 5.5$ Hz, 1H), 3.62 (t, $J = 5$ Hz, 2H), 1.92 (m, 2H), 2.65 (m, 2H), 0.83 (s, 9H), −0.01 (2 s, 6H); ^{13}C NMR (75 MHz): $\delta = 135.8$, 129.8, 129.3, 126.1, 84.2, 83.4, 61.8, 29.8, 27.7, 25.8, 18.1, −5.6.

A suspension of 10 % Pd/C (20 mg) in a solution of carbonate **37** (170 mg, 0.5 mmol), dissolved in ethyl acetate (20 mL), was placed in a hydrogen atmosphere at normal pressure. After 1 h of stirring at room temperature, the mixture was filtered through Celite, and column chromatography of the residue (silica gel, 3:2 pet. ether/ether) provided 145 mg (99 %) of alcohol **38**, $R_f = 0.3$ (85:15 pet. ether/ethyl acetate); IR: $\tilde{\nu} = 3418$, 1472, 1255 cm^{-1}; ^1H NMR (300 MHz): $\delta = 7.25$ (m, 5H), 3.83 (m, 1H), 3.66 (t, $J = 5.3$ Hz, 2H), 2.76 (d, $J = 6.6$ Hz, 2H), 2.53 (d, $J = 3.6$ Hz, 1H), 1.66 (m, 2H), 1.45 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz): $\delta = 138.9$, 129.5, 128.5, 126.4, 72.5, 63.4, 44.0, 33.6, 29.1, 25.8, 18.2, −5.5; anal. calcd for $C_{17}H_{30}O_2Si$: C 69.39, H 10.20; found C, 69.18, H 10.12.

[(2*R)-5-(*tert*-Butyldimethylsilyloxy)-1-phenyl-2-pentyl]diphenylphosphine–borane** (**41**): To a solution of alcohol **38** (390 mg, 1.33 mmol) dissolved in methylene chloride (20 mL) at 0 °C was added, sequentially, triethylamine (673 mg, 6.6 mmol) and methanesulfonyl chloride (305 mg, 2.66 mmol). The mixture was stirred 30 min at 0 °C and 30 min at room temperature at which point aqueous hydrochloric acid (0.5 M, 30 mL) was

0947-6539/99/0503-1064 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 3

added. The mixture was extracted with methylene chloride and the organic extracts washed with a saturated aqueous solution of sodium bicarbonate, dried (Na_2SO_4), and evaporated. The residue was chromatographed (silica gel, 3:2 pet. ether/ether) to give 443 mg (90%) of mesylate **39**, $R_f = 0.8$ (CH_2Cl_2); IR: $\tilde{\nu} = 1472, 1358, 1256, 1173, 1100\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.27$ (m, 5H), 4.87 (quint, $J = 4.16$ Hz, 1H), 3.63 (m, 2H), 2.99 (d, $J = 4.4$ Hz, 2H), 2.49 (s, 3H), 1.75 (m, 4H), 0.87 (s, 9H), 0.03 (s, 6H).

To a degassed (Ar) solution of the mesylate (443 mg, 1.2 mmol) in THF (17 mL) was slowly added lithium diphenylphosphide at $-50\,^\circ C$ (2.4 mmol from a solution prepared by stirring a mixture of 670 mg (3.6 mmol) of diphenylphosphine and *n*-butyllithium (3.6 mmol, 2.25 mL, 1.6 M in hexanes) in THF (12 mL) for 2.5 h at $-35\,^\circ C$). The reaction mixture was stirred 30 min at $-30\,^\circ C$ and 1 h at room temperature and then quenched with 30 mL of degassed water (30 mL). The mixture was extracted with methylene chloride under nitrogen. After drying and evaporating, the resultant crude phosphine was redissolved in degassed THF (15 mL) and borane/dimethylsulfide (365 mg, 3.60 mmol) was added at $0\,^\circ C$. The mixture was stirred for 30 min at $0\,^\circ C$ and 30 min at room temperature, after which it was quenched by addition of water (50 mL). The mixture was extracted with ethyl ether, dried (Na_2SO_4), and evaporated, and the residue purified by column chromatography (silica gel, 95:5 pet. ether/ether) to give 425 mg (75%) of the phosphine borane **41**. M.p. 73–75 °C; $[\alpha]_D = +8.52$ ($c = 2.6$, $CHCl_3$); $R_f = 0.6$ (7:3 pet. ether/ether); IR: $\tilde{\nu} = 2386, 1437, 1255\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.83–7.01$ (m, 15H), 3.27 (m, 2H), 2.94 (m, 1H), 2.75 (m, 2H), 1.8–0.8 (m, 7H), 0.76 (s, 9H), −0.11 (2 s, 6H); ^{13}C NMR (75 MHz): $\delta = 140.2$ ($J_{PC} = 12.7$ Hz), 132.7 ($J_{PC} = 4.6$ Hz), 132.6 ($J_{PC} = 4.6$ Hz), 131.2, 128.9, 128.8, 128.5, 126.4, 62.8, 36.0, 35.8 ($J_{PC} = 40$ Hz), 31.9 ($J_{PC} = 7.3$ Hz), 26.2, 25.8, 18.1, −5.5; ^{31}P NMR (161.906 MHz): 23.84 (s); anal. calcd for $C_{29}H_{42}BOPSi$: C 73.14, H 8.83; found: C 72.87, H 8.93.

[(2*R)-5-Hydroxy-1-phenyl-2-pentyl]diphenylphosphine–borane**: TBAF (1.2 mL of a 1 M solution in THF, 1.2 mol) was added to a cooled (0 °C) solution of phosphine–borane **41** (425 mg, 0.89 mmol) in THF (15 mL) under Ar. The reaction mixture was stirred for 1 h at $0\,^\circ C$ and 2 h at room temperature. A saturated aqueous solution of ammonium chloride was added and the mixture was extracted with ethyl acetate, dried (Na_2SO_4) and evaporated. Flash column chromatography of the residue (silica gel, 1:1 pet. ether/ethyl acetate) provided 260 mg (80%) of the desired primary alcohol. $[\alpha]_D = +17.49$ ($c = 17$, $CHCl_3$); $R_f = 0.5$ (1:1 pet. ether/ethyl acetate); IR: $\tilde{\nu} = 3387, 2385, 1964, 1895, 1484, 1437\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.85–7.07$ (m, 15H), 3.27 (br s, 2H), 2.95 (m, 1H), 2.74 (m, 2H), 1.65 (m, 2H), 1.6–0.6 (br m, 3H), 1.20 (m, 2H); ^{13}C NMR (75 MHz): $\delta = 140.0$ ($J_{PC} = 12.6$ Hz), 132.7 ($J_{PC} = 3.6$ Hz), 132.7 ($J_{PC} = 21.0$ Hz), 131.4, 128.9, 128.8 ($J_{PC} = 8.9$ Hz), 128.6, 126.5, 62.3, 36.1 ($J_{PC} = 4$ Hz), 35.5 ($J_{PC} = 33.1$ Hz), 31.6 ($J_{PC} = 6.9$ Hz), 25.7; ^{31}P NMR (161.903 MHz): $\delta = 23.87$ (br m); HRMS: calcd for $C_{23}H_{25}OP$ [$M^+ - BH_3$]: 348.1643; found: 348.1635.

[(2*R)-5-Cyclopentadienyl-1-phenyl-2-pentyl]diphenylphosphine (44a,b)**: Following the same procedure as already described for the preparation of **39**, the primary alcohol (106 mg, 0.29 mmol), triethylamine (148 mg, 1.50 mmol), and methanesulfonyl chloride (67 mg, 0.59 mmol) were allowed to react. Column chromatography (3:2 pet. ether/ethyl acetate) furnished the mesylate **42** (125 mg, quantitative), $R_f = 0.5$ (CH_2Cl_2); IR: $\tilde{\nu} = 2385, 1437, 1354\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.86$ (m, 4H), 7.48 (m, 6H), 7.26–7.10 (m, 5H), 3.83 (dt, $J = 6.27$, 1.2 Hz, 2H), 3.00–2.61 (m, 3H), 2.78 (s, 3H), 1.65 (m, 2H), 1.36 (m, 2H), 1.6–0.6 (br m, 3H).

Fluoroboric acid dimethyl ether (182.6 mg, 1.36 mmol) was added to a solution of the mesylate **42** (120 mg, 0.27 mmol) in degassed methylene chloride (3 mL) at $-15\,^\circ C$, and the mixture was allowed to warm slowly to room temperature overnight. Slow addition of a degassed satd aqueous solution of sodium bicarbonate (9 mL) quenched the reaction. After 30 min at room temperature, the resulting mixture was extracted with degassed methylene chloride under nitrogen, dried (Na_2SO_4), and evaporated to provide crude air-sensitive phosphine **43**, $R_f = 0.3$ (1:1 pet. ether/ether); IR: $\tilde{\nu} = 1438, 1349\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.70–7.10$ (m, 15H), 3.98 (t, $J = 6.3$ Hz, 2H), 2.91–2.36 (m, 3H), 2.79 (s, 3H), 1.77 (m, 2H), 1.45 (m, 2H): Because of its sensitivity, **43** was used immediately in the next reaction.

Sodium cyclopentadienide (2 M in THF, 1.47 mL, 2.9 mmol) was added to a solution of **43** in THF (6 mL). The reaction mixture was stirred for 1.5 h at room temperature. After addition of degassed water (5 mL), the mixture was extracted with degassed methylene chloride. After drying and evaporating, the residue was purified by short-column chromatography (silica gel, 4:1 pet. ether/ether, degassed) to give 49 mg (45%) of compound **44a,b** as a mixture of double-bond isomers, $R_f = 0.9$ (4:1 pet. ether/ether), IR: $\tilde{\nu} = 1602, 1494, 1479, 1454, 1434, 1366\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.62–7.10$ (m, 15H), 6.37–6.17 (m, Cp), 5.98 (s, Cp), 5.83 (m, Cp), 2.87 (s, Cp), 2.81 (m, 1H), 2.70 (s, Cp), 2.66–2.43 (m, 2H), 2.17 (m, 2H), 1.70–1.30 (m, 4H); ^{13}C NMR (75 MHz): δ (J_{PC} could not be properly assigned for all the carbon signals) = 141.1, 141.0, 134.8, 134.3, 134.0, 133.6, 133.4, 132.4, 130.5, 129.1, 129.1, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 126.5, 126.0, 43.0, 41.0, 37.6 ($J_{PC} = 2.7$ Hz), 37.4 ($J_{PC} = 2.7$ Hz), 36.8 ($J_{PC} = 8.6$), 30.7, 29.8, 29.5, 29.3, 29.1, 27.0, 26.1, 25.9; ^{31}P NMR (161.903 MHz): $\delta = -5.40$ and −5.58 (two Cp isomers): HRMS: calcd for $C_{28}H_{29}P$ [M^+] 396.2007; found: 396.2003.

(4*R*)-4-Phenyl-2-[3-(*p*-toluenesulfonyl)-1-propyl]-4,5-dihydrooxazole (50): *n*-Butyllithium (1.55 M in hexanes, 0.224 mL, 0.347 mmol) was added dropwise to a solution of 2-methyl-(4*R*)-phenyl-4,5-dihydrooxazole (**49**, 53 mg, 0.33 mmol) in DME (1 mL) at $-78\,^\circ C$. The reddish solution was stirred at $-78\,^\circ C$ for 30 min prior to the addition of ethylene oxide (82.8 mg, 18.8 mmol) with a precooled syringe. Slowly (over 6 h) the reaction mixture was warmed to $0\,^\circ C$. After recooling to $-40\,^\circ C$, *p*-toluenesulfonyl chloride (74 mg, 0.390 mmol) was added and the solution allowed to warm to room temperature overnight. Quenching with ice cold satd aqueous sodium bicarbonate followed by extraction with methylene chloride afforded after flash chromatography (silica gel, 1:5 ethyl acetate/pentane) 56 mg (52%) of **50** as a colorless oil. $[\alpha]_D = -38.0(5)$ ($c = 4.6$, $CHCl_3$), $R_f = 0.50$ (EtOAc); IR: $\tilde{\nu} = 1666, 1598, 1493, 1454, 1359\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.78$ (d, $J = 8.3$, 2H), 7.38–7.23 (m, 5H), 7.21–7.15 (m, 2H), 5.10 (t, $J = 9.0$, 1H), 4.57 (m, 1H), 4.16 (t, $J = 6.1$, 2H), 4.02 (m, 1H), 2.48–2.40 (m, 2H), 2.42 (s, 3H), 2.12–2.03 (m, 2H); ^{13}C NMR (75 MHz): $\delta = 167.5, 144.9, 142.3, 133.1, 130.0, 128.8, 128.0, 127.7, 126.6, 74.6, 69.5, 69.4, 25.2, 23.8, 21.5$; HRMS: calcd for $C_{19}H_{21}NO_4S$ [M^+]: 359.1197; found 359.1191.

(4*R*)-2-(3-Cyclopentadienyl-1-propyl)-4-phenyl-4,5-dihydrooxazole (51a,b): Sodium cyclopentadienide (2 M in THF, 2.3 mL, 4.6 mmol) was added to a solution of **50** (800 mg, 2.23 mmol) in THF (70 mL) at room temperature. After 6 h, the cloudy greyish-red solution was poured onto ice water and extracted with methylene chloride. After drying, evaporation, and flash chromatography (silica gel, 1:2 ethyl acetate/pet. ether), 321 mg (57%) of **51a,b** was obtained as an unstable pale yellow oil. $[\alpha]_D = 75.7(25)$ ($c = 3.4$, $CHCl_3$), $R_f = 0.53$ (1:1 ethyl acetate/pet. ether); IR: $\tilde{\nu} = 1665, 1602, 1364\ cm^{-1}$; ^1H NMR (300 MHz): $\delta = 7.38–7.32$ (m, 2H), 7.31–7.21 (m, 3H), 6.50–6.40 (m, Cp), 6.30–6.25 (m, Cp), 6.21 (s, Cp), 6.07 (s, Cp), 5.17 (t, $J = 9.0$, 1H), 4.59 (t, $J = 8.7$, 1H), 4.07 (t, $J = 8.2$, 1H), 2.96 (s, Cp), 2.90 (s, Cp), 2.55–2.45 (m, 2H), 2.42 (t, $J = 7.6$, 2H), 2.03–1.96 (m, 2H); ^{13}C NMR (75 MHz): $\delta = 168.7, 148.6, 142.5, 134.5, 133.9, 132.4, 130.8, 128.7, 127.5, 127.0, 126.5, 74.5, 69.6, 43.2, 41.3, 30.2, 29.3, 27.7, 27.6, 26.1, 25.2$; HRMS: calcd for $C_{17}H_{19}NO$ [M^+]: 253.1475; found: 253.1467.

General methods for formation of ruthenium complexes:

Method A: The desired Ru^{II} complexes were best prepared by dissolving the bidentate cyclopentadienyldiphenylphosphine ligand in degassed (Ar) 1,2-dichloroethane (0.08 M), adding a stoichometric amount of [$(Ph_3P)_3RuCl_2$] at room temperature, and subsequently heating the mixture to reflux for 30 to 60 min. During this time, the color of the solution changed from brownish black to deep red. The mixture was then evaporated to dryness in vacuo. The red residue was dissolved in degassed (Ar) methylene chloride/diethyl ether (1:1, 2 mL) and transferred onto a flash chromatography column filled with neutral aluminum oxide or silica gel as specified. The excess triphenylphosphine eluted first with 20:1 degassed pentane/ether, after which a yellow-orange fraction was eluted by switching to more polar solvents as indicated for each specific compound. If necessary they could be further purified by dropwise addition of a highly concentrated degassed CH_2Cl_2 solution of the complex to a 50-fold amount of degassed hexane. The orange precipitate was collected on a paper filter, washed with pentane and dried in vacuo (0.05 Torr). When dry, the complexes were air-stable. They were routinely stored at $4\,^\circ C$ under Ar.

Method B: The ligand was dissolved in degassed (Ar) toluene (10 mL, 0.03–0.05 M) and cooled to $-78\,^\circ C$, when *n*-butyllithium in hexanes (1.1 equiv, 1.6 M) was slowly added. The mixture was then warmed to room temperature and stirred for 30 min, after which 1.1 equiv of [$(Ph_3P)_3RuCl_2$]

was added to the white suspension and the reaction mixture heated to 90–95 °C for 3 h. The mixture turned bright orange after 20 min. After cooling to room temperature, the solvent was evaporated, and the residue chromatographed (Ar degassed solvents) on silica gel or neutral aluminum oxide as specified. The orange products were collected and purified as described under method A.

Chloro{[2-(diphenylphosphino)phenyl]-η^5-cyclopentadienyl} (triphenylphosphine)ruthenium(II) (5): Ligand **11a,b** was not sufficiently stable to be kept at room temperature for more than 15 min and was therefore immediately transformed to the corresponding Ru^{II} complex **5** by method A on a 725 mg (2.22 mmol) scale to give 1.41 g (87%) of **7** as an orange powder, m.p. 149–151 °C (N_2, sealed tube; decomp at 285–290 °C); IR: $\tilde{\nu}$ = 1956, 1886, 1816, 1586, 1480, 1434 cm^{-1}; ^1H NMR (400 MHz): δ = 8.13–8.05 (m, 2H), 7.52–6.85 (m, 25H), 6.36–6.22 (m, 2H), 5.27 (s, 1H, Cp), 5.11(s, 1H, Cp), 4.49(s, 1H, Cp), 3.15 (s, 1H, Cp); ^{13}C NMR (100 MHz): δ = 153.2 (J_{PC} = 38.8), 140.9 (J_{PC} = 21.1), 139.3 (J_{PC} = 40), 135.0–127.4 numerous aromatic peaks, 114.1 (Cp), 84.5 (J_{PC} = 4.1) (Cp), 83.3 (J_{PC} = 12.5) (Cp), 82.0 (J_{PC} = 9.3) (Cp), 67.2 (Cp); ^{31}P NMR (161.903 MHz): δ = −13.4 (d, J_{PP} = 39.5), −16.1 (d, J_{PP} = 39.5); MS (FAB) 724 (M^+, 70); anal. calcd for $C_{41}H_{33}ClP_2Ru$: C 68.00, H 4.59; found: C 67.95, H 4.66.

Chloro{[3-(diphenylphosphino)-1-propyl]-η^5-cyclopentadienyl} (triphenylphosphine)ruthenium(II) (7): With ligand 3-diphenylphosphinopropylcyclopentadiene (1.90 g, 6.51 mmol), 1.30 g (29%) of the desired complex **7**, m.p. 154 °C (N_2, sealed tube, 225 °C decomp) was obtained using method A and after the same workup and flash chromatography as described for **5**. The product proved to be unstable in chloroform solution at room temperature and not as soluble in benzene as **5**, **6**, or **8**. The relatively low yield is probably due to the oxygen sensitivity of the ligand, which was used for complex formation without extensive purification; IR: $\tilde{\nu}$ = 1958, 1895, 1813, 1480, 1433 cm^{-1}; ^1H NMR (300 MHz): δ = 8.05–7.96 (m, 2H), 7.38–7.00 (m, 19H), 6.94–6.86 (m, 2H), 6.63–6.55 (m, 2H), 5.30 (s, 1H, Cp), 4.57 (s, 1H, Cp), 3.81 (s, 1H, Cp), 3.69 (s, 1H, Cp), 2.55–2.46 (m, 1H), 2.36 (ddd, J = 13.5, 13.5, 6.4, 1H), 2.08–1.84 (m, 1H), 1.83–1.63 (m, 2H), 1.57–1.41 (m, 1H); ^{13}C NMR (75 MHz): δ (aromatic signals show phosphorus coupling, couplings could not all be determined, all peaks listed): δ = 138.4–137.3 (4 lines), 135.2, 135.1, 134.2, 134.1, 132.2, 132.0, 129.4, 128.9, 128.4, 127.8, 127.7, 127.6, 127.4, 127.3, 115.5 (Cp), 97.2 (Cp), 80.4 (J_{PC} = 4.4) (Cp), 77.3 (Cp), 75.6 (Cp), 24.6 (J_{PC} = 24.4), 24.4, 21.1 (J_{PC} = 2.1); ^{31}P NMR (161.903 MHz): δ = 45.7 (d, J_{PP} = 41.0), 27.9 (d, J_{PP} = 41.0): MS (FAB) 690 (M^+, 54); anal. calcd for $C_{38}H_{35}ClP_2Ru$: C 66.13, H 5.11; found: C 66.04, H 5.28.

Chloro{[4-(diphenylphosphino)-1-butyl]-η^5-cyclopentadienyl}(triphenylphosphine)ruthenium(II) (8): When complexation method A was used, ligand **14a,b** (262 mg, 0.856 mmol) led to 101 mg (17%) of the desired complex. After flash chromatography (silica gel, degassed solvents (Ar), 1:8 to 1:1 pet. ether/diethyl ether) and evaporation of the solvents (under Ar), the air-stable solid **8**, m.p. 115–117 °C (N_2, sealed tube), was obtained as an orange powder, R_f = 0.22 (1:5 ether/pet. ether). With complexation method B, 60 mg (0.196 mmol) of ligand **14a,b** gave 51 mg (38% yield) of **8** after the same workup and purification: m.p. 115–117 °C (N_2, sealed tube), IR: $\tilde{\nu}$ = 1481, 1434 cm^{-1}; ^1H NMR (300 MHz): δ = 7.43–6.90 (m, 25H), 4.93 (s, 1H, Cp), 4.77 (s, 1H, Cp), 3.55 (s, 1H, Cp), 3.51 (s, 1H, Cp), 3.26–3.11 (m, 1H), 2.72–2.60 (m, 1H), 2.55–2.40 (m, 1H), 2.18–1.83 (m, 3H), 1.73–1.50 (m, 1H), 0.92–0.81 (m, 1H); ^{13}C NMR (100 MHz): (aromatic signals show J_{PC}'s; the couplings could not be determined for all signals, therefore all peaks are listed): δ = 140.9, 140.5, 139.1, 138.8, 138.7, 138.5, 134.4, 134.1, 133.8, 133.6, 133.6, 133.5, 133.4, 133.3, 128.9, 128.7, 128.5, 128.4, 128.3, 127.5, 127.4, 127.3, 127.1, 127.0, 98.7 (J_{PC} = 7.4, Cp), 85.1 (Cp), 83.1 (J_{PC} = 8.0, Cp), 80.0 (Cp), 70.9 (Cp), 35.7 (J_{PC} = 24.9), 25.6, 25.5, 23.9; ^{31}P NMR (161.903 MHz): δ = 39.9 (d, J_{PP} = 43.2), 34.5 (d, J_{PP} = 43.2); MS(LS/MS): calcd for $C_{39}H_{37}ClP_2Ru$: 704.1; found: 704.1; anal. calcd for $C_{39}H_{37}ClP_2Ru$: C 66.52, H 5.26; found: C 66.30, H 5.41.

Chloro{[4-(diphenylphosphino)-1-butyl]-η^5-(3-benzylcyclopentadienyl)}-(triphenylphosphine)ruthenium(II) (16a,b): The deprotected phosphine of **13** (same procedure as above for **14a,b**) (300 mg, 0.890 mmol) was dissolved in degassed THF (1 mL) at 0 °C. A freshly prepared solution of lithium benzylcyclopentadienide (217 mg, 1.34 mmol in 3.5 mL of THF) was added to the phosphine. After stirring for 1 h at room temperature, degassed water was added (10 mL) and the mixture was extracted with degassed methylene chloride under nitrogen (3 × 20 mL). The extracts were dried (Na_2SO_4) and concentrated. The residue was passed through a short column (silica gel, gradient of pure pet. ether to pet. ether/ether 97/3) to give 200 mg (55%) of ligand **15a,b,c** as a mixture of 3 isomers at the Cp ring.

Complex formation according to method B: *n*BuLi (0.184 mL, 1.6 M in hexanes, 0.294 mmol) was added to a degassed solution of ligand **15a,b,c** (106 mg, 0.268 mmol) in toluene (7 mL) at 0 °C, and the mixture was stirred at room temperature for 1.5 h. [$(Ph_2P)_3RuCl_2$] (270 mg, 0.281 mmol) was added and the mixture heated from room temperature to 90 °C over 15 min and kept at 90 °C for 2.5 h. The resulting deep red solution was cooled and concentrated. The residue was purified through a short plug of silica gel (gradient, pet. ether/ether 8/2 to 1/1). Two yellow fractions were collected.

Diastereomer 16a: 40 mg (20%), m.p. 123–125 °C. R_f = 0.6 (pet. ether/ethyl acetate/methylene chloride); IR: $\tilde{\nu}$ = 1479, 1429 cm^{-1}; ^1H NMR (400 MHz): δ = 7.43 (m, 2H), 7.31–6.98 (m, 26H), 6.82 (m, 2H), 4.37 (s, 1H, Cp), 4.24 (s, 1H, Cp), 3.73 (q, J = 10.52 Hz, 2H), 2.99 (m, 1H), 2.62 (m, 2H), 2.55 (s, 1H, Cp), 2.11 (m, 2H), 1.82 (m, 1H), 1.62 (m, 2H); ^{13}C NMR (100 MHz): δ = 140.0, 139.2, 138.8, 133.8, 133.7, 133.6, 133.5, 129.3, 128.9, 128.3, 127.7, 127.6, 127.5, 127.4, 127.1, 126.9, 126.0, 108.5 (J_{PC} = 4.3 Hz), 88.8 (J_{PC} = 11.7 Hz), 80.0 (J_{PC} = 9.1 Hz), 78.8, 70.0, 33.9 (J_{PC} = 26.3), 32.1, 27.0, 22.6, 22.3; ^{31}P NMR (161.903 MHz): δ = 40.6 (d, J_{PP} = 41.5 Hz), 33.9 (d, J_{PP} = 41.9 Hz); MS (LSIMS): calcd for $F_{46}H_{43}ClP_2Ru$: 794.1; found: 794.1; anal. calcd for $C_{46}H_{43}ClP_2Ru$: C 69.57, H 5.42; found: C 69.57, H 5.24.

Diastereomer 16b: 35 mg (17%), m.p. 118–120 °C, R_f = 0.6 (pet. ether, ethyl acetate, chloroform); IR: $\tilde{\nu}$ = 1481, 1433 cm^{-1}; ^1H NMR (400 MHz): δ = 7.70 (m, 2H), 7.36–7.04 (m, 24H), 6.90 (m, 2H), 6.80 (m, 2H), 4.38 (s, 1H), 3.86 (s, 1H), 3.50 (m, 2H), 3.08 (s, 1H), 2.88 (m, 1H), 2.54 (m, 1H), 2.06 (m, 1H), 1.97 (m, 1H), 1.62 (m, 2H), 1.42 (m, 1H), 1.27 (m, 1H); ^{13}C NMR (100 MHz): δ = 141.2, 140.8, 139.1, 138.8, 134.5, 134.4, 133.5, 133.4, 133.3, 129.2, 128.8, 128.3, 128.2, 127.4, 127.3, 127.1, 127.0, 125.9, 107.2, 100.6, 83.9 (J_{PC} = 7.5 Hz), 75.2 (J_{PC} = 10.9 Hz), 66.9, 33.9 (J_{PC} = 25.7 Hz), 33.5, 26.0, 24.6, 23.6; ^{31}P NMR (161.903 MHz): δ = +38.68 (d, J_{PP} = 40.7 Hz), +32.3 (d, J_{PP} = 41.2 Hz); MS (LSIMS): calcd for $C_{46}H_{43}ClP_2Ru$: 794.1; found: 794.1; anal. calcd for $C_{46}H_{43}ClP_2Ru$: C 69.57, H 5.42; found: C 69.57, H 5.24.

Chloro{[(2*S*,3*R*)-4-(diphenylphosphino)-2,3-(dimethylmethylenedioxy)-1-butyl]-η^5-cyclopentadienyl}(triphenylphosphine)ruthenium(II) (20a,b): By method A, 207 mg (51%) of a yellow orange solid, m.p. 127 °C (N_2, sealed tube, 220 °C decomp), were obtained after one recrystallization from hexane. In solution both diastereomers arising from different stereochemistry at the metal center were present in a ratio of 3:2 (^1H NMR). Analysis was carried out on the mixture; IR: $\tilde{\nu}$ = 1961, 1897, 1815, 1480, 1434 cm^{-1}; ^1H NMR (300 MHz): δ = 7.52–7.24 (m, 10H), 7.21–6.99 (m, 11H), 6.95–6.85 (m, 2.5H), 6.79–6.71 (m, 1.5H), 5.22 (s, 0.6H), 5.10 (dd, J = 14.4, 7.2, 0.4H), 4.98 (s, 0.4H), 4.98–4.88 (m, 0.6H), 4.70 (s, 0.4H), 4.57 (s, 0.6H), 4.07 (s, 0.4H), 3.95–3.82 (m, 0.4H), 3.91 (s, 0.6H), 3.86–3.79 (m, 0.6H), 3.75–3.68 (m, 0.4H), 3.50 (dd, J = 14.6,14.5, 0.6H), 3.24 (dd, J = 12.3, 9.2, 0.6H), 3.13–3.04 (m, 0.6H), 3.01 (s, 0.4H), 3.00–2.89 (m, 0.4H), 2.83–2.71 (m, 0.4H), 2.68–2.57(ddd, J = 14.1, 11.0, 2.9, 0.4H), 2.37 (s, 0.6H), 2.28 (ddd, J = 13.6, 10.8, 2.7, 0.6H), 1.49 (s, 1.8H), 1.46 (s, 1.2H), 1.39 (s, 1.2H), 1.36 (s, 1.8H); ^{13}C NMR (100 MHz): (aromatic signals show J_{PC}'s, couplings could not be determined for all peaks): δ = 139.3–136.4 (10 lines), 134.1 (J_{PC} = 11.5), 133.6 (J_{PC} = 11.1), 133.4–133.2 (4 lines), 132.7 (J_{PC} = 9.0), 131.7 (J_{PC} = 7.7), 130.1, 129.2, 128.4–127.3 (8 lines), 107.2, 107.1, 92.1 (J_{PC} = 5.1), 88.8 (J_{PC} = 5.9), 87.6 (J_{PC} = 5.9), 86.8 (J_{PC} = 9.8), 84.3, 83.2 (J_{PC} = 12.2), 82.0 (J_{PC} = 7.3), 81.5, 79.3, 78.3 (J_{PC} = 11.0), 77.9 (J_{PC} = 13.0), 77.8, 70.2, 69.5, 45.5 (J_{PC} = 24.4), 39.2 (J_{PC} = 24.2), 31.3, 28.6, 27.1, 27.0, 26.9, 26.7; ^{31}P NMR (161.903 MHz): δ = 36.7 (J_{PP} = 42.2), 36.6 (J_{PP} = 43.4), 32.0 (J_{PP} = 42.2), 28.7 (J_{PP} = 43.4); HRMS: calcd for $C_{24}H_{26}O_2PCl$ ($M^+ - Ph_3P$): 514.0372; found: 514.0385; anal. calcd for $C_{42}H_{41}O_2ClP_2Ru$: C 64.98, H 5.32; found: C 65.15, H 5.23.

Chloro{[(2*S*,3*R*)-4-(diphenylphosphino)-2,3-dihydroxy-1-butyl]-η^5-cyclopentadienyl}(triphenylphosphine)ruthenium(II) (21a,b): Cleavage of the ketal **20a,b** (300 mg, 0.385 mmol) in a degassed (Ar) mixture of ethanol (8 mL), 1,2-dichloroethane (0.5 mL) and aqueous hydrochloric acid (0.5 M, 0.8 mL). When the orange suspension was heated to 76 °C, initially a clear red solution was obtained which turned slightly brownish during the course of the 6 h heating process. The reaction mixture was cooled and the solvent evaporated to leave a crude oily solid which was flash chromatographed (silica gel, 1:3 methylene chloride/diethyl ether, gradually increasing the

0947-6539/99/0503-1066 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 3

amount of methylene chloride) to give 270 mg (95%) of an orange-brown solid, m.p. 169–170 °C (N_2, sealed tube). The ^{1}H NMR analyses revealed that a mixture of diastereomers of **21a,b** was present and that the product complex contained 1 equiv of water; this finding was supported by elemental analyses. IR: $\tilde{\nu}$ = 3397, 1967, 1895, 1481, 1434, 1310 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.84–7.78 (m, 0.4H), 7.71–7.63 (m, 4H), 7.59–7.53 (m, 2.8H), 7.46–7.40 (m, 1.2H), 7.15–7.09 (m, 1.2H), 7.06–6.74 (m, 15H), 5.57 (s, 0.4H), 5.15–5.04 (m, 0.4H), 5.03 (s, 0.6H), 4.94 (s, 0.6H), 4.72 (s, 0.4H), 4.55–4.45 (m, 0.4H), 4.20–4.08 (m, 1H), 4.01 (s, 0.4H), 3.93–3.84 (m, 0.4H), 3.82–3.62 (m, 2.2H), 3.60–3.50 (m, 0.4H), 3.42–3.30 (m, 1.2H), 3.09 (s, 0.4H), 2.90–2.79 (m, 1.2H), 2.72–2.63 (m, 0.4H), 2.34–2.17(m, 1H), 1.17–0.90 (br s, 2H, H_2O); ^{13}C NMR (100 MHz, C_6D_6): (aromatic signals show J_{PC}'s, couplings could not be determined for all peaks): δ = 142.5 (J_{PC} = 35.6), 141.9 (J_{PC} = 38.3), 140.0 (J_{PC} = 36.4), 139.4 (J_{PC} = 37.3), 136.8 (J_{PC} = 38.3), 135.2 (J_{PC} = 11.8), 134.0–133.4 (12 lines), 132.4 (J_{PC} = 9.4), 131.9, 129.7, 129.0–127.3 (11 lines), 95.3 (m), 94.1 (J_{PC} = 5.6), 89.3 (J_{PC} = 5.1), 84.6, 83.9 83.5 (J_{PC} = 6.9), 82.7, 80.9 (J_{PC} = 4.6), 75.1, 74.1, 73.6 (J_{PC} = 4.6), 72.9 (J_{PC} = 10.0), 71.3, 68.6, 41.4 (J_{PC} = 24.1), 40.5 (J_{PC} = 23.9), 30.8, 29.8; ^{31}P NMR (161.903 MHz, C_6D_6): δ = 39.0 (d, J_{PP} = 39.5), 37.9 (d, J_{PP} = 41.6), 34.0 (br d, J_{PP} is about 41 Hz), 30.4–29.7 (very br d, no coupling could be determined); MS (FAB) 736 (M^+,10); anal. calcd for $C_{39}H_{39}O_3ClP_2Ru$: C 62.10, H 5.21; found: C 62.33, H 5.41.

Chloro{[(2*S*, 3*R*)-2,3-bis(benzyloxy)-4-(diphenylphosphino)-1-butyl]-η^5-cyclopentadienyl}(triphenylphosphine)ruthenium(II) (22a,b): A mixture of the diol **21a,b** (20 mg, 27.2 mmol), dissolved in DME (1 mL), containing potassium hydride (13.6 mg, 0.119 mmol, 35% dispersion in mineral oil, washed twice with 1 mL of pentane) and freshly distilled benzyl bromide (11.6 mg, 0.068 mmol) were stirred for 45 min at room temperature. The reaction mixture was quenched with one drop of ice-water prior to transfer onto a silica gel column. Flash chromatography (silica gel, gradient of pure pentane to a mixture of 1:2 pentane/diethyl ether) afforded 15 mg (63%) of the bis-benzylated complex **22a,b** as a yellow-orange solid, m.p. 82–83 °C (N_2, sealed tube). R_f = 0.61 (2:1 diethyl ether/pentane). The diastereomeric ratio remained at 3:2, also after heating a benzene solution of the product to 80 °C for 15 min. M.p. 82–83 °C (N_2, sealed tube); IR: $\tilde{\nu}$ = 1960, 1891, 1812, 1480, 1453, 1434 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.73–7.48 (m, 7H), 7.31–6.62 (m, 28H), 5.77 (s, 0.33H), 5.51–5.42 (m, 0.33H), 5.20 (s, 0.66H), 5.08 (d, J = 11.7, 0.33H), 4.99 (d, J = 11.7, 0.33H), 4.78 (s, 0.66H), 4.69 (s, 0.33H), 4.68 (s, 0.66H), 4.57 (d, J = 12.1, 0.33H), 4.49 (d, J = 12.1, 0.33H), 4.41 (d, J = 11.5, 0.66H), 4.39 (d, J = 11.5, 0.66H), 4.30 (s, 0.33H), 4.30 (d, J = 11.5, 0.66H), 4.09 (d, J = 11.5, 0.66H), 4.04–3.96 (m, 1.33H), 3.82–3.73 (m, 0.66H), 3.51–3.39 (m, 0.66H), 3.31–3.22 (m, 0.66H), 3.16 (s, 0.33H), 3.06–2.96 (m, 0.66H), 2.88–2.78 (m, 1H), 2.77 (s, 0.66H), 2.50–2.40 (m, 0.33H), 1.90–1.81 (m, 0.33H); ^{13}C NMR (100 MHz, C_6D_6): (aromatic signals show J_{PC}'s, couplings could not be determined for all peaks): δ = 140.4–139.3 (8 lines), 136.3 (J_{PC} = 10.6), 134.5–133.5 (8 lines), 130.1, 129.1–127.0 (>16 lines), 92.7, 89.7 (J_{PC} = 5.3), 84.9 (J_{PC} = 4.6), 84.6 (J_{PC} = 7.5), 84.3, 83.7 (J_{PC} = 8.8), 83.1, 81.3 (J_{PC} = 4.9), 81.2, 81.1, 80.9, 80.8, 73.5, 73.0, 72.8, 72.1, 71.8, 68.9, 38.6 (J_{PC} = 21.9), 37.6 (dd, J_{PC} = 22.1, 5.7), 27.4, 25.6; ^{31}P NMR (161.9 MHz, C_6D_6): δ = 41.8, 41.6, 41.5 and 41.2 (AB, J_{PP} = 41.7), 40.9 (J_{PP} = 39.5), 35.6 (J_{PP} = 39.5); MS (FAB): 916 (M^+,10); anal. calcd for $C_{53}H_{49}ClO_2P_2Ru$: C 69.31, H 5.38; found: C 69.47, H 5.43.

Chloro{[(2*S*, 3*R*)-2,3-bis(*tert*-butyldimethylsilyloxy)-4-(diphenylphosphino)-1-butyl]-η^5-cyclopentadienyl}(triphenylphosphine) ruthenium(II) (23a,b): Sequential addition of di-*tert*-butylpyridine (185 mg, 0.966 mmol, 2.5 equiv) and TBDMSOTf (263 mg, 1.00 mmol, 2.6 equiv) to a solution of the crude diol **21a,b** (330 mg, 0.387 mmol) in degassed methylene chloride (12 mL) at −10 °C was followed by stirring for 1 h at −10 °C. Then it was allowed to warm to room temperature and stirred for another 10 h. The solvent was reduced to 2 mL by blowing a slow stream of nitrogen over the solution. The crude orange oil was transferred onto a flash column (silica gel, 1:4 to 1:1 diethyl ether/pentane). Separation of the two product diastereomers obtained, **23a** and **23b** (ratio 1:2.5), was achieved by semipreparative HPLC. After drying under high vacuum (0.01 Torr for 24 h), 233 mg (62%) of a yellow solid, m.p. 99–101 °C (N_2, sealed tube), were obtained. The analysis was performed on the original mixture of diastereomers **23a,b**. M.p. 99–101 °C (N_2, sealed tube); R_f = 0.69 (2:1 diethyl ether/pentane); IR: $\tilde{\mu}$ = 1963, 1900, 1472, 1434 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ = 7.75–7.42 (m, 6H), 7.42–7.22 (m, 2H), 7.12–6.86 (m, 16H), 6.81–6.69 (m, 1H), 5.65 (s, 0.71H), 5.59–5.50 (m, 0.71H), 5.14 (s, 0.29H), 4.93 (s, 0.29H), 4.66 (s, 0.71H), 4.47 (t, J = 6.6, 0.29H), 4.40 (s, 0.71H), 4.14–4.06 (m, 0.29H), 3.98–3.91 (m, 0.29H), 3.78 (s, 0.29H), 3.79–3.73 (m, 0.71H), 3.48 (s, 0.29H), 3.44–3.23 (m, 1.42H), 3.19–3.08 (m, 0.71H), 2.93 (s, 0.71H), 2.92–2.85 (m, 0.29H), 2.59–2.43 (m, 0.71H), 2.35–2.25 (m, 0.71H), 1.21 (s, 6.43H), 1.04 (s, 2.57H), 1.00 (s, 9H), 0.85 (s, 2.14H), 0.55 (s, 2.14H), 0.29 (s, 0.86H), 0.25 (s, 0.86H), 0.22 (s, 2.14H), 0.17 (s, 0.86H), −0.02 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6 one of the diastereomers is in much lower quantity in the mixture, not all of its peaks are detected, aromatic signals show J_{PC}'s, couplings could not be determined for all peaks): δ = 142.1–139.7 (6 lines), 136.1, 136.0,134.9, 134.8, 133.9–133.2 (5 lines), 130.1, 129.4, 128.8–126.8 (overlay of many lines), 94.2 (J_{PC} = 6.2), 89.1 (J_{PC} = 6.2), 87.5, 87.3, 82.9, 79.9, 78.0, 77.0, 75.8, 74.4, 74.3, 65.6, 43.4, 40.7 (J_{PC} = 18.6), 33.0, 30.8 (J_{PC} = 4.2), 26.5, 26.3, 26.2, 18.1, 18.0, −3.3, −3.6, −3.6, −3.7, −4.5, −4.7; ^{31}P NMR (161.903 MHz, C_6D_6): δ = 38.1 (J_{PP} = 37.9), 38.0 (J_{PP} = 41.6), 36.0 (J_{PP} = 41.6), 35.6 (J_{PP} = 37.9); MS (FAB) 964 (M^+, 4), 804 (−Cl, 23), 804 (6), 743 (9), 702 (−PPh_3, 24), 667 (−Cl, −PPh_3, 100); anal. calcd for $C_{51}H_{62}O_2ClP_2RuSi_2$: C 63.36, H 6.78; found: C 63.52, H 6.60: HPLC analytical column, flow 1 mL min^{-1}, *n*-heptane with 8% TBME, pressure 880 psi, injection 15 mL, conc. 4 mg mL^{-1}, retention time: minor diastereomer 9.57 min; major diastereomer 10.81 min; semipreparative column, flow 5 mL min^{-1}, *n*-heptane with 8% TBME, pressure 1162 psi, injection 20 mL, conc. 12 mg mL^{-1}, retention time: minor diastereomer 10.20 min, major diastereomer 12.03 min.

Chloro{[(2*R,3*R**)-2,3-(9,10-dihydro-9,10-anthracenediyl)-4-diphenylphosphino-1-butyl]-η^5-cyclopentadienyl}(triphenylphosphine)ruthenium(II) (25a,b)**: Following procedure B, ligand **24a,b** (145 mg, 0.30 mmol) in degassed (Ar) toluene (10 mL), *n*-butyllithium in hexanes (1.6 M, 0.21 mL, 0.33 mmol), and [$(Ph_3P)_3RuCl_2$] (290 mg, 0.30 mmol) after initial chromatography on silica gel (10:4:35 ethyl acetate/methylene chloride/pet. ether) followed by rechromatography on neutral alox (5:4:20 ethyl acetate/methylene chloride/pet. ether, then 2:1:2 ethyl acetate/methylene chloride/pet. ether) gave 128 mg (48%) of an orange powder, m.p. 218 °C (N_2, sealed tube, decomp). R_f = 0.37 (25:10:2 pet. ether/ethyl acetate/methylene chloride). The complex **25a,b** included 1 equiv of ethyl acetate and was a 11:1 mixture of diastereomers. IR: $\tilde{\nu}$ = 1954, 1899, 1481, 1458, 1434 cm^{-1}; ^{1}H NMR (400 MHz): δ = 7.95–7.82 (m, 2H), 7.48–6.78 (m, 29H), 6.46–6.36 (m, 2H), 5.11 (s, 1H, Cp, major), 5.08 (s, 0.09H, Cp, minor), 4.66 (s, 1H, Cp, major), 4.57 (s, 0.09H, Cp, minor), 3.95 (s, 1H), 3.91 (s, 1H, Cp), 3.83 (s, 1H), 3.70 (s, 1H, Cp), 2.49–2.36 (m, 2H), 2.26–2.12 (m, 2H), 1.69–1.60 (m, 1H), 1.33–1.18(m, 1H), 1 equiv EtOAc; ^{13}C NMR (100 MHz): (aromatic signals show J_{PC}'s, couplings could not be determined for all peaks. Only the major diastereomer was assigned): δ = 143.9, 143.7, 143.6, 142.2, 140.9, 140.6, 135.5 (J_{PC} = 9.3), 133.7 (J_{PC} = 10.5), 131.8 (J_{PC} = 8.1), 129.5, 128.6, 128.1, 127.7 (J_{PC} = 8.9), 127.3 (J_{PC} = 7.9), 127.2 (J_{PC} = 9.1), 125.8, 125.0, 123.5, 122.9, 93.0 (Cp), 80.6 (Cp), 78.9 (Cp), 75.8 (J_{PC} = 11.0), 54.7 (J_{PC} = 11.6), 52.5, 39.3, 36.5, 34.4 (J_{PC} = 26.3), 29.3; ^{31}P NMR (161.904 MHz): δ = 43.19 (d, J_{PP} = 42.6, major), 42.58 (d, J_{PP} = 42.3, minor), 39.04 (d, J_{PP} = 42.3, minor), 32.83 (d, J_{PP} = 42.6, major): MS (FAB) 880 (M^+, 18); anal. calcd for $C_{53}H_{45}ClP_2Ru \cdot EtOAc$ (i.e., $C_{57}H_{53}ClO_2P_2Ru$): C 70.69, H 5.51; found: C 70.37, H 5.44.

Chloro{[(2*R,3*R**)-2,3-(9,10-dihydro-9,10-anthracenediyl)-4-diphenylphosphino-1-butyl]-η^5-(3-benzylcyclopentadienyl)}(triphenylphosphine) ruthenium(II) (32a,b)**: Following method B, ligand **31a,b,c** (20 mg, 0.035 mmol) in degassed toluene (2 mL), *n*-butyllithium in hexanes (1.6 M, 0.024 mL, 0.038 mmol), and [$(Ph_3P)_3RuCl_2$] (34 mg, 0.035 mmol) gave, after chromatography on neutral alumina (90:5:5 to 80:10:10 pet. ether/ethyl acetate/methylene chloride), 10 mg (30%) of complex **32a,b**. R_f = 0.5 (70:15:15 pet. ether/ethyl acetate/methylene chloride); IR: $\tilde{\nu}$ = 1478, 1429 cm^{-1}; ^{1}H NMR (400 MHz): δ = 7.88 (m, 2H), 7.35–6.83 (m, 34H), 6.31 (m, 2H), 4.34 (s, 1H, Cp), 3.91 (s, 1H, Cp), 3.82 (s, 1H, Cp), 3.76 (s, 0.25H) minor, 3.72 (s, 0.75H) major, 3.63 (s, 1H), 3.55–3.51 (m, 2H), 2.38 (m, 2H), 2.00 (m, 2H), 1.62 (m, 1H), 1.28 (m, 1H); ^{13}C NMR (100 MHz) (not all the J_{PC} could be assigned): δ = 144.4 (J_{PC} = 31.4 Hz), 143.7, 142.1, 140.9, 140.5, 140.4, 134.1, 131.8 (J_{PC} = 7.1 Hz), 129.6, 129.2, 128.5 (J_{PC} = 21.7 Hz), 127.9, 127.6 (J_{PC} = 9.3 Hz), 127.2 (J_{PC} = 8.1 Hz), 127.0 (J_{PC} = 5.5 Hz), 126.0, 125.8 (J_{PC} = 8.5 Hz), 125.0, 123.6, 122.9, 84.0, 79.6, 76.1 (J_{PC} = 13.4 Hz), 74.2 (J_{PC} = 8.5 Hz), 54.6 (J_{PC} = 10.7 Hz), 52.5, 38.5, 36.6, 33.9, 33.5 (J_{PC} = 25.7 Hz), 29.5 (J_{PC} = 25.5 Hz), 29.5; ^{31}P NMR (161.903 MHz): δ = 44.77 (d, J_{PP} = 39.8 Hz), 34.09 (d, J_{PP} = 40.0 Hz); anal. calcd for $C_{60}H_{51}ClP_2Ru \cdot H_2O$: C 72.90, H 5.40; found: C 72.95, H 5.48.

Chloro{[(4*R)-4-(diphenylphosphino)-5-phenyl-1-pentyl]-η^5-cyclopentadienyl}(triphenylphosphine)ruthenium(II) (46a,b)**: Following method B, *n*-

butyllithium in hexanes (1.6 M, 0.08 mL, 0.127 mmol), **44a,b** (46 mg, 0.120 mmol) in toluene (3 mL), and $[(Ph_3P)_3RuCl_2]$ (117 mg, 0.122 mmol) gave, after chromatography (silica gel, 8:2 to 1:1, degassed pet. ether/ether) 40 mg (45%) of solid orange complex **46a,b** as a 5:1 mixture of diastereomers, m.p. 138–140 °C (sealed tube), $R_f = 0.5$ (1:1 pet. ether/ether); IR: $\tilde{\nu} = 1480$, 1433, 1266 cm^{-1}; ^1H NMR (400 MHz): $\delta = 8.16$ (m, 2H), 7.39–6.96 (m, 26H), 6.72 (m, 2H), 4.99 (s, 1H, Cp major), 4.96 (s, 0.2H, Cp minor), 4.57 (s, 1H, Cp major), 4.54 (s, 0.2H, Cp minor), 4.49 (s, 1H, Cp major), 4.46 (s, 0.2H, Cp minor), 3.07 (m, 1H), 2.87 (m, 1H), 2.63 (m, 1H), 2.46 (m, 1H), 2.30 (m, 2H), 2.20 (s, 1H, Cp major), 1.67–1.15 (m, 3H); ^{13}C NMR (75 MHz): $\delta = 137.8$, 137.3, 135.9 ($J_{PC} = 8.2$ Hz), 134.1 ($J_{PC} = 10.5$ Hz), 131.2 ($J_{PC} = 8.1$ Hz), 129.2, 128.9 ($J_{PC} = 7.8$ Hz), 128.5, 128.4, 128.2, 127.4, 127.3, 127.1, 127.0, 126.1, 94.1 ($J_{PC} = 4.4$ Hz), 90.6 ($J_{PC} = 13,7$ Hz), 81.7, 70.8, 65.9, 47.1 ($J_{PC} = 48.3$ Hz), 29.8, 27.6 ($J_{PC} = 9.5$ Hz), 24.4, 15.2; ^{31}P NMR (161.904 MHz): $\delta = 43.14$ (d, $J_{PP} = 41.5$ Hz); 34.87 (d, $J_{PP} = 41.5$ Hz); MS (LSIMS): calcd for $C_{46}H_{43}P_2Ru$ [$M^+ - Cl$]: 759.2; found: 759.3; anal. calcd for $C_{46}H_{43}ClP_2Ru$: C 69.57, H 5.42; found: C 69.64, H 5.42.

Chloro{[(4*R)-4-(diphenylphosphino)-5-phenyl-1-pentyl]-η^5-(3-benzylcyclopentadienyl)}(triphenylphosphine)ruthenium(II) (47a,b; 48a,b)**: Following the same procedure as described for the preparation of chiral ligand **31a,b,c**, the deprotected phosphine **43** (210 mg, 0.493 mmol) and lithium benzyl cyclopentadienide (119.8 mg, 0.74 mmol) in degassed THF (8 mL) gave, after workup and purification, 62 mg (27%) of ligand **45a,b,c** as a mixture of 3 double-bond isomers at the cyclopentadiene ring, $R_f = 0.2$ (98:2 pet. ether/ether); ^1H NMR (300 MHz): $\delta = 7.65–7.01$ (m, 20H), 6.18–5.65 (m, 2H, Cp), 3.66–3.50 (m, 2H), 2.83–2.41 (m, 4H), 2.20–1.95 (m, 2H), 1.62–1.25 (m, 3H).

Following Method B, ligand **45a,b,c** (62 mg, 0.128 mmol), *n*-butyllithium in hexanes (1.6 M, 0.088 mL, 0.141 mmol) and $[(Ph_3P)_3RuCl_2]$ (128.4 mg, 0.134 mmol) in degassed toluene (3.3 mL) gave, after flash chromatography (silica gel, 9:1 to 7:3 pet. ether/ether), 15 mg (13.3%) of complex **47a,b**:**48a,b** as a mixture of 4 diastereomers. IR: $\tilde{\nu} = 1482$, 1435, 1381 cm^{-1}; ^1H NMR (400 MHz): $\delta = 8.28$ (t, $J = 8.32$ Hz, 2H), 7.43–6.84 (m, 31H), 6.62 (t, $J = 7.84$ Hz, 2H), 4.84 (s, 0.6H, Cp), 4.55 (s, 0.4H, Cp), 4.29 (s, 0.4H, Cp), 4.22 (s, 0.6H, Cp), 3.78–3.60 (m, 2H), 3.36 (m, 0.4H), 3.27 (m, 0.6H), 3.09 (m, 0.4H), 2.91 (m, 0.6H), 2.53 (s, 0.4H, Cp), 2.43 (m, 2H), 2.27 (m, 1H), 2.02 (s, 0.6H, Cp), 1.91 (m, 1H), 1.69 (m, 2H), 1.50–1.15 (m, 3H); ^{13}C NMR (100 MHz): (not all the J_{PC} could be assigned): $\delta = 137.0$ ($J_{PC} = 11.4$ Hz), 136.1 ($J_{PC} = 8.3$ Hz), 134.4 ($J_{PC} = 7.1$ Hz), 134.0 ($J_{PC} = 10.9$ Hz), 133.1 ($J_{PC} = 10.3$ Hz), 131.0 ($J_{PC} = 7.3$ Hz), 129.8–125.4 (20 lines), 109.5, 108.7 ($J_{PC} = 3.6$ Hz), 82.3 ($J_{PC} = 8.7$ Hz), 80.9, 80.2, 80.1, 73.7 ($J_{PC} = 9.5$ Hz), 71.3, 67.6, 44.0 ($J_{PC} = 22.1$ Hz), 40.0 ($J_{PC} = 43.7$ Hz), 40.0 ($J_{PC} = 40.0$ Hz), 37.7, 32.3, 31.9, 31.0, 30.3, 29.7, 28.6, 28.6, 27.8, 27.7, 24.1, 22.8, 19.9; ^{31}P NMR (161.903 MHz): $\delta = 57.3$ (d, $J_{PP} = 37.3$ Hz), 43.7 (d, $J_{PP} = 39.2$ Hz), 43.7 (d, $J_{PP} = 39.3$ Hz), 38.2 (d, $J_{PP} = 40.2$ Hz), 38.2 (d, $J_{PP} = 39.8$ Hz), 31.6 (d, $J_{PP} = 39.0$ Hz), 31.6 (d, $J_{PP} = 39.3$ Hz); MS (LSIMS): calcd for $C_{53}H_{49}ClP_2Ru$: 884.2; found: 884.1; anal. calcd for $C_{53}H_{49}ClP_2Ru$: C 71.99, H 5.55; found: C 72.03, H 5.52.

Chloro{[3-[(1′*R*)-1′-phenyl-2′-hydroxyethylcarbamoyl]-1-propyl]-η^5-cyclopentadienyl}bis(triphenylphosphine)ruthenium(II) (52): Following method A, ligand **51a,b** (308 mg, 1.217 mmol) and $[(Ph_3P)_3RuCl_2]$ gave, after flash chromatography on degassed aluminum oxide (neutral) (1:1 ethyl acetate/pet. ether), 857 mg (76%) of the monohydrate as an orange solid. M.p. 111 °C (N_2 sealed tube); $R_f = 0.43$ (1:1 pet. ether/diethyl ether); IR: $\tilde{\nu} =$ 3675, 3424, 1963, 1905, 1817, 1733, 1676, 1498 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): $\delta = 7.70$ (s, 12H), 7.31–7.15 (m, 5H), 7.13–6.93 (m, 18H), 6.31 (d, $J = 8.24$, 1H), 5.59–5.51 (m, 1H), 4.08 (s, 2H, Cp), 3.75–3.66 (m, 1H), 3.63–3.57 (m, 1H), 3.48 (s, 1H, Cp), 3.44 (s, 1H, Cp), 2.71–2.63 (m, 2H), 2.21–2.00 (m, 4H), 1.70 (s, 1H); ^{13}C NMR (100 MHz): (aromatic signals show J_{PC}'s, couplings could not be determined for all peaks): $\delta = 172.2$, 138.7, 138.6, 138.6, 138.4, 138.3, 138.3, 133.8, 133.7, 132.1, 132.0, 131.9, 128.7, 128.6, 128.0, 127.4, 127.3, 126.9, 108.7, 79.7 ($J_{PC} = 8.2$), 79.4 ($J_{PC} = 8.2$), 76.5, 76.1, 53.6, 47.5, 36.4, 26.1, 25.5; ^{31}P NMR (161.9 MHz, C_6D_6): $\delta = 41.2$ (d, $J_{PP} = 42.0$), 40.8 (d, $J_{PP} = 42.0$); MS (FAB): 949 (M^+, 11); anal. calcd for $C_{53}H_{50}ClNO_2P_2Ru \cdot H_2O$: C 67.05, H 5.52; found: C 66.94, H 5.42.

Chloro{[3-[(4′*R*)-4′-phenyl-4′,5′-dihydrooxazol-2-yl]-1-propyl]-η^5-cyclopentadienyl}bis(triphenylphosphine)ruthenium(II) (53): Following method B, ligand **51a,b** (160 mg, 0.623 mmol) in degassed THF rather than toluene for 12 h at 90 °C gave, after flash chromatography (silica gel, degassed solvents (Ar) 1:1 diethyl ether/pet. ether, 1:1 methylene chloride/diethyl ether), 352 mg (61%) of an orange powder. M.p. 70–72 °C (N_2, sealed tube), $R_F = 0.29$ (1:1 pet. ether/diethyl ether); IR: $\tilde{\nu} = 1665$, 1480, 1434 cm^{-1}; ^1H NMR (400 MHz): $\delta = 7.41–7.28$ (m, 13H), 7.27–7.15 (m, 10H), 7.14–7.01 (m, 2H), 5.13 (t, $J = 9.1$, 1H), 4.58 (dd, $J = 10.2$, 8.4, 1H), 4.06 (t, $J = 8.2$, 1H), 4.01 (s, 2H, Cp), 3.28 (s, 2H, Cp), 2.42 (t, $J = 7.1$, 4H), 2.00–1.92 (m, 2H); ^{13}C NMR (100 MHz): (aromatic signals show J_{PC}'s, couplings could not be determined for all peaks): $\delta = 168.6$, 142.5, 138.7 ($J_{PC} = 19.4$), 138.4 ($J_{PC} = 19.4$), 133.8, 128.6, 128.5, 127.4, 126.6, 107.7, 80.2, 76.6, 74.5, 69.6, 27.8, 26.7, 26.2; ^{31}P NMR (161.9 MHz): $\delta = 40.2$; MS (FAB) 913 (M^+, 22); anal. calcd for $C_{53}H_{48}ClNOP_2Ru$: C 69.61, H 5.29; found: C 69.80, H 5.50.

General procedure for reconstitutive condensation: 12-cyclohexyl-11-oxo-13-tetradecenoic acid ethyl ester (19): Ethyl 10-undecynoate (63 mg, 0.30 mmol) was added at room temperature to a solution of 10 mol% (30 μmol) of catalyst dissolved in degassed toluene (1 mL) followed by sequential addition of indium triflate (15 mol%, 45 μmol) and (*S*)-1-cyclohexyl-2-propen-1-ol (168 mg, 1.2 mmol). The reaction mixture was then placed into a preheated 90 °C oil bath. The heterogeneous solution turned from orange to red and the formation of a fine white solid was observed at the bottom of the glass tube. The reactions were monitored by GC and stopped when no further turnover was detected, or when the alkyne was completely consumed, at which point the solvent was decanted off the solid material and the tube rinsed twice with 1 mL of diethyl ether. After evaporation, the residue was purified by flash chromatography (silica gel, 1:30 diethyl ether/pentane) to give the product. $[\alpha]_D = 49.9(4)$ ($c = 11.8$, $CHCl_3$), which corresponds to 46.8% *ee* by chiral HPLC; $R_f = 0.33$ (1:5 diethyl ether/pentane); IR: $\tilde{\nu} = 1737$, 1713, 1631, 1466, 1449, 1406, 1371 cm^{-1}; ^1H NMR (300 MHz): $\delta = 5.66$ (dt, $J = 16.8$, 9.8, 1H), 5.14–5.05 (m, 2H), 4.12 (q, $J = 7.1$, 2H), 2.87 (t, $J = 9.1$, 1H), 2.51–2.33 (m, 2H), 2.28 (t, $J = 7.6$, 2H), 1.81–1.46 (m, 11H), 1.34–0.75 (m, 14H), 1.25 (t, $J = 7.1$, 3H); ^{13}C NMR (75 MHz): $\delta = 211.9$, 174.0, 135.9, 118.2, 64.7, 60.1, 42.7, 38.9, 34.3, 31.5, 30.1, 29.2, 29.1, 29.1, 29.1, 29.0, 28.9, 26.2, 26.0, 24.8, 23.2, 14.1; HRMS: calcd for $C_{22}H_{38}O_3$]M^+]: 350.2821; found: 350.2825; anal. calcd for $C_{22}H_{38}O_3$: C 75.38, H 10.93; found: C 75.46, H 10.74; chiral HPLC, OD column, 1.5 mL flow, detection 210 nm, 99.1/0.1 *n*-heptane/isopropanol, retention times: major isomer 18.3 min, minor isomer 23.0 min.

5-Cyclopentyl-3-methyl-1-penten-3-one (56): IR (neat): $\tilde{\nu} = 1715$, 1634, 1454, 1405, 1472 cm^{-1}; ^1H NMR (300 MHz): $\delta = 5.79$ (m, 1H)), 5.14 (m, 2H), 3.20 (quint, $J = 7.1$ Hz, 1H), 2.50 (d, $J = 3.87$ Hz, 1H), 2.48 (d, $J = 3.15$ Hz, 1H), 2.23 (hept, $J = 7.4$ Hz, 1H), 1.80 (m, 2H), 1.16 (d, $J = 6.87$ Hz, 3H), 1.05 (m, 2H); ^{13}C NMR (75 MHz): $\delta = 211.7$, 137.7, 116.7, 51.4, 46.9, 35.2, 32.6, 32.5, 24.9, 15.6; HRMS: calcd for $C_{11}H_{18}O$: 166.1358; found: 166.1357.

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