Enantioselective π-Complexation. Synthesis of Enantiomerically Pure Planar Chiral Ruthenocenes

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Reaction of half-sandwich complexes $Cp^*RuL_2^{ch}$, featuring a chiral auxiliary ligand L_2^{ch}, with prochiral cyclopentadienides Cp^{pc-} gave enantiomerically pure (>95% ee) or enriched ruthenocenes Cp^*RuCp^{pc} **4**. For the chiral auxiliary L_2^{ch} were tested a pyridyloxazoline (ref 15), the diolefin nopadiene (ref 16), and the amino acids methionine and proline, which form relatively labile complexes with the Ru(II) fragment Cp^*Ru^+. For the prochiral cyclopentadienide $Cp^{pc}Li$, Li derivatives of 1- *tert*-butyl-3-methylcyclopentadienide, 1-*tert*-butylindenyl, and 1- *tert*-butyl-3-benzylindenyl were used. Determination of enantiomeric excess was achieved through a derivatization procedure generating fulvene cation complexes $[Cp^{pc}RuC_5Me_4{=}CH_2]^+$ (**5**), which, after the addition of (*S*)-α-phenylethylamine, yield mixtures of diastereoisomers $Cp^{pc}RuC_5H_4CH_2NHCH(Me)Ph$ (**6**). The absolute configuration of **4c** (Cp^{pc} = 1-*tert*-butyl-3-benzylindenyl) was determined by X-ray structure analysis of the respective fulvene salt. Asymmetric induction was greatest with the amino acids and was reverted with the epimeric amino acid; thus, (*S*)-proline or -methionine gave (*S*)-ruthenocene **4c** and vice versa.

Planar chiral arene and dienyl complexes have recently proven to be versatile intermediates in synthetic organic chemistry.[1] Due to the complete regiospecificity in, for example, the addition of a nucleophile to an electrophilic π-ligand of a transition metal complex,[2] the newly generated asymmetric carbon atom is formed enantiospecifically depending on the optical purity of the π-complex. Such methodology has been widely used to elaborate a host of functionalities in stereocontrolled reactions via, for example, the (dienyl)$Fe(CO)_3$[+ 3] or (arene)$Cr(CO)_3$[1] moieties.

Although sandwich and half-sandwich complexes with planar chirality, particularly ferrocenes, ruthenocenes, (arene)chromium, and CpMn tricarbonyl derivatives,[4] had been synthesized and their chiroptical properties studied, resolution into enantiomers generally has rested on classical derivatization procedures via diastereoisomers. These can be generated by the introduction of a chiral substituent onto either the π-ligand[5] or, in the case of a half-sandwich complex, the metal (or both).[6]

Strategies to effect face differentiation in the course of the complexation of prochiral (enantiotopic) π-ligands were mostly based on an additional chiral substituent, e.g., a menthyl ester, on this ligand, leading to diastereoisomers with planar chirality as well as central chirality in the side chain. Although the method was successful in the diastereospecific complexation of the $Cr(CO)_3$ unit to an α-hydroxytetraline, with diastereometric induction of >98%,[7] in other cases induction was low and the resulting diastereomeric mixtures had to be separated by recrystallization or chromatography.[8]

In view of the synthetic versatility provided by an element of planar chirality in transition metal complexes on the one hand and the restrictions inherent in the separation of enantiomers or diastereoisomers on the other, enantioselective π-complexation would mark important progress in the direction toward synthesis of enantiomerically pure planar chiral π-complexes. A chiral auxiliary ligand, which may or may not be lost during complexation, could serve as the *si/re* controlling factor during attack of the complexing metal fragment L_nM onto the prochiral π-ligand, e.g., Cp^{pc}. The idea was first pursued by Birch,[9] who attempted this kind of *chirality transfer* by reacting chiral oxa diene $Fe(CO)_3$ complexes (of 16-dehydropregnenolone acetate or pulegone) with suitably substituted cyclohexadienes to generate optically enriched (cyclohexadiene)$Fe(CO)_3$

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complexes. However, neither optical yields, estimated at best around 40% ee, nor chemical yields were in a range that encouraged practical use of the method. Since the intermediate $L^{ch}Fe(CO)_3$ complexes were not isolated, their diastereomeric purity could not be assessed,[10] leaving the reasons for the relatively low chiral induction unclear. In a similar experiment by Wink and co-workers,[11] who examined arene exchange at (naphthalene)$(CO)_2PR(OR')_2{}^{ch}Cr$, inductions likewise were rather low. In this case the chiral phosphine is not exchanged during reaction, leading to a mixture of diastereoisomers.

As a prerequisite for successful enantiosteering of a prochiral π-ligand, the complexation reaction must proceed under mild conditions, implying that the auxiliary ligand must not be too strongly bound in case it has to be released in the course of the complexation. The chiral auxiliary itself should be preferably available from the natural chiral pool or should be easily synthesized from it. Moreover, if it is released during complexation, it could be recovered. Common (acceptor) ligands in transition organometallic complexes in general do not meet these requirements. We recently found a class of Cp*Ru complexes where coligands such as amines or sulfoxides are pure σ-donors[12] and can be expected to be displaced in, for example, a cyclopentadienylation reaction under rather mild conditions. We thus embarked on the direct synthesis of enantiomerically enriched planar chiral ruthenocenes by cyclopentadienylation of such labile half-sandwich complexes as *an entry into enantioselective* π-complexation. For this reason, we developed a methodology to incorporate chiral chelating amines and dienes, as well as amino acids, as ligands into preferably labile Cp*Ru half-sandwich complexes. These have proved to directly yield planar chiral ruthenocenes upon complexation with appropriately substituted cyclopentadienides in good chemical yield and, in the most favorable cases, in rather high optical purity.

$Cp^*RuL^{ch}_2$ Complexes with Bidentate Chiral Auxiliary Ligands L^{ch}_2. Starting from either $[Cp^*Ru(OMe)]_2$ (**1**) or $[Cp^*RuCl]_4$ (**2**), complexes of the type Cp^*RuL_2X were readily prepared with a wide variety of ligands L, including pure σ-donors.[12−14] In analogy to Cp*Ru(bipy)Cl,[13] the corresponding complex with a chiral 2-(2-pyridinyl)-2-oxazoline[15] compound **3a**, known as a ligand in Rh^I complexes that catalyze asymmetric hydrosilylation, was prepared. The NMR spectrum of **3a** indicated a 1:10 ((*S*,*R*):(*R*,*R*)) mixture of diastereoisomers that did not change upon recrystallization and is believed to be the thermodynamic mixture. Complex **3b**, which was obtained from **2** and the chiral diene (+)-nopadiene[16] (Scheme 1), showed but one diastereoisomer in the NMR spectrum.

Amino acids could serve as readily available auxiliaries from the chiral pool. CODRu(amino acid) complexes are known with the composition CODRu(amino acid)Cl_2.[17] Depending on the additional functional groups, an amino acid could function as a bi- or tridentate ligand toward a CpRu* unit. We found that the coordinatively unsaturated precursor **1** reacted smoothly with methionine and also with proline to give **3c** and **3d**, respectively. In the methionine complex **3c**, the amino acid functions as a monoanionic tridentate ligand through carboxylate, amine, and MeS groups. Complexation of methionine to Cp*Ru generates two new chiral centers (at ruthenium and at sulfur), giving rise to four diastereoisomers. Starting from optically pure (*S*)-methionine, NMR spectra of **3c** show the presence of but one diastereoisomer, i.e., the configuration of the amino acid determines the sense of the tripodal arrangement (O, N, S) as well as the configuration at the complexed MeS group. Such diastereoselectivity was previously observed in CODRu(amino acid)Cl_2, where the use of a racemic amino acid led to the mixture of only two enantiomers.[17]

The situation is slightly more complicated with proline, which can function only as a bidentate ligand. The analytical and spectroscopic composition of the bright yellow, extremely air sensitive (pyrophoric!) solid that separates from THF is for Cp*Ru(proline). The compound is soluble without decomposition only in coordinating solvents such as acetonitrile. NMR spectra in this solvent show coordinated proline and one single Cp* singlet. Although a number of Cp*Ru complexes with 16 valence electrons are well documented,[18] no monomeric complex with just two σ-donor ligands exists among them. We suggest a solvent-stabilized monomeric structure for **3d** in acetonitrile solution and a polymeric one in the solid, possibly with the free C═O group of the amino acid as a weak intermolecular link. Although in principle two diastereomeric complexes **3d** can be formed from either (*S*)- or (*R*)-amino acids, respectively, only one has been observed in complexes such as Cp*Rh(proline)Cl or (arene)Ru(proline)Cl,[19] which means that the configuration of the newly formed chiral center at nitrogen is determined by the configuration of the α-carbon. Therefore, also in the case of **3d**, from the two diastereomeric forms possible in solution, whether rapidly interconverting or not, one is expected to be present in large excess.

Cyclopentadienylation with Unsymmetrically Substituted Cyclopentadienides. Prochiral cyclopentadienes $Cp^{pc}H$, 1-*tert*-butyl-3-methylcyclopentadiene, 1-*tert*-butylindene, and 1-*tert*-butyl-3-benzylindene, were synthesized according to or adopted from literature methods.[20] The corresponding lithium cyclopentadienides were prepared by the action of a stoichiometric amount *n*-BuLi on cyclopentadienes. These were added to complexes **3a**−**3d** at low temperature (−78 °C), and

(10) Complexation of Cp*Ru on pullegone to give the the Cp*Ru(oxadiene) complex analogous to the $(CO)_3Fe$ complex of ref 9a (Koelle, U.; Pasch, R. To be published) showed almost no diastereoselectivity, which may be the reason for the low enantiomeric excess in transfer reactions described in ref 9.

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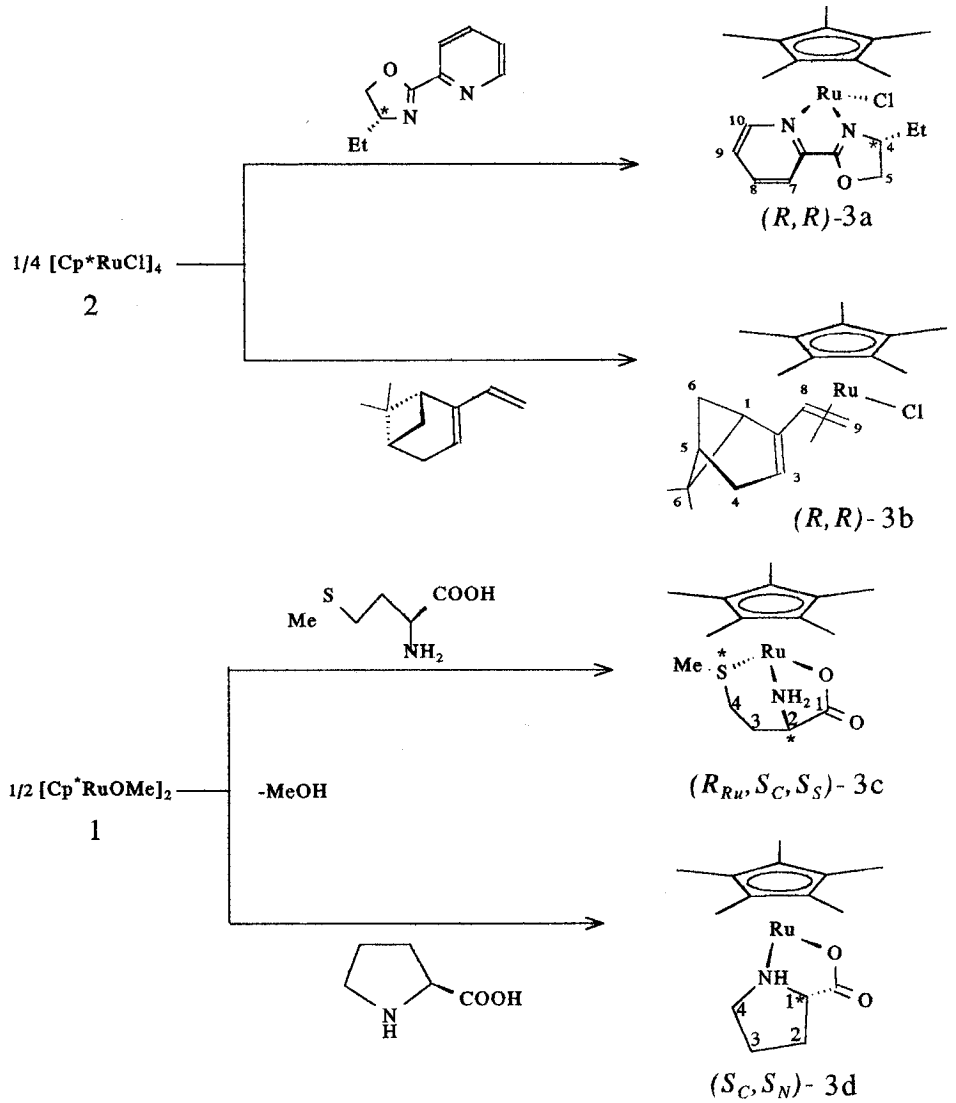
Scheme 1. Synthesis of Chiral Cp*Ru Half-Sandwich Complexes



the mixture was slowly warmed until the reaction started, which occurred around −30 to −10 °C. The mixture was then stirred at this temperature for some hours before workup. Ruthenocenes were purified by chromatography over silylated silica. They are pale yellow oils that were spectroscopically pure, but elemental analysis was difficult in cases where the compound did not solidify. Chemical and optical yields of ruthenocenes **4a**−**4c** are collected in Scheme 2. For the sake of comparison, the same ruthenocenes were synthesized as racemates by cyclopentadienylation of **1** with the respective prochiral lithium cyclopentadienide (Cp^{pc}) in THF, a reaction that gives ruthenocenes in yields of 60−65%.

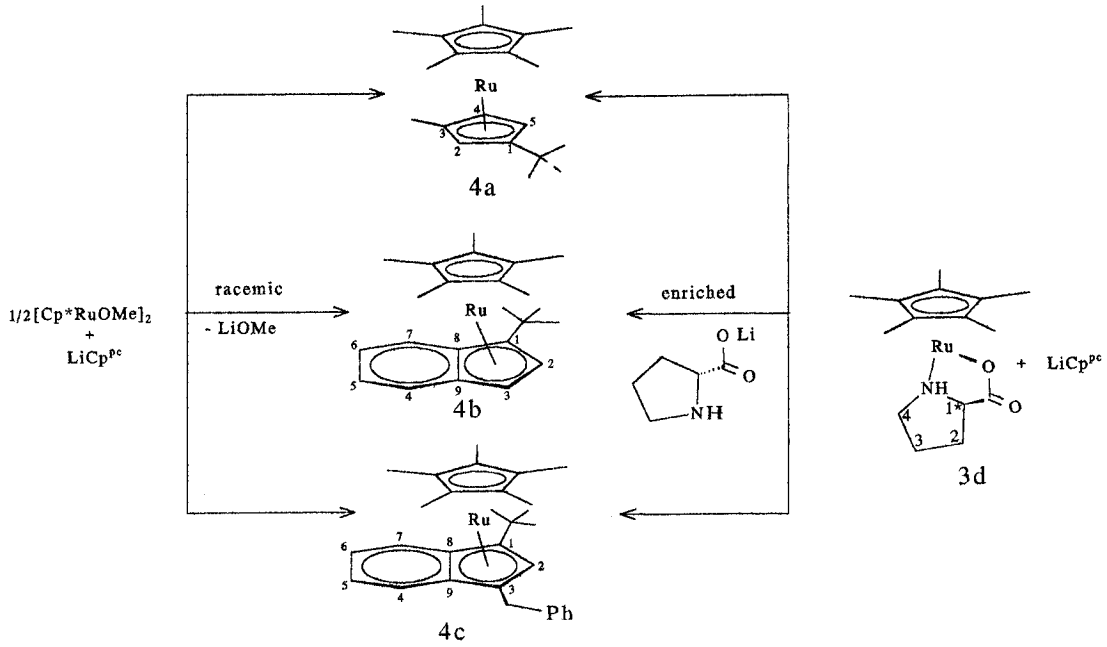
Derivatization, Enantiomeric Purity, and Absolute Configuration. In the present case, determination of the enantiomeric composition poses a particular problem. Ruthenocenes lacking functional groups are not split in the NMR by chiral shift reagents. They are not volatile enough for GC, nor did HPLC on chiral material (DIONEX) give any separation of enantiomers. To determine the enantiomeric composition, we resorted to a derivatization procedure, the principles of which we developed many years ago.[21] Ruthenocenes featuring a Cp* ligand are susceptible to hydride abstraction from a methyl group, giving cationic fulvene complexes in high yield. These are readily recrystallized, which, when followed by hydride addition, can serve as a convenient purification procedure for the ruthenocene. Fortunately hydride abstraction in the present cases occurred exclusively at the Cp* ligand, even if the other Cp ring carried methyl groups as well.

Since these cationic fulvenes are prone to add various nucleophiles at the exocyclic $=CH_2$ group,[21] the specific addition of (*S*)-α-phenylethylamine (Scheme 3) was a straightforward way to obtain diastereoisomers that could be distinguished in the proton (in some cases also the carbon) NMR. Optical yields in Chart 1 are based on these spectra. Figure 1 shows a representative ^1H NMR spectrum of **6c** to illustrate the method. The derivatization as applied to racemates gave diastereoisomers in an exactly 1:1 ratio, proving that no diastereoselectivity is inherent in any of its reaction steps.

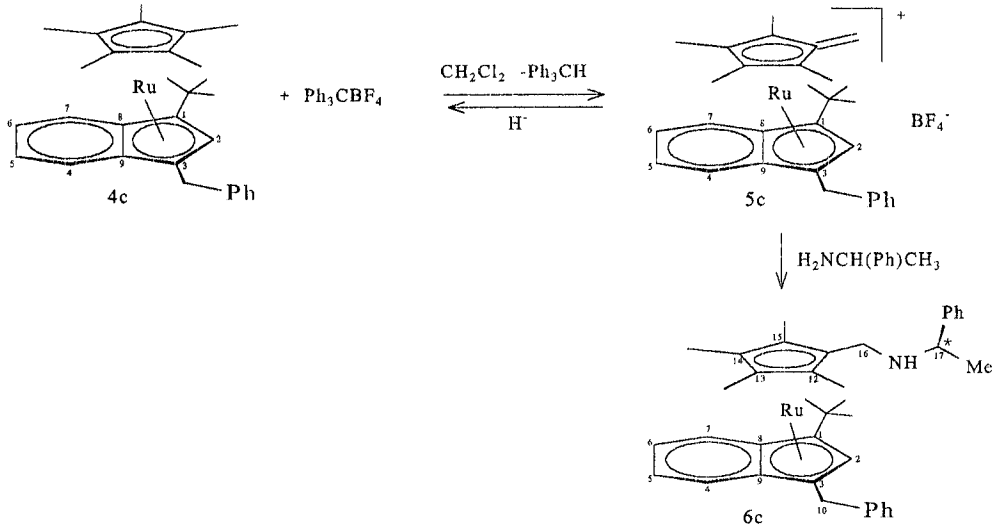
As one can see from Figure 1, signals for diastereoisomers are doubled for Cp* methyl protons, for residual protons in Cp^{pc}, and for the AB pattern of the exocyclic CH_2 group. NOE experiments on **6a** suggest a conformation where the $CH_2NHCHMe(Ph)$ group is located above H^2 of the Cp^{pc} ring, exerting a maximum chemical

(21) Koelle, U.; Grub, J. *J. Organomet. Chem.* **1985**, *289*, 133.

Scheme 2. Synthesis of Racemic and Optically Enriched Ruthenocenes



Scheme 3. Derivatization of Chiral Ruthenocenes (e.g., 4c) Giving diastereomers (e.g., 6c).



anisotropy in this proton as well as in the Me and ^{t}Bu groups. Shift differences are large enough to locate signals from individual diastereomers and, thus, identify (*R*)- and (*S*)-ruthenocenes for **4a**−**c** independently. In this way it was possible to assess the formation of epimeric ruthenocenes (*S*)-**4c** and (*R*)-**4c** as the majority enantiomers with the same enantiomeric excess when (*S*)- and (*R*)-proline and -methionine, respectively, were the auxiliaries.

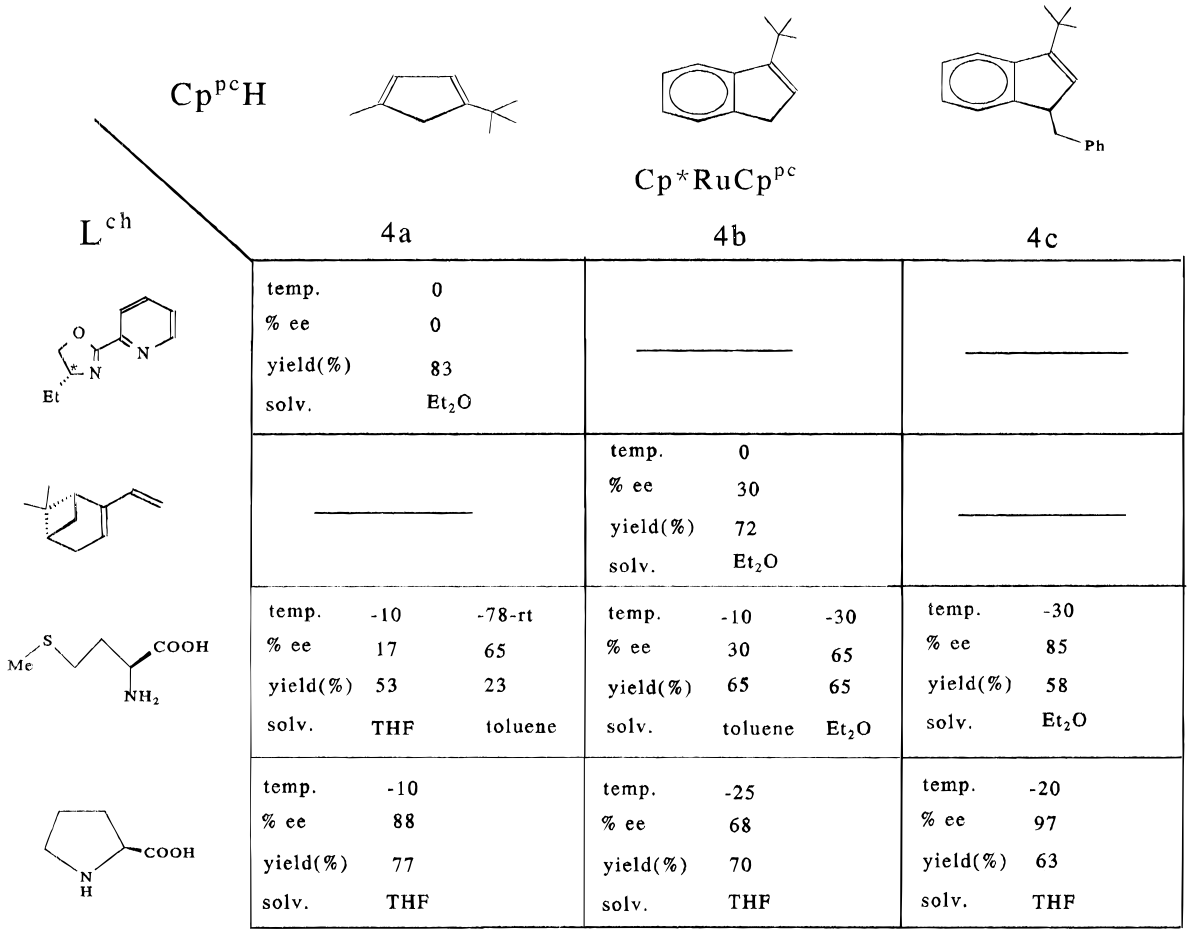
To determine the absolute configuration of one of the chiral ruthenocenes, a single-crystal X-ray structure determination was performed. Since none of the ruthenocenes showed a tendency to form good crystals, particularly when it was enantiomerically pure or enriched, we resorted to crystallizing the corresponding fulvene cations, which must have the same configuration as the parent ruthenocene. Crystals of (tetramethylfulvene)(1-*tert*-butyl-3-benzylindenyl)ruthenium tetrafluoroborate (**5c**), derived from ruthenocene **4c**, were grown by diffusion of ether into a concentrated methylene chloride solution of the fulvene salt. In addition to the structure solution, the measurement of anomalous dispersion of Friedel pairs allowed one to determine the absolute configuration. It is thus shown that (*S*)-methionine and also (*S*)-proline induce a planar (*S*)-configuration (*pS*) of this particular ruthenocene. NMR assignment gives the other diastereoisomer with either (*R*)-amino acid (using (*S*)-α-phenylethylamine); thus, (*R*)-methionine and (*R*)- proline induce a (*pR*)-configuration.[22]

Discussion

As can be seen by inspection of Chart 1, asymmetric induction in the course of π-complexation increases with increasing steric bulk of the substituents at Cp^{pc}. Moreover, the highest enantiomeric purities were obtained in cases where the reaction started at low

(22) The configuration is designated by using the adaptation of the Cahn−Ingold−Prelog Rules to Cp transition metal complexes: Sloan, T. E. In *Topics in Inorganic and Organometallic Stereochemistry*; Geoffrey, G., Ed.; Wiley: New York, **1981**; Vol. 12, p 32.

Chart 1. Yields and Enantiomeric Excess of Chiral Ruthenocenes Obtained with Various Chiral Auxiliaries.



L^{ch}	4a	4b	4c
	temp. 0 % ee 0 yield(%) 83 solv. Et_2O	———	———
	———	temp. 0 % ee 30 yield(%) 72 solv. Et_2O	———
	temp. -10 -78-rt % ee 17 65 yield(%) 53 23 solv. THF toluene	temp. -10 -30 % ee 30 65 yield(%) 65 65 solv. toluene Et_2O	temp. -30 % ee 85 yield(%) 58 solv. Et_2O
	temp. -10 % ee 88 yield(%) 77 solv. THF	temp. -25 % ee 68 yield(%) 70 solv. THF	temp. -20 % ee 97 yield(%) 63 solv. THF

temperature, but the Cp*Ru half-sandwich complex was not completely dissolved in the reaction mixture. A σ-cyclopentadienyl complex as depicted in Figure 3 is generally considered as an intermediate in this type of complexation.[23] For intermediates such as the (σ-cyclopentadienyl)(diene)RuCp*, formed in the case of the nopadiene complex **3b**, this complex is anticipated to be relatively more stable, i.e., the barrier for $\sigma \rightarrow \pi$ conversion should be higher than if the coligands are pure σ-donors. A low barrier for $\sigma \rightarrow \pi$ conversion can be anticipated for amino acid complexes.

Since the orientation of the incoming Cp^{pc} with respect to the Cp*Ru residue will be restricted to that shown in Figure 3 (H on C_2 pointing toward Cp*), site differentiation is determined by the attack of Cp^{pc} from "left or right". For configurationally rigid precursor complexes such as **3a**−**c**, the site of attack is then determined by the most labile (i.e., the most readily substituted) atom at Ru. It therefore seems essential that in these cases precursor half-sandwich complexes are formed as one single diastereoisomer with respect to the configuration at the metal. But even an auxiliary such as bidentate proline, which emerged in this study as the most efficient chiral auxiliary, may still offer a reaction path where the chiral information provided by the amino acid can be retained to a late stage at the reaction coordinate. Figure 3 displays the σ-cyclopentadienyl intermediate that could be formed from **3d** and 1-*tert*-butyl-3-benzylindenyl. Note that the attack of an anion at the metal of a carboxylic acid complex can be compensated for within the carboxylate group, avoiding a negatively charged metal fragment. In the case of **3d**, a dynamic equilibrium between the transition complex of Figure 3 and its constituents, with high preference for one diastereoisomer, could still lead to high optical induction in the product. Obviously the low-energy conformation for this particular case is that depicted in Figure 3 (benzyl group directed toward N, ^{t}Bu directed toward O), since it leads to the experimentally observed configuration of the resulting ruthenocene.

In 1,3-disubstituted cyclopentadienides with $R^1 > R^3$, like the 1-*tert*-butyl-3-methylcyclopentadienide, a 4-σ-complex is the most probable intermediate. Differentiation is then effected through the difference in size between R^3 and H, which may lead to a single preferred conformation in the transition state and ultimately to a single enantiomer. In 1-indenyls a 3-σ-complex would be formed, where stereodifferentiation is between H atoms at the Cp and the arene ring, whereas 1,3-disubstituted indenyls are restricted to form a 2-σ-complex in the transition state (as depicted in Figure 3). In this latter case, R^1 and R^3 are both adjacent to the Ru−C σ-bond providing the full effect of size differentiation, which may explain the high induction found for 1-*tert*-butyl-3-benzylindene. For a ligand transfer reaction that does not pass through a σ-transition state, the factors that determine enantioface differentiation are less well defined, but substituents of different size can be expected to exert a major influence.

(23) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 7523.

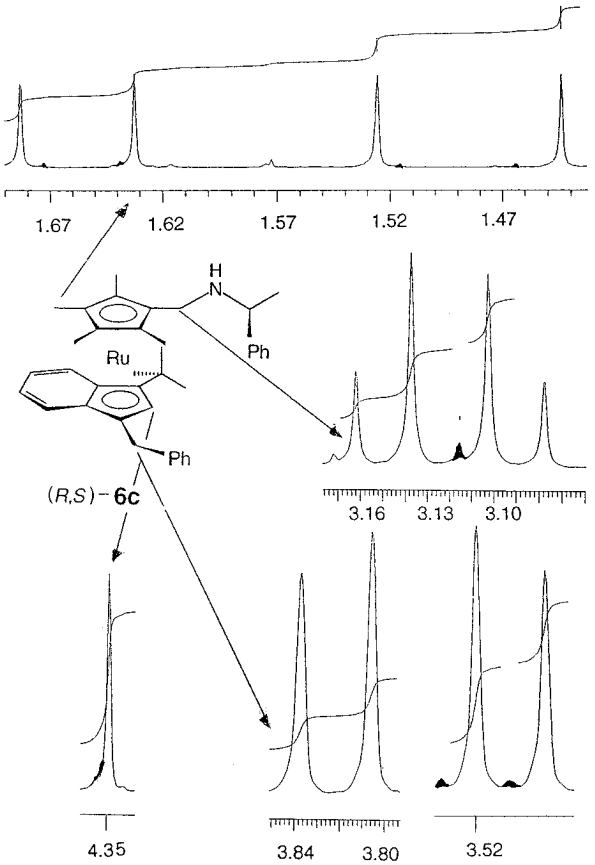


Figure 1. Part of the ^{1}H NMR spectrum of **6c** showing signals that are doubled in the diastereomeric mixture. Major signals are from *(R,S)*-**6c** and minor signals (black) from (*S,S*)-**6c**.

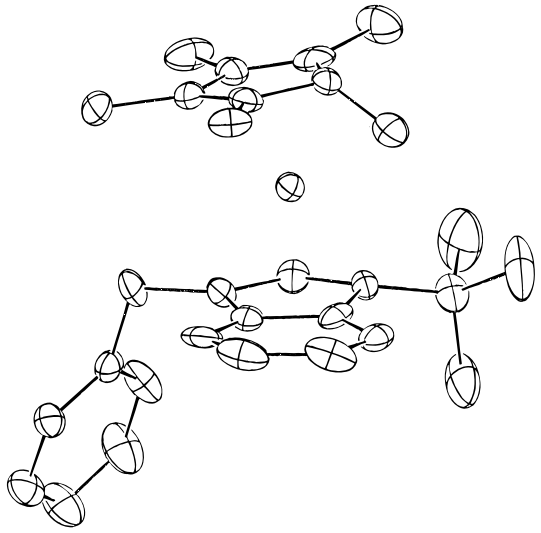


Figure 2. Ortep representation of the cation of (*S*)-(tetramethylfulvene)(1-*tert*-butyl-3-benzylindenyl)ruthenium tetrafluoroborate (**5c**): Ru−C_{ind} 2.23(1), 2.24(1), 2.20(1), 2.265(9), 2.25(1) Å, Ru−C_{fulv} 2.14(1), 2.25(1), 2.252(9), 2.15(1) Å; Ru−*C*═CH_{2exocl} 2.07(1) Å; Ru−C═*C*H_2 exocl 2.30(1) Å.

Experimental Section

All manipulations were conducted under an inert atmosphere of nitrogen using conventional Schlenk tube techniques. Solvents were dried and distilled under nitrogen atmosphere before use. The nuclear magnetic resonance spectra were recorded on Varian Unity 500 or Bruker WP-80 spectrometers. Mass spectra were recorded on a Varian MAT-95 spectrometer,

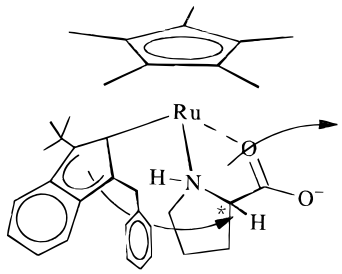


Figure 3. Assumed configuration of the intermediate σ-Cp complex formed from **3d** and 1-*tert*-butyl-3-methylindenide.

UV spectra were recorded on an X-dap diode array spectrophotometer, and CD spectra were recorded on a Jasco J 41c instrument. Elemental analyses were from Microanalytical Laboratories Engelskirchen or the microanalytical laboratory of this institute. 1-*tert*-butyl-3-methylcyclopentadiene, 1-*tert*-butylindene[20] and (*R*)-(+)-4-ethyl-2-(2-pyridinyl)-2-oxazoline[14] were synthesized by adapting literature procedures.

1-*tert*-Butyl-3-benzylindene. To a solution of 5.95 mmol of 1-*tert*-butylindene in 20 mL of THF cooled to −78 °C was added 2.38 mL of BuLi (2.5 M solution in hexane). The mixture was slowly warmed to ambient temperature and stirred for one additional hour. To the solution of 1-*tert*-butylindenyllithium cooled again to −78 °C was added 5.95 mmol of benzyl chloride. After the solution was warmed to room temperature and stirred for 1 h, the solvent was removed and the oily residue was extracted with pentane. The combined extracts were filtered through Celite, the solvent was stripped again, and the residual oil was dried at high vacuum to obtain 4.1 mmol (68% yield) of product (14:1 mixture of tautomers). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): 1-*tert*-butyl-3-benzylindene δ 7.48−6.68 (m, 9H, Ph, H^{4-7}), 6.00 (d, $^3J(H^2,H^3)$ = 2.1 Hz, 1H, H^2), 3.49 (ABX, $^3J(H^3,H^2)$ = 2.1 Hz, $^3J(H^3,$-PhCH*H*) = 8.2 Hz, $^3J(H^3,$PhC*H*H) = 6.4 Hz, 1H, H^3), 2.89, 2.55 (ABX, J_{AB} = 13.4 Hz, $^3J($PhCH*H*,$H^3)$ = 8.2 Hz, $^3J($PhC*H*H,$H^3)$ = 6.4 Hz, 2H, $PhCH_2$), 1.26 (s, 9H, ^{t}Bu); 1-benzyl-3-*tert*-butylindene δ 5.80 (s, 1H, H^2), 2.10 (s, 1H, H^3), 2.99, 2.94 (ABq, J_{AB} = 13.4 Hz, 2H, $PhCH_2$), 1.03 (s, 9H, ^{t}Bu). ^{13}C NMR (500 MHz, C_6D_6, 25 °C): 1-*tert*-butyl-3-benzylindene δ 153.6, 149.3, 144, 140.6 ($C^{8,9,1}$, Ph-C_{ipso}), 131 (C^2), 129.2, 128.5, 126.6 (Ph), 126.4, 124.4, 123.8, 122.5 (C^{4-7}), 49.6 (C^3), 38.6 (Ph*C*H_2), 33.0, 29.4 (^{t}Bu).

3a. To a solution of 0.25 g (0.23 mmol) of $[Cp^*RuCl]_4$ (**2**) in 30 mL of Et_2O was added 0.16 g (0.92 mmol) of (*R*)-(+)-4-ethyl-2-(2-pyridinyl)-2-oxazoline; the color directly turned mauve. The solution was stirred for 2 h, filtered through Celite, and concentrated. At −40 °C, 0.322 g (0.72 mmol, 78% yield) of product separated as a dark mauve powder: de 88%; ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ 8.97 (d/d/d, $^3J(H^{10},H^9)$ = 5.5 Hz, $^4J(H^{10},H^8)$ = 1.5 Hz, ^fJ = 1.0 Hz, 1H, H^{10}), 7.15 (m, 1H, H^7), 6.68 (1H, t/d, $^3J(H^8,H^7,H^9)$ = 7.5 Hz, $^4J(H^8,H^{10})$ = 1.5 Hz, 1H, H^8), 6.55 (d/d/d, $^3J(H^9,H^{10})$ = 5.5 Hz, $^3J(H^9,H^8)$ = 7.5 Hz, $^4J(H^9,H^7)$ = 1.5 Hz, 1H, H^9), 4.15 (d/d, $^3J(H^4,H^5)$ = 8.5 Hz, $^3J(H^4,H^{5'})$ = 6.0 Hz, 1H, H^4), 3.97 (d/d/d, $^2J(H^5,H^{5'})$ = 8.5 Hz, $^3J(H^5,H^4)$ = 8.5 Hz, $^3J(H^{5'},H^4)$ = 6.0 Hz, 2H, $H^5,H^{5'}$), 2.25 (m, 1H, CH_2), 1.36 (m, 1H, CH_2), 0.75 (t, $^3J($Me,$CH_2)$ = 7.5 Hz, 3H, Me), 1.74 (s, 15H, Cp*).

3b. To 0.3 g (0.29 mmol) of $[Cp^*RuCl]_4$ (**2**) in 30 mL of Et_2O was added, at −78 °C, 0.17 g (1.16 mmol) of (+)-nopadiene.[15] After slow warming to room temperature, the mixture was stirred for an additional 3 h. The solvent was stripped, the residue was extracted with hexane, and the solution was filtered through celite, concentrated, and kept at −78 °C. **3b** separated as an orange powder: yield 80% (0.39 g, 0.92 mmol); ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ 3.87 (d/d, $^3J(H^8,H^{9'})$ = 9.5 Hz, $^3J(H^8,H^9)$ = 7.3 Hz, 1H, H^8), 3.44 (d br, $^3J(H^3,H^{4'})$ = 6.1 Hz, 1H, H^3), 2.85 (d/d, $^3J(H^9,H^8)$ = 7.3 Hz, $^2J(H^9,H^{9'})$ = 2.14 Hz, 1H, H^9), 1.75 (d/d, $^3J(H^{9'},H^8)$ = 9.5 Hz, $^2J(H^{9'},H^9)$ = 2.14 Hz, 1H, $H^{9'}$), 2.22 (d br, $^2J(H^4,H^{4'})$ = 17.5 Hz, 1H, H^4), 2.03 (d/d/d/d, $^2J(H^{4'},H^4)$ = 17.5 Hz, $^3J(H^{4'},H^3)$ = 6.1 Hz, $^3J(H^{4'},H^5)$

= 2.5 Hz, ^{f}J = 1.5 Hz, 1H, H$^{4'}$), 1.95 (t/d, ^{3}J(H^{1},H^{7}) = 5.5 Hz, ^{f}J = 1.0 Hz, 1H, H^{1}), 1.85 (m, 1H, H^{5}), 1.54 (m, 1H, H^{7}), 1.10 (d, ^{2}J = 8.6 Hz, 1H, H$^{7'}$), 1.36 (s, 15H, Cp*), 1.23 (s, 3H, Me^{6}), 0.86 (s, 3H, Me$^{6'}$); ^{13}C NMR (500 MHz, C_6D_6) δ 125.2 (C^{2}), 47- (C^{9}), 83.2, 74.6 (C^{8,3}), 93.8, 9.6 (Cp*), 46, 42 (C^{1,5}), 38 (C^{6}), 35.4, 30.2 (C^{4,7}), 26, 21.6 (Me^{6}, Me$^{6'}$).

(R_{Ru},S_C)- or (S_{Ru},R_C)-3c. To 0.19 g (0.36 mmol) of **1** in 20 mL of MeOH was added 0.11 g (0.71 mmol) of (*S*)- or (*R*)-methionine, respectively, and the mixture was stirred for 12 h at ambient temperature. The solvent was stripped, the residue was extracted with toluene, and the solution was filtered through Celite. To the solution, concentrated to about 2 mL, was added ether to precipitate the product as a yellow powder, which was washed successively with ether and hexane and dried at high vacuum: yield 0.19 g (0.5 mmol (71%)); ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ 4.67 (s br, 1H, H^{2}), 2.46 (m, 1H, H^{3}), 2.31 (m, 1H, H$^{3'}$), 2.15 (m, 2H, H$^{4,4'}$), 2.20 (s, 3H, SMe), 1.78 (s, 15H, Cp*); ^{13}C NMR (500 MHz, C_6D_6) δ 181 (CO_2), 76, 10.4 (Cp*), 57.4 (C^{2}), 30.6, 27.4 (C^{3,4}), 21.2 (SMe); MS (70 eV, EI) *m*/*z* (relative intensity) 385 (16) [M$^+$], 341 (3) [M$^+$ − CO_2], 291 (23), 282 (25) [M$^+$ − $MeSC_2H_4CHNH_2$], 233 (20) [Cp*Ru − 4H], 44 (100) [CO_2]. Anal. Calcd for $C_{15}H_{25}NO_2RuS$ (384.5): C, 46.86; H, 6.55; N, 3.64. Found: C, 47.1; H, 6.40; N, 3.57.

(R_{Ru},S_C)- or (S_{Ru},R_C)-3d. To 0.27 g (0.50 mmol) of [Cp*Ru-(μ_2-OMe)]$_2$ (**1**) in 20 mL of THF was added 0.12 g (1.0 mmol) of (*S*)- or (*R*)-proline, and the mixture was stirred for 3 h at ambient temperature; a yellow powder precipitated. This was collected, washed with ether and hexane, and dried *in vacuo* to give 0.3 g (0.86 mmol (87%)) of **3d**: ^{1}H NMR (500 MHz, CD_3CN, 25 °C) δ 4.21 (br d, 1H, H^{2}), 3.27 (m, 2H, H$^{5,5'}$), 2.62, 2.35, 1.79, 1.70 (m, s, m, m, 1H, 1H, 1H, 1H, H$^{3,3',4,4'}$), 1.57 (s, 15H, Cp*); ^{13}C NMR (500 MHz, CD_3CN) δ 181.5 (CO_2), 74.6, 10.3 (Cp*), 63.6 (C1), 53.8, 30.4, 27.4 (C2−C4). Anal. Calcd for $C_{15}H_{23}NO_2Ru$ (350.42): C, 51.41; H, 6.62; N, 4.00. Found: C, 51.25; H, 6.71; N, 4.14.

4a−c from 3a−d. The half-sandwich complex **3**, as specified in Chart 1, was dissolved or suspended in 20 mL of solvent (Chart 1), and an equimolar amount of the appropriate lithium cyclopentadienide, generated *in situ* from the cyclopentadiene and *n*-BuLi, was added at −78 °C. The temperature was slowly increased until a color or solubility change was evident. The mixture was stirred at this temperature for 1−2 h and then warmed to room temperature. The solvent was stripped, the residue was extracted with hexane, and the solution filtered over Celite and chromatographed over silylated silica (Merck 60 treated with Me_3SiCl) with hexane (to remove volatiles). The solvent was then evaporated and the residual yellow oil was dried at high vacuum. Yields and *ee* values are given in Chart 1. **4a**: $[\alpha]^{20}_{436}$ = 15.8° cm^2 (from [Cp*Ru((*R*)-pro)], $c = 2.9 \times 10^{-2}$ g cm^{-3} in *n*-hexane); ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ 4.08 (d/d, ^{3}J(H^{5},H^{4}) = 2.4 Hz, ^{5}J(H^{5},H^{2}) = 1.5 Hz, 1H, H^{5}), 3.99 (d/d, ^{5}J(H^{2},H^{5}) = 1.5 Hz, ^{5}J(H^{2},H^{4}) = 1.5 Hz, 1H, H^{2}), 3.83 (d/d, ^{3}J(H^{4},H^{5}) = 2.4 Hz, ^{5}J(H^{4},H^{2}) = 1.5 Hz, 1H, H^{4}), 1.86 (s, 15H, Cp*), 1.71 (s, 3H, Me^{3}), 1.20 (s, 9H, ^{t}Bu); ^{13}C NMR (500 MHz, C_6D_6) δ 105.6 (C^{1,3}), 74.0, 71.1, 69.7 (C^{2,4,5}), 84.2, 12.1 (Cp*), 31.4, 30.8 (^{t}Bu); UV/vis (*n*-hexane) λ_{max} (ϵ) 263 (286), 302 nm (149); CD (*n*-hexane) λ_{max} ($\Delta\epsilon$) 258 (-2.9×10^{-1}), 283 (8.4×10^{-2}), 317 nm (-1.2×10^{-1}); MS (70 eV, EI) *m*/*z* (relative intensity) 372 (100) [M$^+$], 357 (73) [M$^+$ − Me], 315 (32) [M$^+$ − ^{t}Bu], 231 (4) [Cp*Ru − 6H]. **4b**: ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ 7.44, 6.91, 6.83−6.74 (m, m, m, 1H, 1H, 2H, H$^{4-7}$), 4.47 (d/d, ^{3}J(H^{3},H^{2}) = 2.4 Hz, ^{5}J(H^{3},H^{4}) = 1.0 Hz, 1H, H^{3}), 4.38 (d, ^{3}J(H^{2},H^{3}) = 2.4 Hz, 1H, H^{2}), 1.59 (s, 15H, Cp*), 1.41 (s, 9H, ^{t}Bu); MS (70 eV, EI) *m*/*z* (relative intensity) 408 (17) [M$^+$], 393 (41) [M$^+$ − Me], 372 (5) [Cp*$_2$Ru], 351 (3) [M$^+$ − ^{t}Bu], 231 (4) [Cp*Ru − 6H]. **4c**: $[\alpha]^{20}_{D}$ = 157.6° cm^2 ((*S*)-**4c**, $c = 5.4 \times 10^{-3}$ g cm^{-3} in *n*-hexane); ^{1}H NMR (500 MHz, C_6D_6, 25 °C) δ 7.48−6.73 (m, 9H, Ph, H$^{4-7}$), 4.37 (s, 1H, H^{2}), 3.87, 3.55 (ABq, J_{AB} = 15.7 Hz, 2H, $PhCH_2$), 1.55 (s, 15H, Cp*), 1.37 (s, 9H, ^{t}Bu); ^{13}C NMR (500 MHz, C_6D_6) δ 142 (Ph-C_{ipso}), 128.8−126.8 (Ph), 126.1, 123.8, 121.5, 121.1 (C$^{4-7}$), 98.6, 92.6, 90.4, 80.8 (C^{8,9,1,3}), 82, 10.6 (Cp*), 77.2 (C^{2}), 44 (C^{10}), 32.1, 31.8 (^{t}Bu); UV/vis (*n*-hexane) λ_{max} (ϵ) 271 (1643), 289 (1591), 394 nm (329); CD ((*S*)-**4c**, *n*-hexane) λ_{max} ($\Delta\epsilon$) 259 (−6.3), 307 (1.6), 332 (-7×10^{-1}), 409 nm (6.35); MS (70 eV, EI) *m*/*z* (relative intensity) 498 (9) [M$^+$], 483 (14) [M$^+$ − Me], 441 (2) [M$^+$ − ^{t}Bu], 372 (100) [Cp*$_2$Ru].

5a−c. 4a−c were each dissolved in CH_2Cl_2, an equimolar amount of Ph_3CBF_4 was added, and the solution was stirred for 30 min. After concentration, the solution was diluted with ether to precipitate **5a−c**, respectively, as a yellow powder. The yield in each case after washing and drying was around 90%. **5a**: ^{1}H NMR (80 MHz, $CDCl_3$, 25°C) δ 5.22, 5.19, 5.09 (s, s, s, 1H, 1H, 1H, H^{5,2,4}), 4.87 (m, 2H, CH_2), 2.17, 2.11, 1.82, 1.75, 1.68 (s, s, s, s, s, 3H, 3H, 3H, 3H, 3H, Me), 1.07 (s, 9H, ^{t}Bu). Anal. Calcd for $C_{20}H_{29}BF_4Ru$ (457.33): C, 52.53; H, 6.39. Found: C, 52.74; H, 6.16. **5b**: ^{1}H NMR (80 MHz, $CDCl_3$, 25 °C) δ 7.48−7.16 (m, 4H, H$^{4-7}$), 5.54 (d/d, ^{3}J(H^{3},H^{2}) = 3.0 Hz, ^{4}J(H^{3},H^{4}) = 1.0 Hz, 1H, H^{3}), 5.32 (d, ^{3}J(H^{2},H^{3}) = 3.0 Hz, 1H; H^{2}), 5.25, 3.62 (ABq, J_{AB} = 14.6 Hz, 2H, CH_2), 2.05, 1.95, 1.65, 1.00 (s, s, s, s, 3H, 3H, 3H, 3H, Me), 1.31 (s, 9H, ^{t}Bu). **5c**: ^{1}H NMR (80 MHz, $CDCl_3$, 25 °C) δ 7.44−7.20 (m, 9H, Ph, H$^{4-7}$), 5.54 (s, 1H, H^{2}), 4.31, 3.65 (ABq, J_{AB} = 14.7 Hz, 2H, $PhCH_2$), 5.29, 3.65 (ABq, J_{AB} = 14.6 Hz, 2H, CH_2), 1.77, 1.74, 1.66, 1.26 (s, s, s, s, 3H, 3H, 3H, 3H, Me), 1.34 (s, 9H; ^{t}Bu); MS (FABS) *m*/*z* (relative intensity) [$C_{30}H_{35}Ru$]$^+$ 497 (100) [M$^+$], 481 (16) [M$^+$ − Me − H], 441 (7), 405 (3), 233 (4); MS[BF_4]$^-$ 87 (100). Anal. Calcd for $C_{30}H_{35}BF_4Ru$ (583.48): C, 61.76; H, 6.05. Found: C, 59.55; H, 5.79.

6a−c. 5a−c were each dissolved in CH_2Cl_2, an equimolar amount of (*S*)-phenylethylamine and Et_3N was added, and the solution was stirred for 30 min. The solvent was evaporated and the residue was extracted with hexane. After filtration, the hexane solution was stripped *in vacuo* to give **6a−c**, respectively, as yellow viscous oils in quantitative yield. **6a**: ^{1}H NMR (500 MHz, C_6D_6, diastereoisomer $^{1}/_{2}$) δ 7.43−7.08 (m, 5H, Ph), 4.05 (d/d, ^{3}J(H^{5},H^{4}) = 2.5 Hz, ^{4}J(H^{5},H^{2}) = 1.5 Hz, 1H, H^{5}), 3.99/4.00 (t, ^{4}J(H^{2},H^{4}) = 1.5 Hz, ^{4}J(H^{2},H^{5}) = 1.5 Hz, 1H, H^{2}), 3.82 /3.81 (d/d, ^{3}J(H^{4},H^{5}) = 2.5 Hz, ^{4}J(H^{4},H^{2}) = 1.5 Hz, 1H, H^{4}), 3.79 (q, ^{3}J(H,Me) = 6.5 Hz, 1H, CH), 3.33, 3.30 (ABq, J_{AB} = 12.2 Hz, 2H, CH_2), 1.92, 1.89 (s, s, 3H, 3H, Me^{7,10}), 1.86/1.87, 1.85/1.83 (s, s, 3H, 3H, Me^{8,9}), 1.65 (s, 3H, Me^{3}), 1.29 (d, ^{3}J(Me,H) = 6.5 Hz, 3H, Me), 1.14 (s, 9H, ^{t}Bu); ^{13}C NMR (500 MHz, C_6D_6) δ 145.5, 127.2, 125.6 (Ph), 104.4, 87.2 (C^{1,3}), 83.8−83.1 (C$^{6-10}$), 72.5 (C^{4}), 69.9 (C^{2}), 68.2 (C^{5}), 57.8 (CH), 43.2 (C^{11}), 30, 29.2 (^{t}Bu), 24 (Me), 12.2 (Me^{3}), 10.8−10.2 (Me$^{7-10}$); MS (70 eV, EI): *m*/*z* (relative intensity) 491 (33.6) [M$^+$], 434 (32.8) [M$^+$ − ^{t}Bu], 386 (6.4) [M$^+$− CHMePh], 371 (100) [M$^+$ − CHMe-PhNH], 329 (12) [M$^+$ − ^{t}Bu − CHMePH]. **6b**: ^{1}H NMR (500 MHz, C_6D_6, 25 °C, diastereoisomer $^{1}/_{2}$) δ 7.40−7.01 (m, 5H, Ph), 6.79−6.68 (m, 4H, H$^{4-7}$), 4.45/4.44 (d/d, ^{3}J(H^{3},H^{4}) = 2.4 Hz, ^{4}J(H^{3},H^{4}) = 1.0 Hz, 1H, H^{3}), 4.33/4.34 (d, ^{3}J(H^{2},H^{3}) = 2.4 Hz, 1H, H^{2}), 3.73 (q, ^{3}J(H,Me) = 6.5 Hz, 1H, CH), 3.18, 3.15/3.19, 3.14 (ABq, J_{AB} = 12.2 Hz, 2H, CH_2), 1.69/1.73, 1.66/1.62, 1.60/1.61, 1.48/1.46 (s, s, s, s, 3H, 3H, 3H, 3H, Me$^{11-14}$), 1.36/1.363 (s, 9H, ^{t}Bu), 1.26 (d, ^{3}J(Me,H) = 6.5 Hz, 3H, Me); ^{13}C NMR (500 MHz, C_6D_6) δ 146.8, 128.6−127 (Ph), 126.4, 125.6, 121.4, 121 (C$^{4-7}$), 99.0, 93.4, 90.2 (C^{8,9,1}), 85.6, 83−82.4 (C$^{10-14}$), 75.6, 67.4 (C^{3,2}), 59 (CH), 44.2 (C^{15}), 32.2, 32 (^{t}Bu), 25.2 (Me), 11.2−10.2 (Me$^{11-14}$). **6c**: ^{1}H NMR (500 MHz, C_6D_6, 25 °C, (*S*,*S*)-**6c**/(*R*,*S*)-**6c**) δ 7.48−6.68/7.42−6.70 (m, 14H, Ph, C$^{4-7}$), 4.36/4.35 (s, 1H, H^{2}), 3.83, 3.53/3.82, 3.50 (ABq, J_{AB} = 15.6/16.0 Hz, 2H, $PhCH_2$), 3.72/3.72 (q, ^{3}J(H^{17},Me^{17}) = 6.5 Hz, 1H, H^{17}), 3.12 (s, 2H, CH_2), 3.15, 3.09 (ABq, J_{AB} = 12.5 Hz, 2H, CH_2), 1.67/1.68, 1.64/1.63, 1.52/1.53, 1.47/1.46 (s, s, s, s, 3H, 3H, 3H, 3H, Me$^{12-15}$), 1.264/1.260 (d, ^{3}J(Me^{17},H^{17}) = 6.5 Hz, 3H, Me^{17}), 1.31/1.31 (s, 9H, ^{t}Bu); ^{13}C NMR (500 MHz, C_6D_6) δ 144 (Ph-C_{ipso}),142 (Ph-C_{ipso}), 128.8−126.8 (Ph), 126.1, 123.8, 121.5, 121.1 (C$^{4-7}$), 98.8, 92.8, 90.5, 85.2 (C^{8,9,1,3}), 82.9−82.4, 81.0 (C$^{11-15}$), 77.0 (C^{2}), 59.0 (C^{17}), 44.2 (C^{16}), 33.8 (C^{10}), 32.1, 31.8 (^{t}Bu), 25.0 (Me^{17}), 1.0−10.0 (Me$^{11-14}$); MS (70 eV, EI) *m*/*z* (relative intensity) 617 (16) [M$^+$], 560 (10) [M$^+$ − ^{t}Bu], 512 (11)

[M^+ − PhCHMe], 498 (28) [M^+ − CHMePhN], 106 (100) [CH_2-MePh].

Crystal Structure Determination of 5c. Reflections of an orange plate of approximate dimensions 0.60 × 0.45 × 0.18 mm were collected at 258 K on an ENRAF-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The compound crystallizes in the monoclinic space group $P2_1$ (No. 4) with a = 10.045(2) Å, b = 14.488(4) Å, c = 18.514(3) Å, β = 90.21(2)°, V = 2694(1) Å^3, Z = 4, d_{calc} = 1.438 g cm^{-3}, μ(Mo Kα) = 6.13 cm^{-1}, F(000) = 1200; 6896 reflections were recorded within 3 < θ < 24° in the $+h\pm k\pm l$ hemisphere. Intensity data were collected in the ω scan mode. An empirical absorption correction (min transmission 0.827, max transmission 0.998) on the basis of azimuthal scans[24] was applied before averaging over symmetry equivalent reflections. The structure was solved by conventional Patterson and difference Fourier methods; least-squares full-matrix refinement on F[25] converged for 648 variables and 5149 observations with $I > 1.0\,\sigma(I)$ at R = 0.059, R_w = 0.059 ($w^{-1} = 1/\sigma^2(F_o)$) for the correct enantiomorph (Flack's enantiopol refinement as implemented in SHELXL93[26] converged to 0.01-(6)). For the alternative polarity, R_w = 0.061 was obtained. A final difference Fourier synthesis showed maximal residual electron density of 1.4 e/Å^3 close to one of the Ru atoms.

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Supporting Information Available: Tables of atomic parameters, displacement parameters, and bond distances and angles for **5c**BF4 (21 pages). Ordering information is given in any current masthead page. Additional data on the crystal structure of **5c**BF_4 (atomic coordinates, anisotropic displacment parameters, and structure factors) are also available from the Fachinformationszentrum Karlsruhe, D-76433 Eggenstein-Leopoldshafen, Germany, by quoting the depository number CSD 404544.

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