Planar Chiral Cp*Ru Complexes. 2.[1] Bis(allyl) and -(arene) Complexes Derived from (*R*)-Carvone

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Reaction of $[Cp^*RuOMe]_2$ (**1**) with either enantiomer of the naturally occurring ketonic diterpene carvone or the trimethylsilyl enolate derived thereof leads to homochiral Cp*Ru−π-complexes **6**−**9**, where the Cp*Ru moiety is bound to either the exocyclic double bond or an allyl function derived from it as well as to an enone or ene system in the ring. Full aromatization of the cyclic enone under the same reaction conditions was achieved with 7,8-dihydrocarvone or its trimethylsilyl enolate, respectively, giving complexes **13** and **14**. The carvacrole complex **14** (and consequently also **13**) is shown by the NMR spectra of the diasteroisomers obtained through derivatization with (*S*)-camphorsulfonic acid to be homochiral, thus, central chirality of the carvone has been fully transformed into planar chirality of the carvacrole complex. Compounds **6**, **7**·BF_4, **7**·CF_3SO_3, **8**·CF_3SO_3, and **14**·CF_3SO_3 where characterized by single-crystal X-ray analysis, which allowed for the determination of the absolute configuration of the latter.

Introduction

Planar chiral transition metal complexes have in recent times become increasingly important substrates and targets in organic synthesis. This is due to the highly stereospecific elaborations possible in π-ligand systems complexed to transition metal fragments. Diastereospecific metalation of substituted ferrocenes[2] and arene tricarbonyl Cr complexes[3] as well as carbon−carbon bond forming reactions at cationic dienyl−$Fe(CO)_3$[4] and arene tricarbonyl Cr[5] complexes are intensively studied examples. In cases where the π-ligand is prochiral, planar chirality is generated in the complexation reaction and any successive stereospecific elaborations will lead to enantiomerically pure compounds, only to the extent to which the enantiomeric purity of the starting π-complex can be ascertained. A straightforward strategy to obtain enantiomerically pure or enriched planar chiral π-complexes exists in diastereoselective complexation of π-ligands bearing at least one chiral substituent, such as a menthylcarboxy group,[6] but so far this strategy has been met with limited success with respect to the optical purity of the products, and separation of the diastereoisomers was generally necessary.[7]

High enantiomeric excesses in the course of π-complexation had only been observed in cases where the chiral center is part of an annelated ring close to the unsaturated carbocycle giving rise to diastereotopic faces. Thus, enantiomerically pure (oxohydronaphthalene)$Cr(CO)_3$ was obtained from enantiopure 5-hydroxohydronaphthalene using naphthalene chromium tricarbonyl as a $Cr(CO)_3$ transfer agent.[8] Another possibility to achieve enantioselective π-complexation was the use of chiral intermediates or auxiliary ligands which are lost in the complexation step but can still lead to the differentiation of si/re faces.[9]

A still more rigorous approach is the transformation of a chiral center in the course of the generation of an element of planar chirality, as was exemplified in the synthesis of planar chiral allyl−$Fe(CO)_4$ complexes from chiral allyl ethers.[10] These reactions require the transformation of an sp^3 into an sp^2 carbon atom whereby the unsaturated carbon chain is extended.

Among the metal fragments that have shown particular versatility with respect to this kind of transformations at π-ligands is the Cp*Ru ($Cp^* = \eta^5$-C_5Me_5) fragment. It may be generated either by elimination of methanol from the coordinatively unsaturated alkoxy complex $[Cp^*RuOMe]_2$[11] (**1**) or in the form of the solvent-stabilized cationic complexes $[Cp^*Ru(s)]^+$ (**2**) generated by the action of a noncoordinating acid on **1**.[12] In particular, cations **2** were shown to complex not only to a wide variety of arenes and cyclotrienes but also to effect dehydrogenation and dehydration of cyclic olefins, such as cyclohexene, of enones, such as cyclohexenone,

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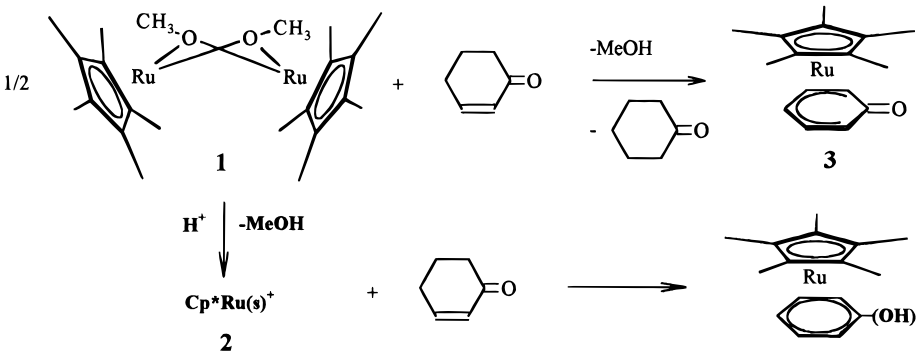
Scheme 1. Reaction of 1 and 2 with Cyclohexenone



and, under more forcing conditions, even saturated cyclic ketones and alcohols to give mostly Cp*Ru-(benzene)$^+$ derivatives.[13] The reaction has been utilized to afford aromatization of ring A in 3-keto steroids, such as testosterone and progesterone, with expulsion of the 17-Me group (as methane) and even of the 1,4-dienonic steroid prednisolone which was degraded under these conditions to 2-methyl-5-hydroxybenzaldehyde complexed to Cp*Ru.[14] Similar reactions have been effected with **2** and ketonic terpenes, in particular carvone (**4**) or carvole ester which gave the corresponding arene complexes with or without loss of the oxygen functionality.[15]

We found that not only **2** but also the neutral methoxy complex **1** aromatizes activated cyclic olefins to give the corresponding oxocyclohexadienyl complexes, e.g., **3** in Scheme 1, at ambient temperature. This observation has led us to utilize **1** as well as **2** for stereospecific transformations of carvone and dihydrocarvone. The results, as detailed below, differ markedly from the ones previously described with the same system.

Results and Discussion

Reactions of Carvone. As shown in Scheme 1, complex **1** reacts with cyclohexenone to give Cp*Ru-(oxocyclohexadienyl) (**3**). Aromatization, under these conditions, requires at least one hydrogen in an allylic position and does not allow quarternary carbon atoms in the ring. Thus, no complexation was observed from **1** and 4,4-dimethylcyclohexenone. In the course of dehydrogenation reactions performed with **2**, elimination of hydroxy and even alkyl groups has been frequently observed.[13−15] In contrast, under the milder conditions applied in the present experiments, those functionalities at the cyclic precursors were preserved. This is important in the present context since oxo, hydroxy, and alkyl groups not only function as stereochemical markers in introducing planar chirality of the product complexes, but, moreover, give the possibility of further elaborating the complexed arene in a stereospecific manner (see below).

Applying the reactions of Scheme 1 to the naturally occurring diterpene carvone (**4**), which is readily available in either enantiomerically pure form, should in principal offer the possibility for an enantioselective complexation of the Cp*Ru moiety to the newly formed arene. Preferential attack of the Cp*Ru fragment from the rear side with respect to the isopropenyl group should lead to planar chiral Cp*Ru complexes in high enantiomeric purity.

Reactions conducted with (*R*)-carvone are shown in Scheme 2. As sources of Cp*Ru, we used **1** or **2**, the latter being generated from **1** and acid in situ. The cyclic enone was either **4** or the trimethylsilyl enolate (**5**) derived from it.

The products formed in the reactions of Scheme 2, however, were not arene complexes but were an allyl−ene (**6**), bisallyl (**7**), or triene (diene−ene) complex (**8**). Primary attack of the Cp*Ru moiety obviously is at the isopropenyl double bond and not at the enone functionality. (Note, however, that cyclic monoenes do not react under these mild conditions.) In **6** and **7**, dehydrogenation has occurred at the isopropenyl group. This finding is in accord with previous observations where the reaction of **1** with propylene has led to allyl complexes in high yield under similar conditions.[16] **6**/**7** as well as **8**/**9** form Brønsted acid/base pairs where deprotonation of **7** and **8** is effected with triethylamine in acetone. Although the formation of **6** as indicated in Scheme 2 was clean by NMR, it proved difficult to separate the product from excess carvone. Samples for crystallization and analysis are therefore better obtained via deprotonation of **7**.

In order to facilitate aromatization in the course of the complexation, carvone was converted into its trimethylsilyl enolate (**5**). In this case, however, **2** simply complexed to the preformed η^6-system of double bonds with no further dehydrogenation. Note, however, the hydrogen shift from the 5-position in **5** to the 6-position in **8**. Hydrolysis of the silyl enol ether appears to be quite facile in the cationic complex and may proceed with methanol being formed with the generation of **2** from **1**.

When using **2** as the source of Cp*Ru, care has to be taken not to bring the carvone in contact with an acidic medium since it undergoes a facile acid-catalyzed rearrangement to the respective phenol (carvacrole). Once the arene is formed independent of the metal fragment, this latter process will give the arene complex[12,17] but

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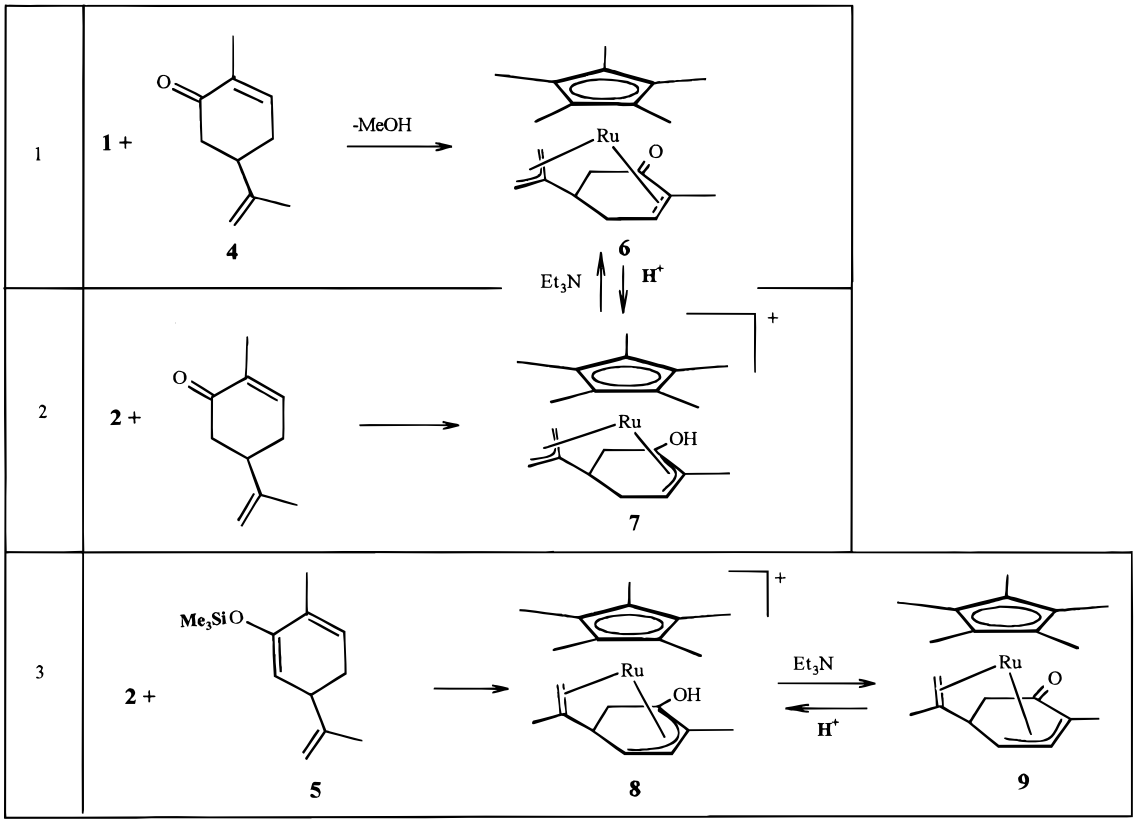
Scheme 2. Reactions Conducted with Carvone



1 = [Cp*RuOMe]$_2$, 2 = 1 + CF_3SO_3H

without any stereochemical preference. The result of Chaudret et al.[15] who had obtained [Cp*Ru(carvacrole)]-CF_3SO_3 (**14**) from the same reaction essentially as a racemic mixture is probably due to this sequence. Reactions leading to **7** and **8** have, therefore, been conducted in such a way as to mix **1** in a slight stoichiometric excess with triflic acid to ensure complete consumption of the latter prior to the addition of **4**.

We verified that neither **6** nor **7** rearranged into **13** or **14** under the reaction conditions, i.e., at ambient temperature. The bis(allyl) complex **7** rearranged cleanly to **14** at 100 °C in CH_2Cl_2 over 50 h. Determination of the specific rotation, however, showed the product to be racemic ($[\alpha]_{546}^{25} = 0$). Heating **7** in toluene at 100 °C gave the toluene complex $[Cp^*Ru(tol)]^+$, together with free carvone. This result suggests that rearrangement requires decomplexation of carvone and recomplexation as carvacrol, formed by adventitious traces of acid with the loss of stereochemical information. The reaction of **1** with carvacrole is one way to obtain racemic **13** (and **14**) which is needed for comparison (vide infra). This reaction was shown by NMR to proceed via the bridged phenol complex $[Cp^*Ru(\mu\text{-}OR)]_2$, R = 2-Me-5-isopropylphenol, which slowly converted to **13**.[18]

Complexes **6**−**9** were identified by their ^1H and ^{13}C NMR spectra, as given in the Experimental Section. Ambiguities in the assignment of carbon atoms in the ring as well as ring hydrogens could be resolved in all cases by use of two-dimensional $^1H/^{13}C$ COSY and $^1H/^1H$ NOESY spectra. The latter, in particular, allowed the location of the isopropenyl group in **9** to be assigned as being directed toward CH_2 in the oxocyclohexenyl ring.

All of the complexes **6**−**9** are formed with 100% stereospecifity. The ligand geometry in these cases allows only one orientation with respect to the Cp*Ru moiety and, thus, determines the configuration at Ru as the newly formed chiral center. In addition, **6**, **7**, and **8** have been shown by X-ray structure analysis to be pure enantiomers. Possible elaboration at the enone or allylic function (such as addition of nucleophiles) is therefore expected to generate new chiral centers with high optical purity.

Reactions of 7,8-Dihydrocarvone. Since we could not transform any of the allylic or ene−diene structures of **6**−**9** into arenes in a stereospecific way, a second set of experiments was conducted where complexation at the exocyclic double bond was blocked by hydrogenation of carvone to 7,8-dihydrocarvone **10**, which is easily accomplished using a PtO_2 catalyst. Results of reactions using **10** or the silyl enol ether (**11**) derived thereof are summarized in Scheme 3. Reaction with **2** under the same conditions as performed with carvone now led to aromatization of the ring, but even under those mild conditions dehydration was favored over dehydrogenation to give the achiral *p*-cymene complex **12**. The desired oxocyclohexadienyl complex **13** was only obtained in the absence of acid with **1** as the source of Cp*Ru, which reacted with either **10** or the the silylenolate **11** (Scheme 3, entries 2 and 3).

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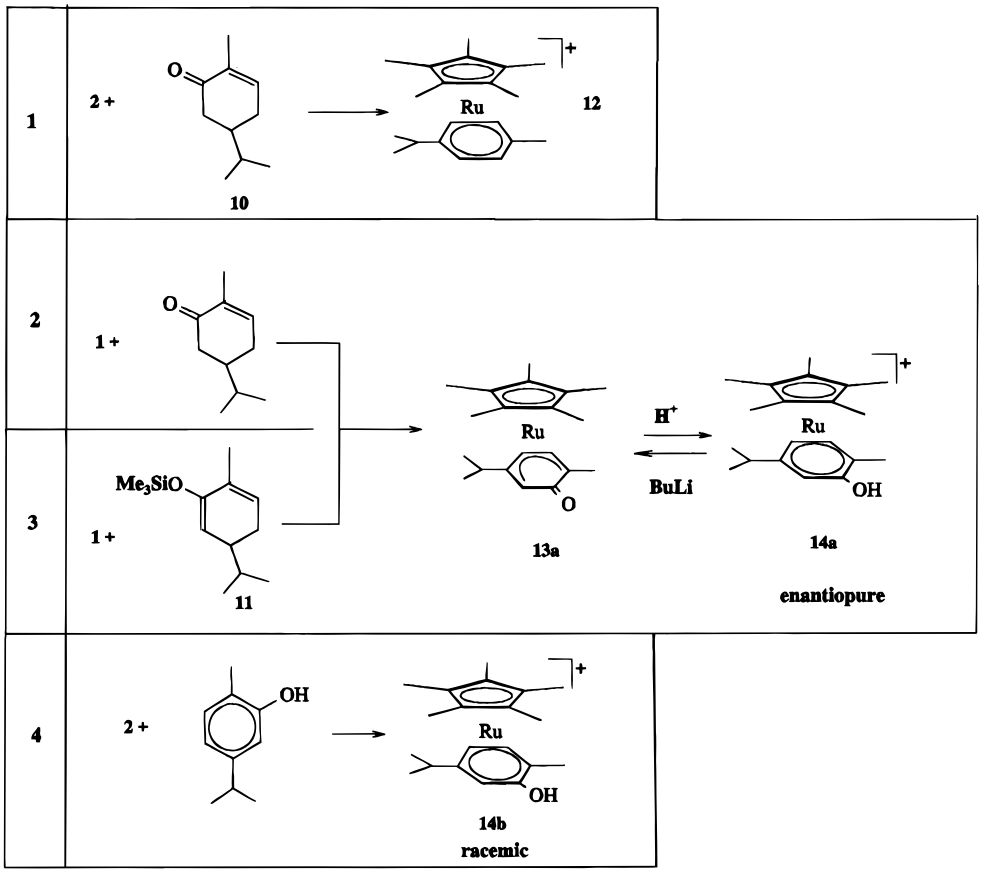
Scheme 3. Reactions Conducted with 7,8-Dihydrocarvone



1 = [Cp*RuOMe]$_2$, 2 = 1 + CF_3SO_3H

Note that in the course of aromatization the chiral center at C5 is lost and the oxocyclohexadienyl ligand is now prochiral. However, since attack of the Cp*Ru moiety is expected to principally be from the face opposite to the isopropyl group, in the case of e.g. (*R*)-dihydrocarvone it will appear on the si-side of the planar aromatic cycle. Conversion of **13a** into the phenol cation **14a** by acid will not change the stereochemistry. In addition **14b** was prepared as a racemate by reacting aromatic carvacrole, generated from **4** and triflic acid, see above, with **2** (entry 4 in Scheme 3).

In order to assess the optical purity of **13a**/**14a** and the racemic nature of **13b**/**14b**, respectively, both forms of **13** were converted into diastereomeric carvacrole camphorsulfonates (**15a**/**b**) by esterification with homochiral (*S*)-camphorsulfonyl chloride (Scheme 4). Thus, **15b** derived from racemic **13b** showed doubling of signals in the ^{1}H NMR, most easily seen in the doublet of CH_2 protons of the camphorsulfonyl residue close to the SO_3 group near 3.6 ppm. The same spectra of **15a**, derived from **13a** consisted of only one set of signals (apart from some **14** which was formed in the esterification procedure due to the presence of some camphorsulfonic acid) proving 100% enantiomeric purity of the arene complexes within the limits of NMR detection.

As outlined in Scheme 4, the neutral complex **13** was reacted with other electrophiles such as MeI, MeCOCl, and Ph_2PCl in a similar manner. This protocol is in principal suited to generate enantiopure arene complexes with a wide variety of functionalities. In some of the products, however, the O−E bond has been found to be sensitive to hydrolysis.

Molecular Structures of 6, 7$^+$, 8, and 14. The molecular structures of the compounds **6**, **7**·CF_3SO_3, **7**·BF_4, **8**, and **14** were elucidated by single-crystal X-ray diffraction. Pertinent distances and angles are collected in Table 1, where data have been arranged in the same order for all independent molecules, thus enabling comparison and allowing differences in the structures to be easily noted.

In the neutral complex **6** (Figure 1), Ru is bound to carbon atoms C2 and C3 of the ring and to three carbon atoms C8−C10 of the isopropenyl group which adopts an *endo* conformation with respect to the Cp*Ru moiety. Distances to the allylic carbons are quite normal, whereas one of the olefinic carbons is about 0.1 Å further apart than in comparable ethylene complexes of the Cp*Ru moiety.[16,19] Likewise bond lengths and angles within the carbon framework compare well with those found for Ru ene−allyl systems. The bond angles at Ru in **6** compare well with those in Cp*Ru(allyl)(propene). The angles C_{olef}−Ru−$C_{t-allyl}$ are 87.7 and 78.3° in **6** and are 85.6 and 90° in Cp*Ru(allyl)(propene).[16] Thus, in **6** the ene and allyl parts are only slightly closer together than in a complex where the same ligand types at Cp*Ru are free to arrange in space.

Complex **7** was measured as the $CF_3SO_3^-$ salt but showed disorder in the anion. Subsequent structure determination as the BF_4^- salt unfortunately revealed four independent molecules in the unit cell. Both salts crystallize in the space group $P2_1$ and show the

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Scheme 4. Derivatization of the Carvacrole Complex

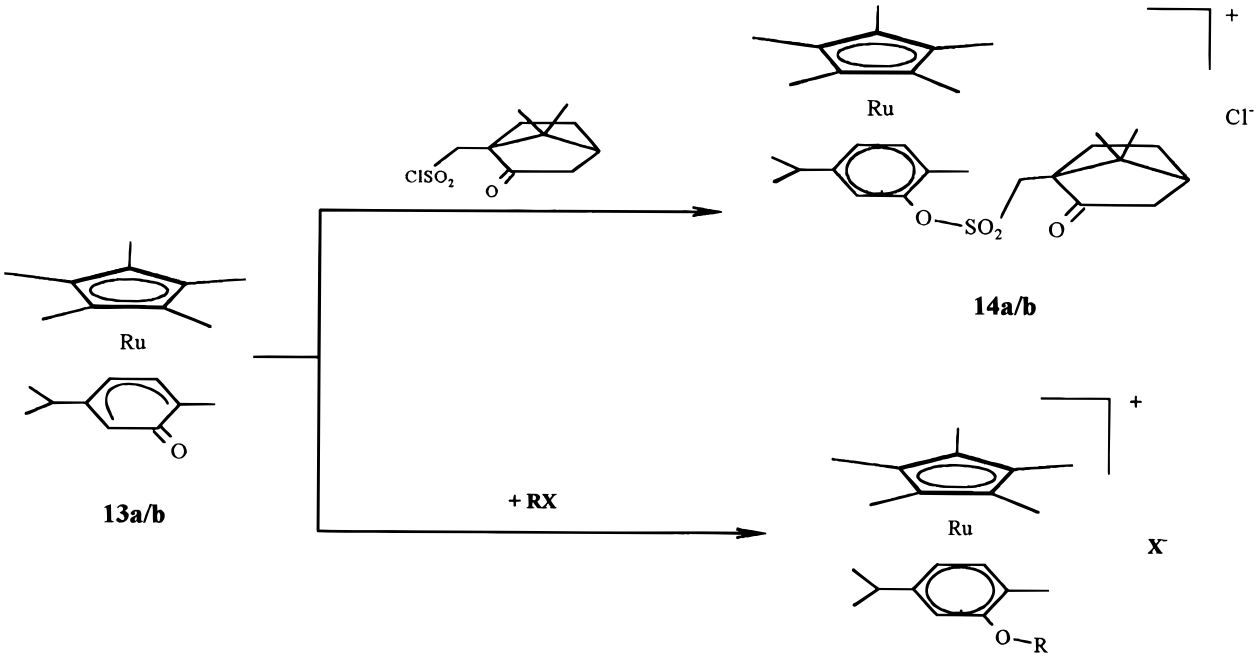

Table 1. Bond Distances and Bond Angles of 6, 7, 8, and 14

	6	**7**·CF_3SO_3	**7**·BF_4				**8**·CF_3SO_3	**14**·CF_3SO_3	
			Bond Distances						
Ru−C2	2.231(6)	2.25(1)	2.24(1)	2.16(1)	2.20(1)	2.23(1)	2.271(4)	2.23(1)	2.25(1)
Ru−C3	2.133(6)	2.25(1)	2.18(1)	2.23(1)	2.29(1)	2.22(1)	2.173(4)	2.33(1)	2.19(1)
Ru−C4							2.276(4)	2.16(2)	2.21(2)
Ru−C5								2.21(2)	2.25(2)
Ru−C6								2.21(2)	2.26(2)
Ru−C7		2.49(1)	2.46(1)	2.31(1)	2.41(1)	2.42(1)	2.534	2.25(1)	2.14(2)
Ru−C8	2.130(5)	2.14(1)	2.15(1)	2.15(1)	2.14(1)	2.17(1)	2.320(4)		
Ru−C9	2.189(6)	2.16(2)	2.18(1)	2.21(2)	2.17(2)	2.17(2)	2.250(4)		
Ru−C10	2.199(6)	2.13(2)	2.21(1)	2.26(2)	2.21(1)	2.25(1)			
Ru−$C_{Cp^*-plane}$	1.896	1.907	1.884	1.888	1.891	1.897	1.855	1.810(1)	1.798(1)
C2−C3	1.432(8)	1.43(2)	1.41(2)	1.40(2)	1.39(2)	1.41(2)	1.434(6)	1.37(2)	1.35(2)
C3−C4	1.517(8)	1.49(2)	1.52(2)	1.56(2)	1.47(2)	1.51(2)	1.390(6)	1.52(2)	1.40(2)
C4−C5	1.522(8)	1.53(2)	1.49(2)	1.56(2)	1.48(2)	1.52(2)	1.495(6)	1.46(2)	1.42(2)
C5−C6	1.499(9)	1.56(2)	1.52(2)	1.49(2)	1.53(2)	1.55(2)	1.518(6)	1.42(2)	1.38(2)
C6−C7	1.51(1)	1.49(2)	1.43(2)	1.55(2)	1.49(2)	1.45(2)	1.505(6)	1.42(2)	1.32(2)
C2−C7	1.48(1)	1.40(2)	1.35(2)	1.32(2)	1.39(2)	1.42(2)	1.386(5)	1.44(2)	1.43(2)
C5−C8	1.509(9)	1.46(2)	1.50(2)	1.49(2)	1.49(2)	1.53(2)	1.505(6)	1.55(2)	1.50(2)
C8−C9	1.403(9)	1.40(2)	1.33(2)	1.40(2)	1.39(2)	1.39(2)	1.389(6)	1.56(2)	1.42(3)
C8−C10	1.456(8)	1.44(2)	1.42(2)	1.38(2)	1.42(2)	1.40(2)	1.507(6)	1.45(2)	1.59(2)
O1−C7	1.245(8)	1.35(1)	1.33(2)	1.32(2)	1.39(2)	1.35(2)	1.354(5)	1.37(1)	1.47(1)
C1−C2	1.51(1)	1.49(2)	1.54(2)	1.57(2)	1.48(2)	1.49(2)	1.498(5)	1.53(2)	1.54(2)
			Bond Angles						
C2−C3−C4	118.6(6)	117(1)	116(1)	114(1)	122(1)	118(1)	120.4(4)	113(1)	121(1)
C3−C4−C5	105.8(5)	111(1)	108(1)	107(1)	110(1)	109(1)	123.8(4)	123(1)	122(1)
C4−C5−C6	108.1(6)	106(1)	108(1)	107(1)	108(1)	108(1)	110.5(4)	118(1)	118(1)
C5−C6−C7	112.9(6)	111(1)	109(1)	109(1)	107(1)	107(1)	110.4(3)	119(1)	116(1)
C6−C7−C2	118.2(6)	121(1)	123(1)	117(1)	126(1)	124(1)	120.4(4)	121(1)	130(1)
C7−C2−C3	119.3(7)	117(1)	116(1)	123(1)	112(1)	114(1)	115.4(4)	124(1)	113(1)
C4−C5−C8	107.0(5)	108(1)	109(1)	108(1)	109(1)	108(1)	96.8(3)	120(1)	116(1)
C6−C5−C8	111.5(6)	106(1)	108(1)	110(1)	107(1)	109(1)	111.1(4)	122(1)	126(1)
C9−C8−C10	114.6(6)	108(2)	115(1)	116(1)	114(1)	116(1)	121.1(4)	114(1)	105(1)
C5−C8−C9	119.9(7)	123(2)	117(1)	124(1)	120(1)	119(1)	117.0(4)	107.9(9)	115(1)
C5−C8−C10	124.4(7)	125(2)	124(1)	118(1)	123(1)	120(1)	121.3(4)	115(1)	110(1)
C2−C7−O1	121.9(7)	117(1)	113(1)	120(1)	115(1)	113(1)	124.5(4)	116(1)	110(1)
C6−C7−O1	119.8(7)	117(1)	119(1)	115(1)	115(1)	116(1)	112.0(4)	122(1)	120(1)
C1−C2−C3	120.7(7)	121(1)	121(1)	115(1)	124(1)	124(1)	121.3(4)	118(1)	125(1)
C1−C2−C7	113.3(5)	121(1)	123(1)	122(1)	121(1)	122(1)	122.6(4)	118(1)	122(1)

same enantiomer. Ru is bound to two allylic systems, one made up of C3−C2−C7 and the other of C9−C8−C10 in *endo*- and *exo*-conformations, respectively (Figure 2). This *endo*- and *exo*-conformation has been observed in other cationic CpRu and LRu (bis(allyl)) complexes as well,[20] with Ru−C_{allyl} distances in the

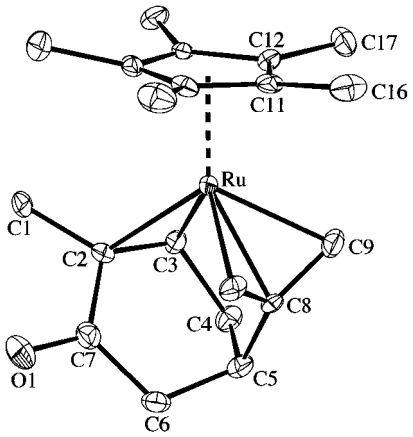

Figure 1. PLATON[28] representation of **6**, showing atom numbering scheme and 30% probability ellipsoids. For bond distances and angles, see Table 1.

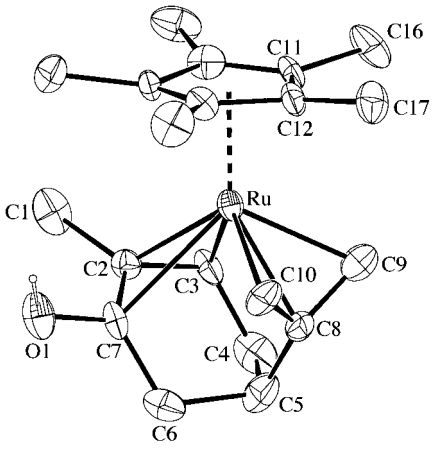

Figure 2. PLATON representation of the cation of **7**·CF_3SO_3, showing atom numbering scheme and 30% probability ellipsoids. For bond distances and angles, see Table 1.

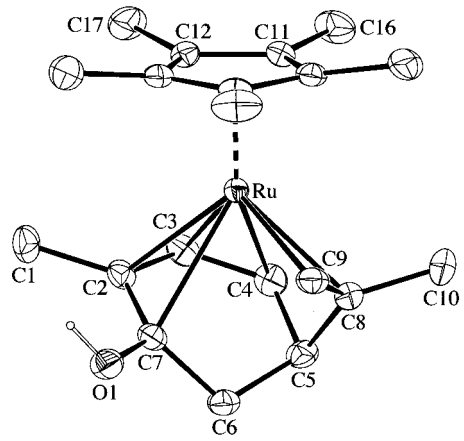

Figure 3. PLATON representation of the cation of **8**·CF_3SO_3, showing atom numbering scheme and 30% probability ellipsoids. For bond distances and angles, see Table 1.

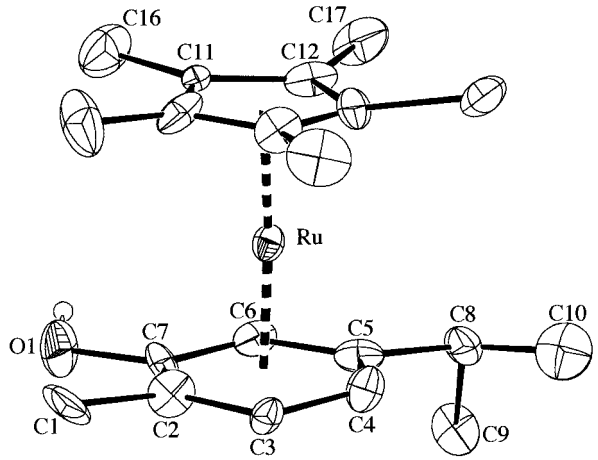

Figure 4. PLATON representation of the cation of **14**·CF_3SO_3, showing atom numbering scheme and 30% probability ellipsoids. For bond distances and angles, see Table 1.

same range. The shortest distances are encountered for the bonds between Ru and the central carbon atoms of both allyl moieties, C2 and C8, see Table 1. Note the slightly shorter distance Ru−C10, disposed roughly *trans* to C7, as compared to Ru−C9 and also the very long distance Ru−C7 at the border of the normal range for Ru−carbon bonds. The six-membered ring adopts a skewed boat conformation with the isopropenyl group in an axial position. As can be seen from the C−C−C bond angles in Table 1, the Cp*Ru unit in the bis(allyl) complex is bound to a strainless carbon skeleton, which may explain the ready formation of this system under the mild reaction conditions employed.

Cation complex **8** was also crystallized as the triflate salt. The Cp*Ru unit is complexed to the olefinic double bond of the isopropenyl group and to a diene system of the ring, i.e., the starting enol ether acts together with the isopropenyl group as an η^6-ligand (Figure 3). The diene system is characterized by two short (1.390(6) and 1.386(5) Å) and one long (1.434(6) Å) carbon−carbon bond. The distance Ru−C7 (2.534 Å) is outside the normal range for Ru−C bonding, but the bond is indispensable to be in keeping with the required electron count. Also in this molecule bond angles in the dienol ligand are close to those in an unstrained carbon skeleton.

The geometry of the two independent cation molecules in the unit cell of homochiral **14a**, crystallized as the triflate salt, conform largely to the shape found in many known Cp*Ru(arene)$^+$ cations (Figure 4).[12] The phenolic hydroxyl group is hydrogen bonded to a sulfonate oxygen of the anion. The distances of the isotropically refined O*H* proton to OSO_2 are 1.824(9) and 1.60(1) Å. The Ru−Cp^*_{plane} distance in this complex is distinctly less than in the allyl and dienyl complexes **6**−**8**, an observation which underlines the stronger back-bonding capabilities[21] of the allyl and ene−diene ligands in the latter as compared to an arene. The absolute configuration could be assigned reliably by refinement of Flack's enantiomorph polarity parameter[22] (see Experimental Section) and is the one expected from attack of the Cp*Ru unit at the face opposite to the isopropyl group. Note that stereoselectivity in this case is much larger than the diastereoselectivity observed when complexing Cp*Ru to the aromatic A ring of estrogenic steroids.[14,23]

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Conclusion

It was shown that aromatization of dihydrocarvone by a Cp*Ru fragment under the appropriate reaction conditions can proceed with complete transformation of the central chirality of the starting terpene into planar chirality of the resulting π-arene complex. Since the dehydrogenative complexation has been observed, apart from the Cp*Ru fragment, with other Ru(II) moieties also, e.g., $Ru(H_2O)_6^{2+}$,[24] the reaction may, under appropriate conditions, provide a route not only to chiral sandwich but also to chiral arene Ru half-sandwich complexes.

Experimental Section

Experiments were conducted under nitrogen with anhydrous, nitrogen-saturated solvents. The NMR spectra were recorded on Bruker WH 250 and Varian Unitiy 300 and 500 instruments. Chiroptical data were obtained with a Perkin-Elmer 241 polarimeter and a Jasco J-41c spectrophotometer (CD). Elemental analyses were performed by the microanalytical laboratory of the institute.

(5*R*)-(−)-5-Isopropyl-2-methylcyclohex-2-en-1-one ((*R*)-(−)-dihydrocarvone)[25] (10). (*R*)-(−)-Carvone (33.3 g, 0.22 mol) in 50 mL of ethanol was hydrated at ambient temperature with 0.22 mol of hydrogen over a PtO_2 catalyst to form (*R*)-(−)-dihydrocarvone. After consumption of the calculated amount of hydrogen, the solution was filtered from the catalyst and the product *distilled in vacuo*. Yield: 32 g (95%). $[\alpha]_{546}^{25} = -49$ (hexane, $c = 1.51 \times 10^{-2}$ g·cm^{-3}). ^{1}H NMR (500 MHz, $CDCl_3$): 0.872 (d, $J = 6.7$ Hz, 3H, *i*-Pr), 0.876 (d, $J = 6.7$ Hz, 3H, *i*-Pr), 1.53 (sept, $J = 6.7$ Hz, 1H, **H**C(CH$_3$)$_2$), 1.73 (ddd, $J = 2.5$, 1.3, 1.3 Hz, 3H, Me), 1.80−2.45 (aliphatic protons, 5H, C**H**$_2$, C**H**$_2$, **H**CCH(CH$_3$)$_2$), 6.70 (m, 1H, **H**C=CMe). ^{13}C NMR (125.6 MHz, $CDCl_3$): 15.6 (Me), 19.4, 19.5 (*i*-Pr), 29.8, 42.0 (**C**H$_2$, **C**H$_2$), 31.9, 41.9 (H**C**CH(CH$_3$)$_2$), 135.3 (H**C**=CMe), 145.3 (HC=**C**Me), 200.7 (**C**=O).

(3*R*)-(+)-3-Isopropenyl-6-methyl-1-(trimethylsiloxy)cyclohexa-1,5-diene[26] (5). To 5 mL (35.7 mmol) of diisopropylamine in 20 mL of Et_2O was added 35.7 mmol (14.3 mL of a 2.5 M solution of BuLi in hexane) of BuLi at −78 °C. After being warmed to ambient temperature, the solution was recooled to −78 °C and 5.5 mL (35.7 mmol) of (*R*)-(−)-carvone was added dropwise. At ambient temperature, 4.6 mL (35.7 mmol) of trimethylsilyl chloride was added. Following evaporation of the ether, the remaining silyl enol ether was dissolved in hexane, the solution was filtered over Celite to remove LiCl, the solvent was removed, and the product was distilled at 10^{-2} Torr. Yield (90%). $[\alpha]_{546}^{25} = +81$ (hexane, $c = 7.55 \times 10^{-3}$ g·cm^{-3}). ^{1}H NMR (500 MHz, $CDCl_3$): 0.19 (s, 9H, $SiMe_3$), 1.68 (ddd, $J = 1.9$, 1.9, 1.9 Hz, 3H, **Me**C=CH), 1.71 (dd, $J = 1.0$, 1.0 Hz, 3H, **Me**C=CH$_2$), 2.08 (dddq, $J = 16.5$, 12.5, 4.0, 2.1 Hz, 1H, −C**H**$_2$), 2.16 (dddq, $J = 16.8$, 8.5, 4.9, 1.8 Hz, 1H, −C**H**$_2$), 2.99 (dq, $J = 2.1$, 1.4 Hz, 1H, =C**H**$_2$), 4.76 (m, 2H, =C**H**$_2$, **H**C=COSiMe$_3$), 5.54 (m, 1H, **H**C=CMe). ^{13}C NMR (125.6 MHz, $CDCl_3$): 0.1 ($SiMe_3$), 17.3 (**Me**C=CH), 20.5 (**Me**C=CH$_2$), 28.6 (**C**H$_2$), 41.8 (H**C**CH(CH$_3$)=CH$_2$), 105.8 (H**C**=COSiMe$_3$), 110.0 (=**C**H$_2$), 123.1 (H**C**CMe), 131.9, 148.6, 149.8 (**C**=CH$_2$, HC**C**Me, **C**OSiMe$_3$).

(3*R*)-(+)-3-Isopropyl-6-methyl-1-(trimethylsiloxy)cyclohexa-1,5-diene (11). Procedure used was similar to that described above. Yield: 90%. $[\alpha]_{546}^{25} = +109$ (hexane, $c = 1.31 \times 10^{-2}$ g·cm^{-3}). ^{1}H NMR (300 MHz, $CDCl_3$): 0.18 (s, 9H, $SiMe_3$), 0.86 (d, $J = 6.7$ Hz, 3H, *i*-Pr), 0.87 (d, $J = 6.7$ Hz, 3H, *i*-Pr), 1.59 (sept$_{br}$, $J = 6.7$ Hz, 1H, **H**C(CH$_3$)$_2$), 1.66 (ddd, $J = 1.7$, 1.7, 1.7 Hz, 3H, Me), 1.83−2.20 (alophatic protons, 3H, CH$_2$, **H**CCH(CH$_3$)$_2$), 4.78 (d$_{br}$, $J = 3.7$ Hz, 1H, **H**C=COSiMe$_3$), 5.53 (m, 1H, **H**C=CMe). ^{13}C NMR (75.4 MHz, $CDCl_3$): 0.2 ($SiMe_3$), 17.3 (Me), 19.8, 19.9 (*i*-Pr), 26.3 (**C**H$_2$), 31.6 (H**C**(CH$_3$)$_2$), 40.3 (H**C**CH(CH$_3$)$_2$), 106.2 (H**C**=COSiMe$_3$), 123.6 (H**C**=CMe), 131.9, 149.5 (**C**Me, **C**OSiMe$_3$).

(5*R*,1*R*)-[(1-Hydroxy-η^3-5-isopropenyl-2-methyl-η^3-cyclohex-1-en-3-yl)(η^5-pentamethylcyclopentadienyl)-ruthenium] Trifluoromethanesulfonate ((*R*)-7·CF$_3$SO$_3$). To 250 mg (0.43 mmol) of $[Cp^*RuOMe]_2$ in 10 mL of acetone was added 0.8 mmol (70 μL) of CF_3SO_3H. The solution was cooled to −78 °C, and 0.86 mmol (0.135 mL) of (*R*)-(−)-carvone was added. After the mixture had reached room temperature, hexane was slowly added to precipitate the product. The brownish precipitate was repeatedly redissolved in acetone and precipitated by addition of hexane to finally yield 0.322 g (70%) of a yellow powder. Fp: 165 °C. $[\alpha]_{546}^{25} = -352$ (acetone, $c = 9.85 \times 10^{-3}$ g·cm^{-3}). ^{1}H NMR (500 MHz, CD_2Cl_2): 1.73 (s, Cp*, 15H), 1.83 (s, H1, 3H), 3.21 (ddd, H3, $J = 4.0$, 1.2, 1.2 Hz, 1H), 1.37 (d$_{br}$, H4, $J = 14.4$ Hz, 1H), 1.73 (dm, H4′, $J = 14.4$ Hz, 1H), 2.56 (m, H5, 1H), 1.73 (d, H6, $J = 16.0$ Hz, 1H), 2.32 (ddd, H6′, $J = 16.0$, 4.0, 1.5 Hz, 1H), 1.59 (s, H9$_{anti}$, 1H), 3.28 (d, H9$_{syn}$, $J = 3.4$ Hz, 1H), 2.01 (s$_{br}$, H10$_{anti}$, 1H), 3.57 (d$_{br}$, H10$_{syn}$, $J = 3$ Hz, 1H). ^{13}C NMR (125.6 MHz, CD_2Cl_2): 9.9, 101.7 (Cp*), 16.1 (C1), 80.0 (C2), 55.9 (C3), 33.3 (C4), 32.6 (C5), 28.8 (C6), 140.8 (C7), 110.5 (C8), 59.9 (C9), 58.3 (C10), 120.9 (q, $CF_3SO_3^-$, $J_{CF} = 320$ Hz). IR (KBr, ν, cm^{-1}): 3158 (m), 3003 (m), 2907 (m), 1554 (w), 1470 (m), 1444 (m), 1386 (m), 1352 (m), 1296 (s), 1236 (s), 1222 (s), 1157 (s), 1028 (s), 638 (s). MS (FAB): *m*/*z* (I_{rel}) +VE 387 (100, $M^+ - CF_3SO_3^-$), 371 (7, $M^+ - CH_4 - CF_3SO_3^-$), 357 (2, $M^+ - C_2H_5 - CF_3SO_3^-$), 343 (1, $M^+ - i$-Pr $- CF_3SO_3^-$), 233 (3, $(Cp^*Ru)^+ - 4H$); −VE 149 (100, $CF_3SO_3^-$). Anal. Calcd for $C_{21}H_{29}F_3O_4RuS$: C, 47.10; H, 5.46. Found: C, 47.08; H, 5.63.

(5*R*,1*R*)-[(1-Hydroxy-η^3-5-isopropenyl-2-methyl-η^3-cyclohex-1-en-3-yl)(η^5-pentamethylcyclopentadienyl)-ruthenium] Tetrafluoroborate ((*R*)-7·BF$_4$). The same procedure as given above using HBF_4 instead of CF_3SO_3H.

(5*S*,1*S*)-[(1-Hydroxy-η^3-5-isopropenyl-2-methyl-η^3-cyclohex-1-en-3-yl)(η^5-pentamethylcyclopentadienyl)-ruthenium] Trifluoromethanesulfonate ((*S*)-7·BF$_4$). Prepared in the same manner as the (*R*)-enantiomer using (*S*)-carvone. $[\alpha]_{546}^{25} = +329$ (acetone, $c = 4.4 \times 10^{-3}$ g·cm^{-3}).

(5*R*,2*R*)-(η^3-5-Isopropenyl-2-methyl-η^2-cyclohex-2-en-1-one)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (6). To 200 mg (0.37 mmol) of **7**·CF$_3$SO$_3$ in 10 mL of acetone was added 55 μL (0.39 mmol) of triethylamine. The solvent was removed *in vacuo*, and the oily residue was extracted with hexane. Cooling the yellow hexane solution to −25 °C yielded 0.130 g (90%) of (5*R*,R_{Ru})-(η^3-5-isopropenyl-2-methyl-η^2-cyclohex-2-ene-1-one)(η^5-pentamethylcyclopentadienyl)ruthenium-(II) as yellow crystals. Fp: 162 °C. $[\alpha]_{546}^{25} = -13$ (acetone, $c = 1.48 \times 10^{-2}$ g·cm^{-3}). ^{1}H NMR (500 MHz, acetone-d_6): 1.68 (s, Cp*, 15H), 1.20 (s, H1, 3H), 2.29 (ddd, H3, $J = 3.3$, 1.1, 1.1 Hz, 1H), 1.80 (d$_{br}$, H4, $J = 13.2$ Hz, 1H), 2.01 (dd, H4′, $J = 13.2$, 4.6 Hz, 1H), 2.59 (ddd$_{br}$, H5, $J = 4.6$, 2.1, 1 Hz, 1H), 1.43 (ddd, H6, $J = 17.5$, 3.3, 1 Hz, 1H), 1.65 (ddd, H6′, $J = 17.5$, 3.1, 2.1 Hz, 1H), 0.77 (s, H9$_{anti}$, 1H), 2.65 (d, H9$_{syn}$, $J = 3$ Hz, 1H), 1.06 (s, H10$_{anti}$, 1H), 2.35 (d, H10$_{syn}$, $J = 3$ Hz, 1H). ^{13}C NMR (125.6 MHz, acetone-d_6): 10.4, 96.6 (Cp*), 21.7 (C1), 56.8 (C2), 56.5 (C3), 34.0 (C4), 32.3 (C5), 41.4 (C6), 203.3 (C7), 106.1 (C8), 47.8 (C9), 46.7 (C10). IR (KBr, ν, cm^{-1}): 2850 (m), 1627 (s), 1377 (m), 1362 (m), 1327 (m), 1305 (m), 1029 (m). MS (70 eV, EI): *m*/*z* (I_{rel}) 385 (100, $M^+ - H$), 371 (89, $M^+ - CH_3$), 358 (22, $M^+ - C_2H_4$), 343 (37, $M^+ - i$-Pr), 232 (24, $(Cp^*Ru)^+ - 5H$). Anal. Calcd for [$C_{20}H_{28}ORu$]: C, 62.31; H, 7.32. Found: C, 61.96; H, 7.40.

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(5*S*,1*R*)-[(1-Hydroxy-η^2-5-isopropene-2-methyl-η^4-cyclohexa-1,3-diene)(η^5-pentamethylcyclopentadienyl)ruthenium(II)] Trifluoromethanesulfonate (8·CF_3SO_3). Prepared analogous to **7** from 250 mg (0.43 mmol) of **1**, 0.8 mmol (70 μL) of CF_3SO_3H, and 0.86 mmol (0.190 mL) of **5**. Yield: 0.322 g (70%). Fp: 145 °C dec. $[\alpha]_{546}^{25} = -349$ (acetone, $c = 8.65 \times 10^{-3}$ g·cm^{-3}). ^{1}H NMR (500 MHz, CD_2Cl_2): 1.72 (s, Cp*, 15H), 1.99 (d, H1, J = 0.5 Hz, 3H), 4.57 (d, H3, J = 6.6 Hz, 1H), 2.44 (ddd, H4, J = 6.5, 5.3, 1.2 Hz, 1H), 3.34 (ddd, H5, J = 5, 5, 1.5 Hz, 1H), 1.24 (ddd, H6, J = 15.4, 4.9, 0.7 Hz, 1H), 1.31 (ddd, H6′, J = 15.5, 1.4, 1.4 Hz, 1H), 2.03 (s, H10, 3H), 2.75 (d, $H9_{syn}$, J = 1 Hz, 1H), 3.19 (d, $H9_{anti}$, J = 1.5 Hz, 1H). ^{13}C NMR (125.6 MHz, CD_2Cl_2): 10.2, 93.7 (Cp*), 14.4 (C1), 76.4 (C2), 77.8 (C3), 33.9 (C4), 34.3 (C5), 23.3 (C6), 145.9 (C7), 60.3 (C8), 23.2 (C10), 49.3 (C9), 120.9 (q, $CF_3SO_3^-$, J_{CF} = 320 Hz). IR (KBr, ν, cm^{-1}): 3275 (m), 2917 (m), 1551 (s), 1484 (m), 1385 (m), 1289 (s), 1258 (s), 1227 (s), 1206 (s), 1157 (s), 1099 (m), 1033 (s), 978 (m), 637 (s). MS (FAB): m/z (I_{rel}) +VE 387 (100, $M^+ - CF_3SO_3^-$), 385 (75, $M^+ - H_2 - CF_3SO_3^-$), 371 (6, $M^+ - CH_4 - CF_3SO_3^-$), 233 (3, $(Cp^*Ru)^+ - 4H$); −VE 149 (100, $CF_3SO_3^-$). Anal. Calcd for [$C_{21}H_{29}F_3O_4RuS$]: C, 47.10; H, 5.46. Found: C, 47.19; H, 5.55.

(5*S*,2*S*)-(η^2-5-Isopropen-2-methyl-η^3-cyclohex-2-en-1-one-4-yl)(η^5-pentamethylcyclopentadienyl)ruthenium-(II) (9). Prepared by deprotonation of **8** (200 mg, 0.37 mmol) with Et_3N in acetone. Yield after extraction into hexane was 0.130 g (90%) as orange crystals. Fp: 163 °C. $[\alpha]_{546}^{25} = +146$ (acetone, $c = 5.95 \times 10^{-3}$ g·cm^{-3}). ^{1}H NMR (500 MHz, CD_2Cl_2): 1.66 (s, Cp*, 15H), 1.41 (s, H1, 3H), 3.89 (d, H3, J = 5.8 Hz, 1H), 2.65 (ddd, H4, J = 6.7, 5.8, 1.2 Hz, 1H), 3.05 (ddd, H5, J = 6.5, 5.5, 2.1 Hz, 1H), 0.97 (ddd, H6, J = 16.2, 2.1, 1.2 Hz, 1H), 1.07 (dd, H6′, J = 16.2, 5.5 Hz, 1H), 1.88 (s, H9, 3H), 1.47 (d, $H10_{syn}$, J = 1.2 Hz, 1H, H_g), 2.05 (d, $H10_{anti}$, J = 1.2 Hz, 1H, $H_{g'}$). ^{13}C NMR (125.6 MHz, CD_2Cl_2): 10.4, 90.3 (Cp*), 18.3 (C1), 43.9 (C2), 82.9 (C3), 24.9 (C4), 34.6 (C5), 34.8 (C6), 201.8 (C7), 58.5 (C8), 27.3 (C9), 43.7 (C10). IR (KBr, ν, cm^{-1}): 2947 (w), 2888 (m), 1625 (s), 1377 (m), 1349 (m), 1311 (m), 1021 (m), 704 (w). MS (70 eV, EI): m/z (I_{rel}) 385 (100, $M^+ - H$), 371 (78, $M^+ - CH_3$), 357 (24, $M^+ - C_2H_5$), 343 (48, M^+ − *i*-Pr), 232 (28, $(Cp^*Ru)^+ - 5H$). Anal. Calcd for [$C_{20}H_{28}ORu$]: C, 62.31; H, 7.32. Found: C, 62.24; H, 7.57.

(5*R*)-(η^5-5-Isopropyl-2-methyl-1-oxocyclohexadienyl)-(η^5-pentamethylcyclopentadienyl)ruthenium(II) (13). (a) To 0.37 g (1.27 mmol) of [Cp*RuOMe]$_2$ dissolved in 10 mL of benzene was added 0.4 mL (2.54 mmol) of (*R*)-(−)-dihydrocarvone. After 4 days at 30 °C, the solvent was removed *in vacuo* and excess dihydrocarvone was extracted with hexane. The residual orange brown solid was dissolved in Et_2O, and the solution was filtered over Celite. On concentration of the solution, 0.23 g (47%) of product precipitated as a colorless solid. Fp: 177 °C. $[\alpha]_{546}^{25} = +1.6$ (acetone, $c = 5.0 \times 10^{-3}$ g·cm^{-3}). ^{1}H NMR (500 MHz, $CDCl_3$): 1.74 (s, Cp*, 15H), 1.77 (s_{br}, H1, 3H), 5.00 (d, H3, J = 5.5 Hz, 1H), 4.72 (dd, H4, J = 5.5, 1.0 Hz, 1H), 4.87 (s_{br}, H6, 1H), 2.25 (sept, H8, J = 6.9 Hz, 1H), 1.12 (d, H9, H10, J = 6.9 Hz, 3H), 1.12 (d, J = 6.9 Hz, 3H). ^{13}C NMR (125.6 MHz, $CDCl_3$): 10.1, 89.6 (Cp*), 14.8 (C1), 109.6 (C2), 87.1, 76.6, 75.4 (C3, C4, C6), 87.5 (C5), 149.1 (C7), 31.0 (C8), 22.3, 23.2 (C9, C10). IR (KBr, ν, cm^{-1}): 3034 (w), 2955 (m), 2904 (m), 1555 (s), 1500 (m), 1477 (m), 1379 (m), 1363 (m), 702 (m). MS (70 eV, EI): m/z (I_{rel}) 385 (63, $M^+ - H$), 371 (100, $M^+ - CH_3$), 358 (7, $M^+ - C_2H_4$), 343 (8, M^+ − *i*-Pr), 233 (14, $(Cp^*Ru)^+ - 4H$). Anal. Calcd for [$C_{20}H_{28}ORu$]: C, 62.31; H, 7.32. Found: C, 62.00; H, 7.43. (b) As performed above using **11** instead of **4**, yield 47%.

(1*S*)-[(η^6-5-Isopropyl-2-methylphenol)(η^5-pentamethylcyclopentadienyl)ruthenium(II)] Trifluoromethanesulfonate ((*S*)-14·CF_3SO_3). **13a** (0.2 g, 0.52 mmol) was treated in acetone with 50 μL (0.52 mmol) of CF_3SO_3H. The reddish brown acetone solution was passed over silylated silica, eluted with acetone, concentrated, and cooled to −78 °C to separate 0.264 g (95%) of brown crystals. Fp: 190 °C. $[\alpha]_{546}^{25} = +83$ (acetone, $c = 1.20 \times 10^{-3}$ g·cm^{-3}). ^{1}H NMR (500 MHz, $CDCl_3$): 1.82 (s, Cp*, 15H), 5.30 (d, H3, J = 5.8 Hz, 1H), 5.13 (d_{br}, H4, J = 5.8 Hz, 1H), 6.14 (s_{br}, H6, 1H), 1.99 (s, H1, 3H), 2.50 (sept, H8, J = 7.0 Hz, 1H), 1.19 (d, H9, H10, J = 7.0 Hz, 3H), 1.26 (d, J = 7.0 Hz, 3H), 9.36 (s_{br}, OH, 1H). ^{13}C NMR (125.6 MHz, $CDCl_3$): 9.9, 93.7 (Cp*), 13.2 (C1), 110.1 (C2), 86.7, 81.0, 75.7 (C3, C4, C6), 88.8 (C5), 129.6 (C7), 30.8 (C8), 22.5, 22.8 (C9, C10), 120.9 (q, $CF_3SO_3^-$, J_{CF} = 320 Hz). IR (KBr, ν, cm^{-1}): 3096 (m), 2973 (w), 2920 (w), 1536 (w), 1476 (m), 1453 (w), 1406 (m), 1387 (m), 1327 (m), 1298 (s), 1237 (s), 1221 (s), 1165 (s), 1030 (s), 638 (s). MS (FAB): m/z (I_{rel}) +VE 387 (100, $M^+ - CF_3SO_3^-$), 371 (8, $M^+ - CH_4 - CF_3SO_3^-$), 357 (2, $M^+ - C_2H_5 - CF_3SO_3^-$), 343 (1, M^+ − *i*-Pr − $CF_3SO_3^-$), 233 (3, $(Cp^*Ru)^+ - 4H$); −VE 149 (100, $CF_3SO_3^-$). Anal. Calcd for [$C_{21}H_{29}F_3O_4RuS$]: C, 47.10; H, 5.46. Found: C, 46.53; H, 5.45.

(1*S*)-[(η^6-1-(*S*)-Camphorsulfonyl-5-isopropyl-2-methyl phenolate)(η^5-pentamethylcyclopentadienyl)-ruthenium(II)] Chloride (15a·Cl). When an ether solution of 0.043 g (0.17 mmol) of (1*S*)-(+)-camphor-10-sulfonyl chloride was added to 0.066 g (0.17 mmol) of **13a** dissolved in ether, the product separated as a white solid, which was washed two times with ether and dried. Yield: 0.104 g (96%). ^{1}H NMR (500 MHz, $CDCl_3$): 1.88 (s, Cp*, 15H), 6.59 (d_{br}, H3, J = 5.8 Hz, 1H), 6.06 (d_{br}, H4, J = 5.8 Hz, 1H), 6.18 (s_{br}, H6, 1H), 2.24 (s, H1, 3H), 2.68 (sept, H8, J = 6.9 Hz, 1H), 1.228 (d, H9, H10, J = 6.9 Hz, 3H), 1.230 (d, J = 6.9 Hz, 3H), 3.80 (d, H11, H11′, J = 14.9 Hz, 1H), 3.36 (d, J = 14.9 Hz, 1H), 1.88 (m, H14, H14′, 1H), 2.37 (ddd, J = 18.6, 4.0, 4.0 Hz, 1H), 2.12 (dd, H15, J = 4.4, 4.4 Hz, 1H), 1.42 (ddd, H16, H16′, J = 13.0, 9.4, 4.0 Hz, 1H), 2.03 (m, 1H), 1.70 (m, H17, H17′, 1H), 2.29 (ddd, J = 15.0, 12.0, 4.0 Hz, 1H), 0.89 (s, H19, H20, 3H), 1.07 (s, 3H). ^{13}C NMR (125.6 MHz, $CDCl_3$): 10.2, 96.1 (Cp*), 13.9 (C1), 110.6 (C2), 86.5 (C3), 89.5 (C4), 95.2 (C5), 80.5 (C6), 119.4 (C7), 30.3 (C8), 22.4, 22.9 (C9, C10), 50.0 (C11), 58.2 (C12), 213.4 (C13), 42.4 (C14), 42.8 (C15), 26.7 (C16), 25.7 (C17), 48.2 (C18), 19.4, 19.6 (C19, C20).

(1*R*,1*S*)-[(η^6-(*S*)-Camphorsulfonyl-5-isopropyl-2-methyl phenolate)(η^5-pentamethylcyclopentadienyl)-ruthenium(II)] Trifluoromethanesulfonate (15b). To 0.2 g (0.34 mmol) of [Cp*RuOMe]$_2$ in 5 mL of acetone was added 60 μL (0.69 mmol) of CF_3SO_3H and subsequently 107 mL (0.69 mmol) of 5-isopropyl-2-methylphenol (carvacrol). The resulting phenol complex was precipitated by addition of 50 mL of ether, redissolved in acetone, and precipitated to give 0.18 g (50%) as the triflate salt. After drying under high vacuum, the complex was treated in ether with an equimolar amount of *n*-BuLi to generate the neutral oxocyclohexadienyl complex **13b**. To the mixture containing **13**, LiCl, and CF_3SO_3Li in ether was added an equimolar amount of (*S*)-(+)-camphor-10-sulfonyl chloride. The resulting solid was separated, washed with ether, and dried under high vacuum. It was freed from LiCl by dissolving in $CHCl_3$, where only the $CF_3SO_3^-$ salt is soluble, filtering off the solid, and evaporating the solvent. ^{1}H NMR (500 MHz, $CDCl_3$): 1.86, 1.87 (s, Cp*, 15H), 6.05, 6.07 (d_{br}, H3, J = 6.1 Hz, 1H), 5.83, 5.85 (d_{br}, H4, J = 6.0 Hz, 1H), 6.16, 6.16 (s_{br}, H6, 1H), 2.20, 2.22 (s, H1, 3H), 2.675, 2.680 (sept, H8, J = 7.0 Hz, 1H), 1.236, 1.256 (d, H9, H10, J = 7.0 Hz, 3H), 1.250, 1.256 (d, J = 7.0 Hz, 3H), 3.79, 3.81 (d, H11, H11′, J = 15.0 Hz, 1H), 3.30, 3.40 (d, J = 15.0 Hz, 1H), 1.4−2.5 (aliphatic protons, H14, H14′, H15, H16, H16′, H17, H17′, 7H), 0.89, 0.92 (s, H19, H20, 3H), 1.070, 1.085 (s, 3H). ^{13}C NMR (125.6 MHz, $CDCl_3$): 9.92, 9.94, 96.33, 96.35 (Cp*), 13.90, 13.95 (C1), 111.25, 111.32 (C2), 85.88, 86.04 (C3), 88.82, 88.82 (C4), 95.39, 95.53 (C5), 80.40, 80.89 (C6), 119.49, 119.96 (C7), 30.31, 30.38 (C8), 22.41, 22.46, 22.76, 22.81 (C9, C10), 49.57, 50.05 (C11), 58.04, 58.25 (C12), 213.49, 214.00 (C13), 42.47, 42.47 (C14), 42.68, 42.94 (C15), 26.80, 26.86 (C16), 25.30, 25.84 (C17), 48.36, 48.49 (C18), 19.29, 19.31, 19.49, 19.53 (C19, C20).

(1*R*,1*S*)-[(η^6-1-Acetyl-5-isopropyl-2-methyl phenolate)-(η^5-pentamethylcyclopentadienyl)ruthenium(II)] Trifluoromethanesulfonate (16). To 895 mg (1.67 mmol) of **14b** (prepared by reaction of 450 mg (0.84 mmol) of [Cp*RuOMe]$_2$

Table 2. Crystal Data, Data Collection Parameters, and Convergence Results of the X-ray Structure Determinations

	6	**7**·CF_3SO_3	**7**·BF_4	**8**·CF_3SO_3	**14**·CF_3SO_3
formula	$C_{20}H_{28}ORu$	$C_{21}H_{29}F_3O_4RuS$	$C_{20}H_{29}BF_4ORu$	$C_{21}H_{29}F_3O_4RuS$	$C_{21}H_{29}F_3O_4RuS$
fw	385.52	535.59	473.33	535.59	535.59
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)	$P2_1$ (No. 4)
a, Å	8.884(3)	8.671(3)	8.872(3)	9.819(6)	15.054(6)
b, Å	9.397(5)	14.437(8)	14.999(6)	14.115(5)	10.923(4)
c, Å	20.806(7)	9.053(2)	30.49(1)	16.01(1)	15.178(9)
β, deg		102.26(2)	94.87(4)		112.64(3)
V, Å^3	1737(2)	1107(1)	4043(5)	2219(4)	2304(2)
d_{calcd}, g cm^{-3}	1.474	1.606	1.457	1.605	1.544
Z	4	2	8	4	4
F(000)	800	548	1812	1096	1096
μ(Mo Kα), cm^{-1}	8.85	8.32	7.51	8.31	8.00
T, K	213	203	203	213	293
scan range, deg	$3 < \theta < 28$	$3 < \theta < 28$	$3 < \theta < 25$	$3 < \theta < 29$	$0.5 < \theta < 27$
total no. of data	8576	5354	14580	3323	10396
no. of unique obsd data	3039 ($I > 1.0\sigma(I)$)	2084 ($I > 0.5\sigma(I)$)	8591 ($I > 2.0\sigma(I)$)	3100 ($I > 1.0\sigma(I)$)	10005 (all data)
no. of variables	199	268	957	272	541
R, R_w, wR2[a]	0.047, 0.035, na	0.0690, 0.053, na	0.064, 0.064, na	0.029, 0.038, na	0.035, na, 0.083
GOF	0.914	1.050	1.460	1.382	0.891
max residuals density, e Å^{-3}	1.08	0.71	1.76	0.34	0.61

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. wR2 $= [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

with 259 μL (1.68 mmol) of cavacrol and 148 μL (1.68 mmol) of CF_3SO_3H in CH_2Cl_2 at −78 °C in 99% yield) was added, at −78 °C, 1 equiv of *n*-butyllithium in 20 mL of Et_2O. After having reached ambient temperature for a short time, the mixture was recooled to −78 °C and 119 μL (1.67 mmol) of acetyl chloride was slowly added. The mixture was warmed to ambient temperature, and the solvent was evaporated. After extensive drying *in vacuo*, the residue was dissolved in CH_2Cl_2 and LiCl was removed by filtering over Celite. Addition of ether precipitated an oil, which solidified on drying *in vacuo* to an off white powder. Yield: 770 mg (80%). ^{1}H NMR (500 MHz, $CDCl_3$): 1.83 (s, Cp*, 15H), 5.92 (d, H3, J = 6.0 Hz, 1H), 5.72 (d_{br}, H4, J = 6.0 Hz, 1H), 5.81 (s_{br}, H5, 1H), 2.01 (s, H1, 3H), 2.60 (sept, H8, J = 7.0 Hz, 1H), 1.21 (d, H9, H10, J = 7.0 Hz, 3H), 1.21 (d, J = 7.0 Hz, 3H), 2.29 (s, CH_3CO, 3H). ^{13}C NMR (125.6 MHz, $CDCl_3$): 9.8, 95.7 (Cp*), 13.1 (C1), 111.0 (C2), 88.3 (C3), 81.3 (C4), 95.0 (C5), 85.2 (C6), 119.3 (C7), 30.6 (C8), 22.3, 22.6 (C9, C10), 168.5 (C=O), 20.2 (CH_3CO), 120.6 (q, $CF_3SO_3^-$, J_{CF} = 320 Hz).

(1*S*)-[(η^6-(Diphenylphosphinito)-5-isopropyl-2-methylbenzene)(η^5-pentamethylcyclopentadienyl)ruthenium(II)] Chloride (17). To 100 mg (0.26 mmol) of **13a** in 10 mL of diethyl ether was added 48 μL (0.26 mmol) of $ClPPh_2$ at ambient temperature. A white solid precipitated from which the supernatant liquid was decanted. It was washed twice with ether and dried *in vacuo*. Yield: 0.125 g (80%). ^{1}H NMR (250 MHz, $CDCl_3$): 1.87 (s, Cp*, 15H), 6.19 (d, H3, J = 5.9 Hz, 1H), 5.69 (d, H4, J = 5.9 Hz, 1H), 6.09 (s, H6, 1H), 2.22 (s, H1, 3H), 2.52 (sept, H8, J = 6.9 Hz, 1H), 1.01 (d, H9, H10, J = 6.9 Hz, 3H), 1.09 (d, J = 6.9 Hz, 3H), 7.4−7.9 (aromatic protons, 10H, PPh_2).

(1*S*)-[(η^6-5-Isopropyl-1-methoxy-2-methylbenzene)(η^5-pentamethylcyclopentadienyl)ruthenium(II)] Iodide (18). To 100 mg (0.26 mmol) of **13a** in 5 mL of acetone was added 0.1 mL (1.6 mmol) of MeI, which was warmed 4 h to 45 °C. The solvent was removed *in vacuo* and the oily residue was washed three times with hexane and dried *in vacuo* to yield 110 mg (80%) of a viscous oil. ^{1}H NMR (250 MHz, $CDCl_3$): 1.82 (s, Cp*, 15H), 1.97 (s, H1, 3H), 5.82 (d, H3, J = 5.9 Hz, 1H), 5.51 (d, H4, J = 5.9 Hz, 1H), 6.12 (s, H6, 1H), 2.80 (sept, H8, J = 6.8 Hz, 1H), 1.17 (d, H9, H10, J = 6.8 Hz, 3H), 1.24 (d, J = 6.8 Hz, 3H), 3.81 (s, OMe, 3H). ^{13}C NMR (62.7 MHz, $CDCl_3$): 10.7, 94.2 (Cp*), 13.4 (C1), 110.2 (C2), 88.4, 82.7, 72.4 (C3, C4, C6), 89.6 (C5), 131.0 (C7), 30.5 (C8), 22.0, 24.3 (C9, C10), 58.3 (OMe).

X-ray Structure Determinations. Geometry and intensity data were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.7107 Å, graphite monochromator). Crystal data, data collection parameters, and convergence results are compiled in Table 2. Only in the case of **8**·CF_3SO_3 was an empirical absorption correction on the basis of azimuthal scans[27] applied (min transmission 0.905, max transmission 0.996) before averaging over symmetry-equivalent reflections. The structures were solved by Patterson syntheses (**6**, **7**·CF_3SO_3, **8**·CF_3SO_3) or direct methods.[28] In the least-squares refinement procedures on F[29] in the case of **6**−**8** and on F^2 [30] for **14**·CF_3SO_3, hydrogen atoms were included in calculated positions with C−H = 0.98 Å and U_{iso}(H) = 1.3U_{eq}(C). Disorder of the trifluoromethyl group was encountered in the anion of **7**·CF_3SO_3.

Two independent molecules in the asymmetric unit of **14**·CF_3SO_3 show pseudoinversion symmetry. Only the oxygen atoms of the arene ligand result as disordered upon tentative refinement in the centric supergroup $P2_1/a$, and therefore, during the refinement of this structure considerable correlation was encountered and is still feasible in displacement parameters and details of the molecular geometry. However, the presence of about 50 significant intensity data with $h01$, $h \neq 2n$, and the fact that single crystals show optical activity excludes the possibility of a centric space group. Flack's enantiomorph polarity parameter[22] indicates the correct assignment of the enantiomorph: this parameter refined to a value of 0.05(5).

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Supporting Information Available: Tables of X-ray data, positional and thermal parameters, bond distances, and bond angles for **6**, **7**·CF_3SO_3, **7**·BF_4, **8**·CF_3SO_3, and **14**·CF_3SO_3 (39 pages). Ordering information is given on any current masthead page.

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