Novel Concepts in Directed Biaryl Synthesis, 68[+]
Enantioselective Organic Syntheses Using Chiral Transition Metal Complexes, 9[++]
Atropo-Diastereoselective Ring Opening of Biaryl Thionolactones Using [CpRu{(*S*,*S*)-CHIRAPHOS}]$^+$ as a Chiral Auxiliary

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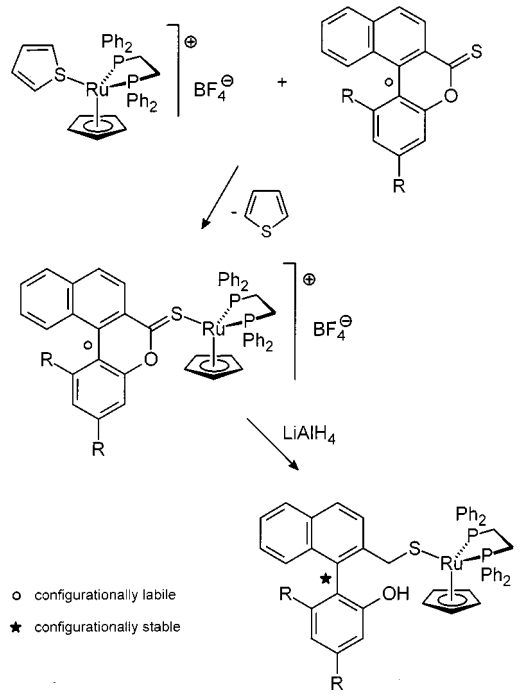
Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

Keywords: Biaryls / Lactones / Nucleophilic additions / Ruthenium / S ligands

The substitution-labile thiophene complex [CpRu{(*S*,*S*)-CHIRAPHOS}(SC_4H_4)]BF_4 (**2**) [(*S*,*S*)-CHIRAPHOS = (2*S*,3*S*)-bis(diphenylphosphanyl)butane], prepared from [CpRu{(*S*,*S*)-CHIRAPHOS}Cl] (**1**), thiophene, and $AgBF_4$, reacted with the biaryl-thionolactones **3a–f** to give the corresponding S-coordinated complexes **4a–f** in high yields. The structure of **4c**, which crystallized as the pure (*S*,*S*,*P*) diastereoisomer, was determined by X-ray crystallography. Coordination of the ruthenium fragment caused an elongation of the C=S bond, a contraction of the C–O bond within the lactone ring and a flattening of that ring. Single hydride transfer with $LiBEt_3H$ converted **4a–f** into the thiolactolate complexes **5a–f** in good yields and diastereoselectivities. An X-ray structure determination of the major isomer of **5a** revealed it to be the (*S*,*S*,*S*,*P*) diastereoisomer. Protonation with NH_4PF_6 converted **5a–f** into the corresponding ring-opened thioaldehyde complexes **6a–f**. Alkylation of **5a** with methyl iodide resulted in Ru–S cleavage to give the oxothioacetal **7a** and [CpRu{(*S*,*S*)-CHIRAPHOS}I] (**8**). Full reduction of **4a–f** with $LiAlH_4$ produced the thiolate complexes **9a–f** in high yields and 6–74% *de*. Methylation at sulfur converted **9a–c** into the corresponding thioether complexes **10a–c**, which were cleaved to **8** and the free methyl thioethers **11a–c** without isomerization of the biaryl axis.

Introduction

Natural products containing a chiral, configurationally stable biaryl axis are attracting considerable attention due to their widespread pharmacological activities.[3][4] Their stereocontrolled synthesis remains a fascinating challenge. One of the most efficient synthetic pathways consists of the preparatively facile formation of a bridged, but still configurationally labile biaryl system followed by an atropo-diastereo- or atropo-enantioselective ring-opening step.[5] The necessary element of chirality may already be present in the molecule,[6] or it may be introduced either by the reagent[7] or by attaching a chiral auxiliary to the bridged biaryl substrate.[8] We have previously demonstrated that configurationally unstable biaryl thionolactones can easily be introduced as ligands into half-sandwich ruthenium complexes. Double nucleophilic addition of hydride converts the coordinated thionolactones into axially chiral racemic thiolates (Scheme 1).[9]



Scheme 1. Coordination and ring opening of biaryl thionolactones

[+] Part 67: Ref.[2]
[++] Part 8: Ref.[1]

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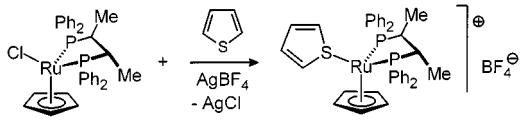
By using a similar but chiral, enantiomerically pure complex it should be possible to achieve a diastereoselective ring cleavage of the thionolactone. The coordinatively unsaturated complex fragment [CpRu{(*S*,*S*)-CHIRAPHOS}]$^+$ [(*S*,*S*)-CHIRAPHOS = (2*S*,3*S*)-bis(diphenylphosphanyl)-butane] appeared to be a promising candidate.[10] This chiral auxiliary has previously been employed by us, and with considerable success, in the diastereoselective oxidation of coordinated thioethers.[11–14]

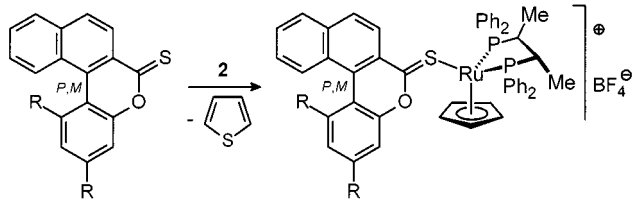
Results

The synthesis of thionolactone complexes by ligand exchange requires a reactive starting material.[9] Thus, [CpRu{(*S*,*S*)CHIRAPHOS}Cl] (**1**) was treated with silver tetrafluoroborate in the presence of thiophene to give the enantiomerically pure thiophene complex **2** in almost quantitative yield (Equation 1).



1 **2** (95%) (1)

Compound **2** is a yellow, crystalline, air-sensitive material. Its ^{1}H-NMR spectrum exhibits, *inter alia*, the typical AA′XX′ pattern at δ = 5.81 and 6.83 indicating the presence of a thiophene ligand. The reaction of **2** with the thionolactones **3a**–**f** at room temperature was accompanied by an immediate color change from yellow to dark purple. The pure thionolactone complexes were readily purified by chromatography and isolated in almost quantitative yields as deep purple crystalline solids (Equation 2).



3a - f **4a - f** (91 - 96%) (2)

R	H	OMe	Me	Et	*i*-Pr	*t*-Bu
	a	**b**	**c**	**d**	**e**	**f**
de (%)		10[a]	10	14	20	6

[a] at 210 K

The ^{31}P-NMR spectra of **4a**–**f** reveal a dynamic process whose rate depends on the size of the substituent R. The limiting cases are marked by **4a** (R = H), which even at 210 K exists as a mixture of rapidly equilibrating diastereoisomers, and **4c**–**f** (R = Me, Et, *i*Pr, *t*Bu), which up to 380 K exhibit two separate sets of signals for the two diastereoisomers. With the exception of R = *t*Bu, the diastereomeric ratio increases slightly with the size of R. Compound **4b** (R = OMe) shows two sets of signals at 210 K in a 55:45 ratio (10% *ee*) which coalesce at 263 K. A standard lineshape analysis yielded an activation barrier for this process of $\Delta G^{\neq}$ = 48 kJ mol^{-1}. ^{1}H-NMR spectra of samples of **4c** and **4d**, if recorded immediately after dissolution at 253 K, gave distinctly higher diastereomeric ratios. This indicates that, for those two compounds, the epimerization of the biaryl axis has a half-life at this temperature in the range of a few minutes. In the ^{13}C-NMR spectra at 295 K the thiocarbonyl function gives rise to one (**4a, b**) or two (**4c**–**e**) signals at δ = 200, which are split into doublets of doublets due to coupling with the nonequivalent phosphorus nuclei. A single crystal of **4c** was subjected to an X-ray structure determination. Figure 1 shows a view of the cation.

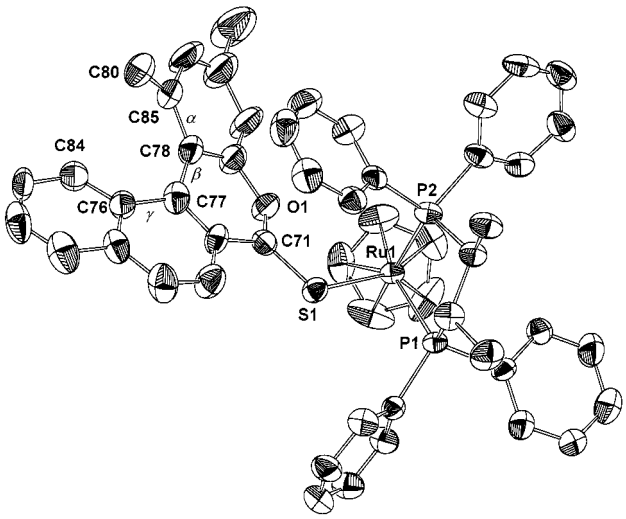
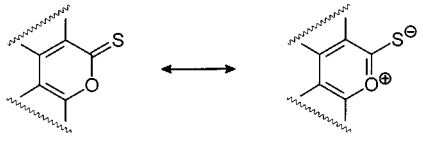


Figure 1. Structure of the Cation of [CpRu{(*S*,*S*)-CHIRAPHOS}($SC_{19}H_{14}O$)]BF_4 (**4c**) (hydrogen atoms omitted); selected bond lengths (pm) and angles (deg): Ru(1)–P(1) 227.8(2), Ru(1)–P(2) 231.2(2), Ru(1)–S(1) 233.1(2), C(71)–S(1) 165.5(8), C(71)–O(1) 134.3(10); P(1)–Ru(1)–P(2) 83.40(7), P(1)–Ru(1)–S(1) 85.42(7), P(2)–Ru(1)–S(1) 89.09(8), C(71)–S(1)–Ru(1) 114.0(3), C(71)–S(1)–Ru(1)–P(1) 169.3(5), C(71)–S(1)–Ru(1)–P(2) 86.0(5), C(80)–C(85)–C(78)–C(77) 15.2(25), C(85)–C(78)–C(77)–C(76) 27.3(23), C(78)–C(77)–C(76)–C(84) 20.0(20)

The coordination geometry around the ruthenium atom is adequately described as octahedral, in which the C_5H_5 ligand occupies three adjacent sites. All bond lengths to ruthenium are similar those in the closely related thioaldehyde complex [CpRu(dppe)(η^1-S=CHC_6H_4OMe)]PF_6.[15] The two angles S–Ru–P(1) and S–Ru–P(2) are markedly different as a result of the fixed configuration of the five-membered Ru{(*S*,*S*)-CHIRAPHOS} chelate ring. The bonding within the thionolactone ring can be described in terms of two canonical forms **A** and **B** (Scheme 2).



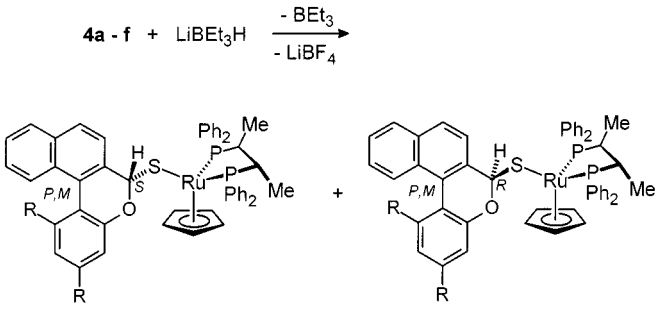
A **B**

Scheme 2. Resonance forms of the thionolactone ring

The coordination of a cationic metal complex at sulfur is expected to increase the contribution of the benzenoid resonance form **B** by dissipating the negative charge. Indeed, the C=S bond in the complex is 2 pm longer than in the uncoordinated thionolactone **3c**,[9] while the C(71)−O bond within the lactone ring of the complex is shorter by 1.6 pm. The two aryl moieties are helically twisted; of the two possible forms, only the *P* diastereoisomer is found in the crystal (see Figure 1). This helical distortion is a result of the steric repulsion between the *ortho* methyl group and the hydrogen atom in the 8-position of the naphthyl part. As seen in other cases,[16] the sum of the dihedral angles α [C(80)−C(85)−C(78)−C(77)], β [C(85)−C(78)−C(77)−C(76)], and γ [C(78)−C(77)−C(76)−C(84)] (Figure 1) can serve as a measure of this distortion. At 62.5°, this sum is only marginally different from the corresponding value for uncoordinated **3c** (63.6°).[9] The individual contributions to this sum, however, differ markedly; β in particular is distinctly smaller in the complex **4c** (27.3°) than in uncoordinated **3c** (33.4°). This flattening of the lactone ring, which has been observed previously for complexes of the analogous oxolactones,[8] hints at some degree of "aromatization" as expressed by the resonance form **B** (Scheme 2). The orientation of the biaryl-thionolactone ligand within the complex is another conspicuous feature of the structure of **4c**. The C=S group and the Ru−P(1) bond are nearly in the same plane, while the Ru−P(2) bond is almost perpendicular to that plane (Figure 1). As a result, one diastereomorphous half space around the thionolactone function is shielded by one of the phenyl groups of the (*S*,*S*)-CHIRAPHOS ligand, while the other half space remains exposed.

Treatment of the thionolactone complexes **4a**−**f** with $LiBEt_3H$ in THF at −70°C followed by slowly warming to 20°C was accompanied by a color change to yellow. Workup by extraction with benzene and freeze-drying gave the yellow, crystalline, slightly air-sensitive thiolactolate complexes **5a**−**f** in very good yields (Equation 3).

The room-temperature NMR spectra of these compounds indicate the presence of two (**5a**, **b**) or four (**5c**−**f**) diastereoisomers. The ^{31}P-NMR spectrum of **5b** consists of two broad signals which, upon cooling to 270 K, decoalesce into two AX spin systems due to a slowed inversion of the biaryl axis. The activation barrier could not be determined precisely but seems to be somewhat higher than that of the helimerization of **4b**. In the ^{13}C-NMR spectra the thioacetal carbon gives rise to a resonance at $\delta = 90$ with a 5 Hz coupling to only one of the phosphorus nuclei. This hints at an unsymmetrical arrangement of the thiolactolate ligand in the coordination sphere of the ruthenium atom, with one dihedral angle C−S−Ru−P close to 90° and the other close to 180°. Interestingly, for the two opposing helimers of the major diastereoisomer, the signals in the ^{1}H-NMR spectrum of the HC(S)O group are separated by up to 1.58 ppm. An inspection of the molecular structure of **5a** (see below) suggests that this may be due to differing anisotropy effects of one of the phenyl groups of the CHIRAPHOS ligand.



R		(*S*,*P*)	(*S*,*M*)	[(*R*,*P*) + (*R*,*M*)] (%)
H	**a**	93		7
OMe	**b**	65	28[a]	7
Me	**c**	52	38	< 10
Et	**d**	53	37	< 10
i-Pr	**e**	55	35	< 10
t-Bu	**f**	45	45	< 10

[a] at 220 K

(3)

An X-ray structure determination was carried out on a crystal of the major diastereoisomer of **5a**, Figure 2 shows a view of the molecule.

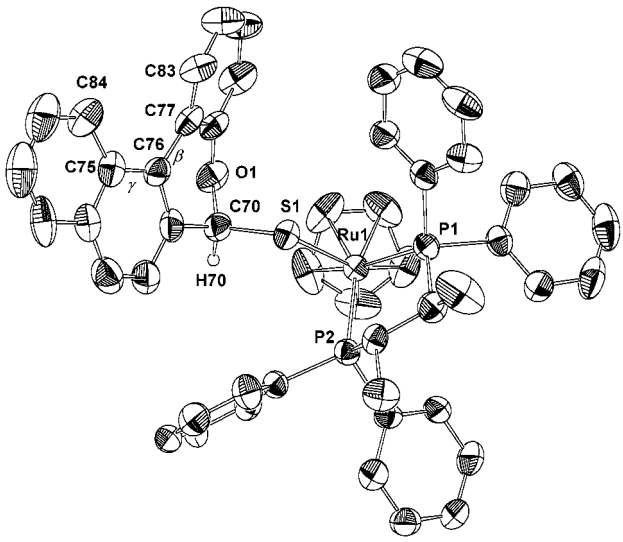


Figure 2. Structure of the Cation of [CpRu{(*S*,*S*)-CHIRAPHOS}($SC_{17}H_{11}O$)] (**5a**) [hydrogen atoms omitted, except for H(70)]; selected bond lengths (pm) and angles (deg): Ru(1)−P(1) 227.0(2), Ru(1)−P(2) 225.7(2), Ru(1)−S(1) 242.2(2), C(70)−S(1) 180.2(7), C(70)−O(1) 144.2(9); P(1)−Ru(1)−P(2) 84.41(7), P(1)−Ru(1)−S(1) 88.37(6), P(2)−Ru(1)−S(1) 81.78(6), C(70)−S(1)−Ru(1) 109.1(3), C(70)−S(1)−Ru(1)−P(1) 167.8(3), C(70)−S(1)−Ru(1)−P(2) 72.4(3). C(83)−C(77)−C(76)−C(75) 26.5(10), C(77)−C(76)−C(75)−C(84) 10.9(10)

The [CpRu{(*S*,*S*)-CHIRAPHOS}] part is almost identical to that of **4c** with the exception of the orientation of one phenyl group of the chiral chelate ligand. The hydride addition has led to an increase of the Ru−S and C−S bond lengths by 9 and 15 pm, respectively. Also, the C−O bond within the former lactone ring is longer by 10 pm. The configuration at the newly formed stereocenter is *S* while the biaryl axis of the crystalline compond has a fixed *P* configuration. The dihedral angles within the biaryl system

(β = 26.5°, γ = 10.9°) still indicate a sizable distortion. These values should, however, not be compared to those of **4c** where the interaction of the *ortho* methyl substituent at the phenyl group greatly contributes to the extent of the helical distortion.[16][17] In order to prove the identity of the single crystal as the bulk material of **5a** unambiguously, a powder diffraction diagram was recorded and compared with the pattern calculated from the single crystal data, which resulted in a perfect match (Figure 3).

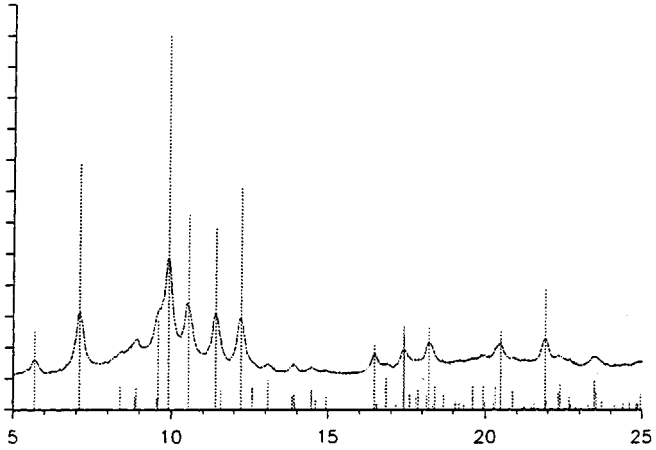
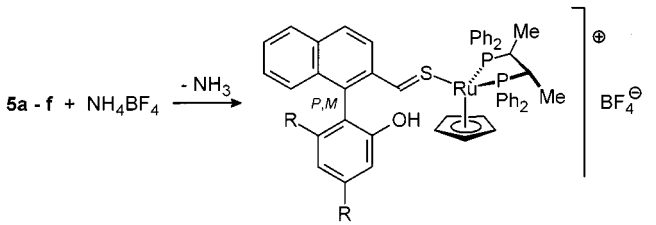


Figure 3. [CpRu{(*S*,*S*)-CHIRAPHOS}($SC_{17}H_{11}O$)] (**5a**), comparison of measured powder diffraction diagram (trace) and calculated diffraction pattern (bars)

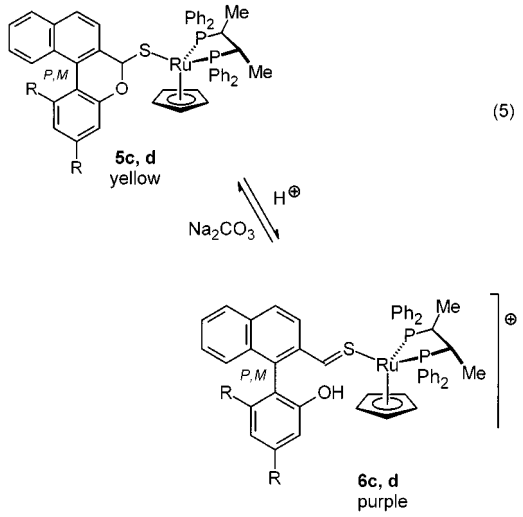
When exposed to traces of moisture or acid, solutions of the thiolactolate complexes **5a**−**f** occasionally turned deep purple, which is the characteristic color of thioaldehyde complexes.[15] Indeed, treatment of **5a**−**f** (as diastereomeric mixtures, Equation 3) with an excess of NH_4BF_4 in acetone (Equation 4) resulted in a quantitative transformation (as judged by NMR spectroscopy) into the corresponding thioaldehyde complexes **6a**−**f**.



6a - f (62 - 75%) (4)

R	H	OMe	Me	Et	*i*-Pr	*t*-Bu
	a	**b**	**c**	**d**	**e**	**f**
de (%)	5	8	12	12	23	0

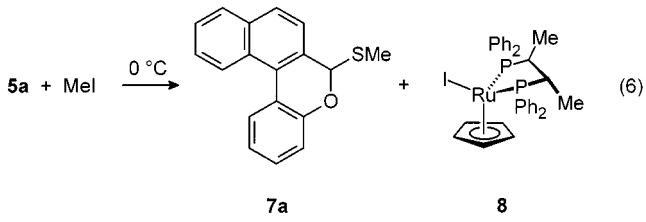
While **6a** was stable only in the presence of NH_4BF_4, the substituted derivatives could be isolated in good yields as deep purple crystalline solids. A similar opening of the thiolactolate could be achieved with various Lewis acids. Thus, when $LiBF_4$ was added to a solution of **5b** in acetone and the solvent removed under reduced pressure, a color change from yellow to purple was observed. According to the ^1H and ^{13}C-NMR spectra complete conversion into the thioaldehyde complex **6b** had taken place with 4% *de.* A similar result was obtained upon treatment of a solution of **5a** in THF with [$ZrCl_4(THF)_2$]. The red reaction mixture was worked up by addition of NH_4BF_4 in acetone and chromatography over silica and yielded **6a** with 20% *de.* Protonation and ring opening are reversible: Stirring suspensions of **6c** or **6d** and sodium carbonate in benzene produced clear yellow solutions, from which **5c** and **5d**, respectively, were isolated in reasonable yields (Equation 5).



(5)

As expected, **6a**−**f** were formed as mixtures of diastereoisomers in these reactions. The diastereomeric excess depends somewhat on the conditions used and increases slightly with increasing size of R; again R = *t*Bu (**6f**) is a conspicuous exception. The presence of a thioaldehyde functionality is unambiguously deduced from the characteristic low field signals in the ^1H (d = 9.7−10.3) and ^{13}C NMR (d = 210−217) spectra. The carbon resonance is split into an apparent triplet caused by roughly equal couplings to the two nonequivalent phosphorus nuclei.

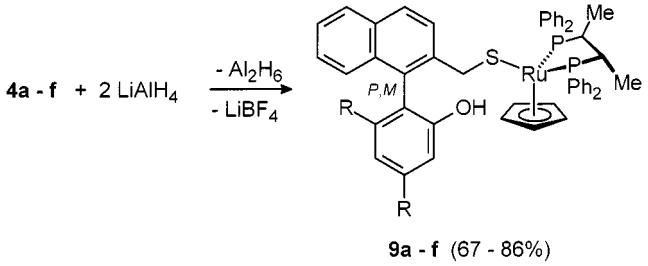
In an attempt to detach the thiolactolate ligand from the metal, **5a** was treated with methyl iodide at 0°C (Equation 6).



(6)

Within a few days complete conversion into the free monothioacetal **7a** and the known iodo complex **8**[12] took place. Chromatographic separation yielded **7a** as an impure yellow oil, which was identified spectroscopically. Full re-

duction of the thionolactone complexes **4a**−**f** was achieved with an excess of $LiAlH_4$ (Equation 7).



9a - f (67 - 86%)

R	H	OMe	Me	Et	*i*-Pr	*t*-Bu
	a	**b**	**c**	**d**	**e**	**f**
de (%)	52	8	74	33	33	6

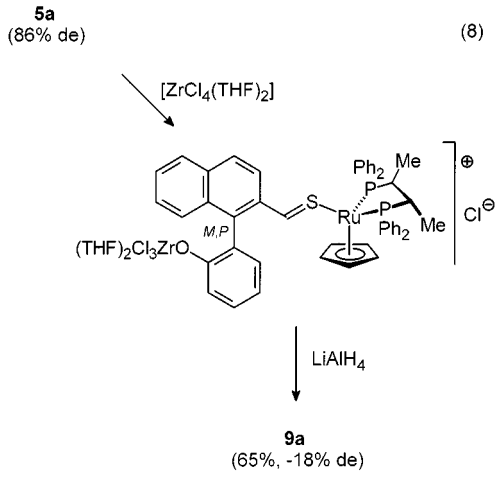
(7)

The highest diastereoselectivities were obtained by combining the reagents at −70°C, keeping the mixtures for 8 h at this temperature, and then allowing them to slowly warm to 20°C. Workup by chromatography over silica gel gave good yields of the yellow crystalline thiolate complexes **9a**−**f**. Their ^{13}C-NMR spectra show a signal at $\delta = 40$ for the benzylic carbon atom, which is split due to coupling with two nonequivalent phosphorus nuclei. The absolute values of the two coupling constants differ considerably, one of them being smaller than 1 Hz in some instances. This again hints at an unsymmetric orientation of the thiolate ligand in the coordination sphere of the ruthenium atom. The chemical shift difference of the diastereotopic benzylic protons is another noteworthy feature. It is consistently small (0.08−0.48 ppm) for the major diastereoisomer and large (0.93−1.46 ppm) for the minor one. Since chemical shift differences in these systems are mainly caused by anisotropy effects of the various aryl groups, we are confident that all major and minor isomers have the same configuration of the biaryl axis.

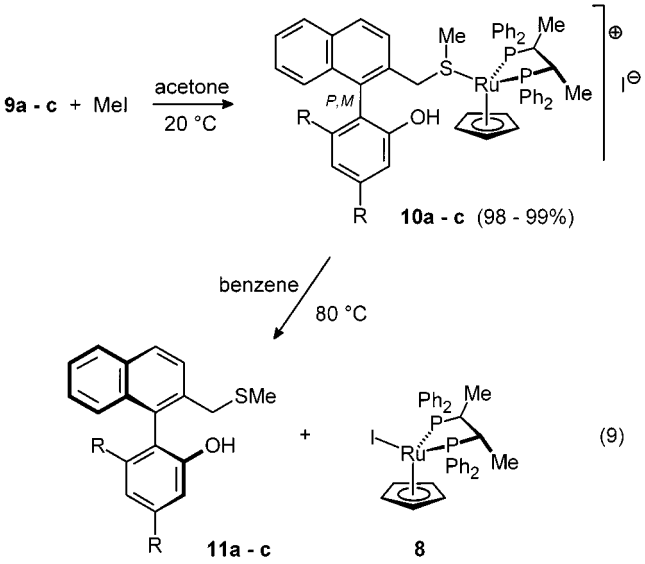
Some experiments aimed at finding ways to influence the diastereoselectivity of the ring-opening reaction were carried out. Thus, reduction of a sample of the thiolactolate **5c** (20% de) at −70°C with $LiAlH_4$ in THF gave the ring-opened thiolate complex **9c** in 61% yield and only 10% *de*. Under the same conditions, $LiBEt_3H$ was much more efficient producing **9c** in 80% yield and 50% *de*. In a similar experiment, a sample of **5a** with 86% *de* was treated at −70°C in THF with $[ZrCl_4(THF)_2]$ whereupon its color changed to red. It was kept at this temperature for 8 h to ensure complete ring opening to the thioaldehyde intermediate, and then $LiAlH_4$ was added (Equation 8).

This time, the thiolate complex **9a** was obtained with 65% yield and 18% *de* but with *opposite diastereoselectivity*, i. e. the minor diastereoisomer of Equation 7 was now the major one (hence the minus sign in Equation 8).

The demetalation of the thiolate complexes was achieved in two steps. Alkylation of **9a**−**c** with methyl iodide gave the thioether complexes **10a**−**c** in quantitative yields as light-yellow crystalline materials. The ionic nature of the



products is apparent from their insolubility in less polar media. The newly introduced methyl group gives resonances in the ^{1}H and ^{13}C-NMR spectra at $\delta = 1$ and 25, respectively. When the salts **10a**−**c** were heated in benzene a smooth ligand substitution took place, giving the iodo complex **8** and the liberated thioethers **11a**−**c** (Equation 9).



(9)

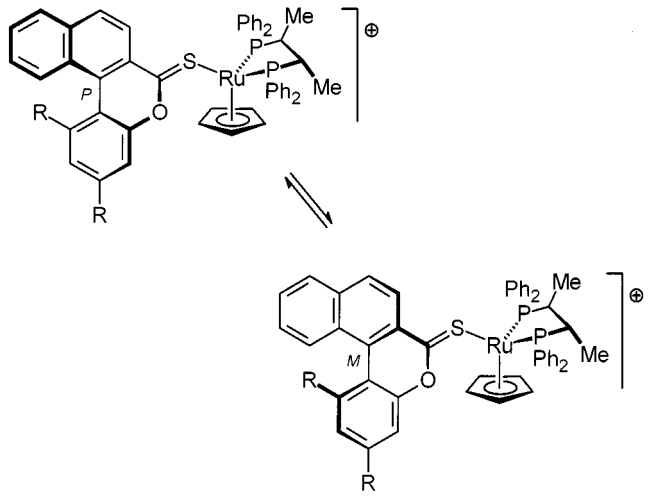
R	H	OMe	Me
	a	**b**	**c**
ee (%)	50 (*P*)	8 (*M*)	74 (*P*)

The latter were isolated after chromatography as slightly yellow oils and their enantiomeric purity checked by HPLC on a chiral phase.[18] The enantiomeric ratios of **11a**−**c** thus obtained were identical to the diastereomeric ratios of the starting complexes **9a**−**c** (Note that the change of the stereochemical descriptor for **11b** is due only to formal reasons, because of the higher priority of the MeO substituent). Finally, a comparison of the CD spectrum of **11c** with that of authentic (*M*)−**11c**[18] showed that the reaction sequence described here had yielded the *P* enantiomer.

Discussion

The work described here is part of an ongoing effort to use chiral transition metal complexes as auxiliaries for various types of enantioselective organic transformations.[19−22] Previously we have shown that double hydride addition to achiral ruthenium complexes of thionolactones leads to a smooth ring-opening reaction.[9] It was expected, therefore, that with the use of similar, but chirally modified, metal templates an atropo-diastereoselective opening of the thionolactone ring could be achieved. The required chiral thionolactone complexes **4a**−**f** are readily accessible by a ligand exchange reaction starting with the highly labile thiophene complex **2,** which in turn was obtained in excellent yield in close analogy to known syntheses.[9][23]

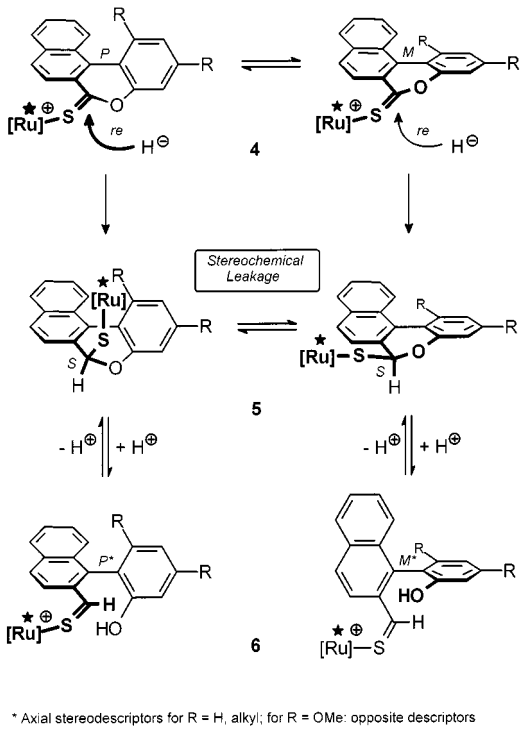
The structure determination of **4c** revealed some interesting aspects. First of all, the compound crystallized as a single diastereoisomer with *P* configuration at the biaryl axis, whereas in solution both diastereoisomers are of almost equal energy. In the solid state, the lactone carbon atom is perfectly shielded from the *si* side by one of the phenyl groups of the (*S*,*S*)-CHIRAPHOS ligand (Figure 1). It is thus tempting to hope that nucleophiles will add from the *re* side with high diastereoselectivity. This, however, is perhaps a too simplistic view. In solution, a dynamic equilibrium between both diastereoisomers [(*S*,*S*,*P*) and (*S*,*S*,*M*)] exists (Scheme 3), whose interconversion rate depends strongly on the size of R.



Scheme 3. Helimerization of the biaryl axis of thionolactone complexes **4a**−**e**

The limiting cases are marked by an immeasurably rapid equilibration, even at low temperature, for R = H (**4a**), and a slow interconversion in the range of several minutes for R = Me, Et, *i*Pr, *t*Bu (**4c**−**f**). This helimerization process is fundamental to an understanding of the stereoselectivity of the hydride addition, which depends on the relative rates of *re* versus *si* attack on both diastereoisomers, as well as the rate of their interconversion. An important clue to the solution structures of the thionolactone complexes comes from the observation of two fairly different ^3J(P,C) couplings of the C=S group for each of the diastereoisomers of **4b**−**f**. This indicates that the two dihedral angles C−S−Ru−P also remain unequal in solution. Furthermore, the (*S*,*S*,*M*) diastereoisomer must have a similar structure with a near coplanar arrangement of C(71), S(1), Ru(1), and P(1). This can be deduced unequivocally from the fact that, in the room temperature NMR spectra of **4a** and **4b**, the ^{13}C signal of the thionolactone group still appears as a doublet of doublets with two unequal couplings. If the inversion of the biaryl axis were accompanied by a rotation of the Ru−S bond such as to expose the *si* side for nucleophilic attack, the couplings ^3J(P,C) of the two diastereoisomers should average out and make the signal at δ = 200 appear as a triplet. The conclusion, therefore, is that for both diastereoisomers of the thionolactone complexes **4a**−**f**, *re* addition is strongly favoured over *si* addition (Equation 3). Molecular models, however, seem to indicate that the (*S*,*S*,*M*) diastereoisomers are, for steric reasons, less accessible and therefore less prone to react with any nucleophiles.

The structure determination of **5a** shows that, as expected, the (*S*,*S*,*S*) diastereoisomer is the major product. From an inspection of Figure 2 we can also see that a *P* configuration of the biaryl axis necessarily implies an axial positioning of the S−Ru unit and an equatorial one of the H substituent at the six-membered thiolactolate ring. It is unlikely that a minor change of the remote substituents R would invert the direction of the hydride addition (see above). Thus it is safe to assume that the major diastereoisomer of **5b** has the (*S*,*S*,*S*) configuration as well. For this compound the helimerization can be slowed down sufficiently to observe separate NMR signals for the (*S*,*S*,*S*,*P*) and (*S*,*S*,*S*,*M*) helimers, which at 253 K are present in a 60: 40 ratio (both helimers of the (*S*,*S*,*R*) diastereoisomer were present in too low a concentration to be assigned with certainty). The *M* helimer has the hydrogen atom in an axial position, which leads to a characteristic[24] high-field shift to δ = 3.72. These results then help to assign the relative (and absolute) configurations of the two major isomers of **5c**−**f** unambiguously. In all cases these are characterized by a large shift difference of the S(O)CH hydrogen atom, which means that the most abundant isomer has this hydrogen atom in an equatorial and the second isomer in an axial position. This implies that the two major isomers must have opposite configurations at the biaryl axis and identical configurations at the tetrahedral carbon atom. Further support for this interpretation is supplied by the stereochemical outcome of the protonation − ring opening reaction (Equation 4). The observed low diastereoselectivity clearly reflects the ratios of the two major isomers of the starting complexes **5a**−**f**. This facile ring opening is driven by the steric strain caused by the *ortho* substituent R, and produces a highly reactive thioaldehyde function which readily takes up a second hydride.[15] On the other hand, by its reversibility under basic conditions (Equation 5), the facile formation of a thioaldehyde intermediate is a serious obstacle in the attempted atropo-enantioselective ring opening reaction since it provides a "stereochemical leakage" (Scheme 4).



Scheme 4. Stereochemical leakage in the hydride addition-ring-opening sequence

As already explained for the oxo analogs[2,5,24,25] the thioaldehyde complexes *P*-**6** can cyclize back to the thiolactolate complexes *S*,*P*-**5**, equilibrate to *S*,*M*-**5**, and then burst open out of both helimeric forms of **5** to eventually give *P*- and *M*-**6**. In favourable cases, this leakage may be overcome as shown by the rapid reaction of **4c** with $LiAlH_4$, which produces **9c** with 74% *de* (Equation 7). A variation of the hydride reagent or a masking of the phenolic oxygen by addition of a strong Lewis acid (Equation 8) does indeed change the stereochemical outcome of the reduction. However, this did as yet not lead to a significant improvement, since the two configurations of the biaryl axis are already present in roughly equal amounts in the intermediates **5a**−**f**.

Conclusions

The work presented here demonstrates that transition metal complexes can be used successfully as chiral auxiliaries in the atropo-diastereoselective ring opening of configurationally unstable biaryllactones. A distinct advantage of the use of stable complexes is the possibility to isolate and structurally characterize important intermediates and thus gain detailed information on their stereochemical properties. The stereochemical leakage, however, provided by the facile helimerization and ring-opening of the thiolactolate intermediates, is still a major obstacle. Nevertheless, a further development of this strategy should be possible by combining the hydride reagent with a bulky, less reactive Lewis acid capable of discriminating between the (*S*,*S*,*S*,*P*) and (*S*,*S*,*S*,*M*) diastereoisomers of the thiolactolate intermediates **5**.

Experimental Section

All experiments were carried out in Schlenk tubes under an atmosphere of nitrogen in suitably purified solvents. Water was distilled under nitrogen immediately before use. − IR: Perkin−Elmer 283, Bruker IFS 25. − ^{1}H NMR: Bruker AMX 400, δ values relative to TMS. − ^{13}C NMR: Bruker AMX 400, δ values relative to TMS. Assignments were routinely checked by DEPT. In some cases the signals in the ^{13}C-NMR spectra for quaternary carbon atoms were too weak to be detected. − ^{31}P NMR: Bruker AMX 400, δ values relative to 85% H_3PO_4. The signals in the ^{1}H- and ^{13}C-NMR spectra of the (*S*,*S*)-CHIRAPHOS ligand are very similar for all compounds and have therefore been omitted from the lists of spectral data. − Elemental analyses: Analytical Laboratory of the Institut für Anorganische Chemie. The following starting materials were obtained as described in the literature: [CpRu{(*S*,*S*)-CHIRAPHOS}Cl] (**1**),[26] thionolactones **3a**−**f**,[9][17] $[ZrCl_4(THF)_2]$.[27] All other reagents were used as purchased.

[CpRu{(*S*,*S*)-CHIRAPHOS}(SC_4H_4)]BF_4 (2): To a solution of **1** (0.40 g, 0.64 mmol) and thiophene (0.50 g, 5.95 mmol) in dichloromethane (50 mL) was added $AgBF_4$ (0.125 g, 0.64 mmol) 0°C and the resulting mixture stirred vigorously for 30 min. The solution was then filtered over Celite, the filtrate evaporated to 2 mL, and the product precipitated by adding diethyl ether. The product thus obtained may still contain traces of silver salts but is usually pure enough for further reactions. An analytical sample was obtained by recrystallization from dichloromethane/ether. Yield 0.29 g (95%), yellow crystalline powder, m.p. 60°C (dec). − ^{1}H NMR (400 MHz, CD_2Cl_2, 20°C): δ = 4.24 (s, 5 H, C_5H_5), 5.81, 6.83 (AA′XX′-system, N = 6.1 Hz, 4 H, SC_4H_4). − ^{31}P NMR (162 MHz, CD_2Cl_2, 20°C): δ = 69.8 [d, ^2J(P,P) = 41 Hz], 81.3 [d, ^2J(P,P) = 41 Hz]. − $C_{37}H_{37}BF_4P_2RuS$ (763.6) calcd C 58.20, H 4.88; found C 57.99, H 5.16.

Synthesis of the Thionolactone Complexes 4a−f: To a solution of **2** (0.15 g, 0.20 mmol) in dichloromethane (8 mL) was added the appropriate thionolactone (0.20 mmol). The color immediately changed to deep purple. The mixture was stirred for 12 h, then evaporated to 2 mL and the product precipitated by adding diethyl ether and pentane. Further purification by chromatography over a short (10 cm) silica column with dichloromethane as an eluent, followed by crystallization from dichloromethane/pentane gave deep purple crystalline powders.

4a: Yield 179 mg (95%), m.p. 176°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 4.73 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 84.0 (s, C_5H_5), 199.4 [dd, ^3J(P,C) = 8 Hz, ^3J(P,C) = 5 Hz, C=S] − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 69.7 [d, ^2J(P,P) = 38 Hz], 84.1 [d, ^2J(P,P) = 38 Hz]. − $C_{50}H_{43}BF_4OP_2RuS$ (941.8) calcd. C 63.77, H 4.60; found C 62.93, H 5.02.

4b: Yield 188 mg (94%), m.p. 189°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 3.77 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 4.70 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 55.5 (s, OCH_3), 56.4 (s, OCH_3), 84.1 (s, C_5H_5), 199.2 [dd, ^3J(P,C) = 8 Hz, ^3J(P,C) = 5 Hz, C=S]. − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C): δ = 69.6 [d, ^2J(P,P) = 37 Hz], 84.2 [d, ^2J(P,P) = 37 Hz]. − ^{31}P NMR (162 MHz, $CDCl_3$, −60°C): δ = 65.5 [d, ^2J(P,P) = 37 Hz], 69.1 [d, ^2J(P,P) = 37 Hz], 83.9 [d, ^2J(P,P) = 37 Hz], 84.2 [d, ^2J(P,P) = 37 Hz]. − $C_{52}H_{47}BF_4O_3P_2RuS$ (1001.8) calcd. C 62.34, H 4.73; found C 62.29, H 4.63.

4c: Yield 186 mg (96%), m.p. 186°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) (both diastereoisomers): δ = 2.08 (s, 6 H, CH_3), 2.43 (s, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 4.72 (s, 5 H, C_5H_5), 4.73 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) (both diastereoisomers): δ = 21.3 (s, CH_3), 21.4 (s, CH_3), 23.4 (s, CH_3), 23.5 (s, CH_3), 84.0 [t, ^2J(P,C) = 2 Hz, C_5H_5], 198.3 [dd, ^3J(P,C) = 8 Hz, ^3J(P,C) = 5 Hz, C=S], 199.5 [dd, ^3J(P,C) = 9 Hz, ^3J(P,C) = 5 Hz, C=S]. − ^{31}P NMR (162 MHz, $CDCl_3$, 20°C) (both diastereoisomers): δ = 69.6 [d, ^2J(P,P) = 37 Hz], 71.5 [d, ^2J(P,P) = 38 Hz], 83.9 [d, ^2J(P,P) = 38 Hz], 84.0 [d, ^2J(P,P) = 37 Hz]. − $C_{52}H_{47}BF_4OP_2RuS$ (1001.8) calcd. C 64.40, H 4.88; found C 64.17, H 5.02.

4d: Yield 184 mg (92%), m.p. 141°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) (both diastereoisomers): δ = 1.36 [t, ^3J(H,H) = 7.6 Hz, 2 × 3 H, CH_3], 1.37 [t, ^3J(H,H) = 7.6 Hz, 2 × 3 H, CH_3], 2.53 −2.37 (m, 4 H, CH_2), 2.79 [q, ^3J(H,H) = 7.5 Hz, 2 H, CH_2], 2.83 [q, ^3J(H,H) = 7.7 Hz, 2 H, CH_2], 4.75 (s, 5 H, C_5H_5), 4.77 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C (both diastereoisomers): δ = 14.9 (s, CH_3), 15.0 (s, CH_3), 28.60 (s, CH_2), 28.66 (s, CH_2), 28.70 (s, CH_2), 28.73 (s, CH_2), 84.0 (s, C_5H_5), 84.1 (s, C_5H_5), 198.4 (br, C=S), 199.5 [dd, ^3J(P,C) = 9 Hz, ^3J(P,C) = 5 Hz, C=S]. − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C (both diastereoisomers): δ = 69.4 [d, ^3J(P,P) = 37 Hz]. 71.7 [d, ^3J(P,P) = 38 Hz], 83.8 [d, ^3J(P,P) = 38 Hz], 84.2 [d, ^3J(P,P) = 38 Hz]. − $C_{54}H_{51}BF_4OP_2RuS$ (997.9) calcd. C 64.92, H 5.15, S 3.20; found C 64.06, H 5.17, S 3.34.

4e: Yield 187 mg (91%), m.p. 163°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) (both diastereoisomers): δ = 0.60 [d, ^3J(H,H) = 6.7 Hz, 2 × 3 H, CH_3], 0.84 [d, ^3J(H,H) = 6.7 Hz, 2 × 3 H, CH_3], 1.37 [d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3], 1.39 [d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3], 1.50 [d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3], 1.51 [d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3], 3.03 [sep, ^3J(H,H) = 6.7 Hz, 2 H, CH], 3.11 [sep, ^3J(H,H) = 6.7 Hz, 2 H, CH], 4.72 (s, 5 H, C_5H_5), 4.76 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) (both diastereoisomers): δ = 20.6 (s, CH_3), 23.4 (s, CH_2), 23.7 (s, CH_2), 23.7 (s, CH_2), 23.8 (s, CH_2), 27.7 (s, CH_3), 27.7 (s, CH_3), 84.1 (s, C_5H_5), 84.2 (s, C_5H_5), 198.3 [dd, ^3J(P,C) = 8 Hz, ^3J(P,C) = 5 Hz, C=S], 199.4 [dd, ^3J(P,C) = 9 Hz, ^3J(P,C) = 5 Hz, C=S]. − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C) (both diastereoisomers): δ = 69.1 [d, ^3J(P,P) = 38 Hz], 71.7 [d, ^3J(P,P) = 38 Hz], 83.8 [d, ^3J(P,P) = 38 Hz], 84.2 [d, ^3J(P,P) = 37 Hz]. − $C_{56}H_{55}BF_4OP_2RuS$ (1025.9) calcd. C 65.48, H 5.14, S 3.12; found C 64.39, H 5.23, S 2.99.

4f: Yield 203 mg (96%), m.p. 90°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) (both diastereoisomers): δ = 0.96 (s, 9 H, CH_3), 0.97 (s, 9 H, CH_3), 1.44 (s, 9 H, CH_3), 1.46 (s, 9 H, CH_3), 4.68 (s, 5 H, C_5H_5), 4.74 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 31.1 (s, CH_3), 31.2 (s, CH_3), 32.78 (s, CH_3), 32.81 (s, CH_3), 35.0 [s, C(*t*Bu)], 35.1 [s, C(*t*Bu)], 39.56 [s, C(*t*Bu)], 39.6 [s, C(*t*Bu)], 84.1 (s, C_5H_5), 84.3 (s, C_5H_5), 198.5 [dd, ^3J(P,C) = 8 Hz, ^3J(P,C) = 5 Hz, C=S], 199.5 [dd, ^3J(P,C) = 9 Hz, ^3J(P,C) = 4 Hz, C=S]. − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C): δ = 69.1 [d, ^3J(P,P) = 38 Hz], 71.3 [d, ^3J(P,P) = 38 Hz], 83.8 [d, ^3J(P,P) = 38 Hz], 84.2 [d, ^3J(P,P) = 38 Hz]. − $C_{58}H_{59}BF_4OP_2RuS$ (1054.0) calcd. C 66.02, H 5.64, S 3.03; found C 65.03, H 5.63, S 3.36.

Synthesis of the Thiolactolate Complexes 5a−f: A solution of the lactone complex (0.10 mmol) in THF (10 mL) was treated at −70°C with 0.11 mL of a 1 M solution of $LiBEt_3H$ in the same solvent. Within a few minutes the color of the solution changed from deep purple to brownish-yellow. After allowing the mixture to warm to 20°C the solvent was removed under vacuum and the residue extracted with benzene (8 mL). After filtration over Celite the mixture was evaporated to 2 mL, frozen, and the remaining benzene sublimed off under vacuum. The products were isolated as yellow crystalline powders. Compounds **5d−f** were invariably obtained contaminated with a trace of the corresponding thioaldehyde complex **6d−f**.

5a: Yield 75 mg (88%), m.p. 74°C (dec). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), major diastereoisomer: δ = 4.86 (s, 5 H, C_5H_5), 5.31 [d, 1 H, ^4J(P,H) = 0.8 Hz, S(O)CH]; minor diastereoisomer: δ = 4.71 (s, 5 H, C_5H_5), 6.10 [br, 1 H, S(O)CH]. − ^{13}C NMR (100 MHz, C_6D_6, 20°C), major diastereoisomer: δ = 82.6 (s, C_5H_5), 90.7 [d, ^3J(P,C) = 7 Hz, S(O)CH]; minor diastereoisomer: δ = 83.6 (s, C_5H_5), 92.9 [br, S(O)CH]. − ^{31}P NMR (161 MHz, C_6D_6, 20°C), major diastereoisomer: δ = 77.1 [d, ^3J(P,P) = 32 Hz], 87.7 [d, ^3J(P,P) = 32 Hz]; minor diastereoisomer: δ = 74.8 [d, ^3J(P,P) = 42 Hz], 87.1 [d, ^3J(P,P) = 42 Hz]. − $C_{50}H_{44}OP_2RuS$ (856.0) calcd. C 70.01, H 5.18, S 3.75; found C 69.01, H 5.14, S 3.48.

5b: Yield 79 mg (86%), m.p. 136°C (dec). − ^{1}H NMR (400 MHz, [D_8]toluene, −20°C), major diastereoisomer, both helimers: δ = 3.41 (s, 3 H, OCH_3), 3.28 (s, 3 H, OCH_3), 3.32 (s, 3 H, OCH_3), 3.48 (s, 3 H, OCH_3), 3.72 [s, 1 H, S(O)CH], 4.74 (s, 2 × 5 H, C_5H_5), 5.31 [s, 1 H, S(O)CH]; minor diastereoisomer: δ = 4.62 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, C_6D_6, 20°C), both diastereoisomers: δ = 55.0 (s, OCH_3), 55.3 (s, br, OCH_3), 82.9 (s, br, C_5H_5), 91.3 [s, S(O)CH]. − ^{31}P NMR (162 MHz, [D_8]toluene, −20°C), major diastereoisomer: δ = 72.7 [d, ^3J(P,P) = 34 Hz], 75.5 [d, ^3J(P,P) = 34 Hz], 87.0 [d, ^3J(P,P) = 34 Hz], 87.2 [d, ^3J(P,P) = 34 Hz]. − $C_{52}H_{48}O_3P_2RuS$ (916.0) calcd. C 68.18, H 5.28, S 3.50; gef. C 67.88, H 5.43, S 3.44.

5c: Yield 76 mg (86%), m.p. 68°C (dec). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), major helimer: δ = 2.19 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 4.84 (s, 5 H, C_5H_5), 5.45 [d, 1 H, ^4J(P,H) = 1.2 Hz, S(O)CH]; minor helimer: δ = 2.17 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 3.87 [s, 1 H, S(O)CH], 4.80 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, C_6D_6, 20°C), major helimer: δ = 21.6 (s, CH_3), 23.0 (s, CH_3), 82.4 (s, C_5H_5), 90.6 [d, ^3J(P,C) = 5 Hz, S(O)CH]; minor helimer: δ = 21.5 (s, CH_3), 22.6 (s, CH_3), 83.7 (s, C_5H_5), 94.5 [d, ^3J(P,C) = 6.2 Hz, S(O)CH]. − ^{31}P NMR (162 MHz, C_6D_6, 20°C), major helimer: δ = 75.8 [d, ^3J(P,P) = 34 Hz], 87.5 [d, ^3J(P,P) = 34 Hz]; minor helimer: 74.1 [d, ^3J(P,P) = 37 Hz], 87.2 [d, ^3J(P,P) = 37 Hz]. − $C_{52}H_{48}OP_2RuS$ (884.0) calcd. C 70.65, H 5.47; found C 70.74, H 5.32.

5d: Yield 71 mg (78%), m.p. 91°C (dec). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), both helimers: δ = 1.07 [t, ^3J(H,H) = 7.5 Hz, 2 × 3 H, CH_3], 1.15 [t, ^3J(H,H) = 7.6 Hz, 2 × 3 H, CH_3], 1.32 [t, ^3J(H,H) = 7.6 Hz, 2 × 3 H, CH_3], 2.51 [q, ^3J(H,H) = 7.7 Hz, 4 × 2 H, CH_2], 3.99 [s, 1 H, S(O)CH], 4.82 (s, 5 H, C_5H_5). 4.86 (s, 5 H, C_5H_5), 5.41 [d, ^4J(P,H) = 1.2 Hz, 1 H, S(O)CH]. − ^{13}C NMR (100 MHz, C_6D_6, 20°C), both helimers: δ = 14.3 (s, CH_3), 15.7 (s, CH_3), 15.8 (s, CH_3), 17.1 (s, CH_3), 28.6 (s, CH_2), 29.4 (s, CH_2), 29.4 (s, CH_2), 29.6 (s, CH_2), 82.5 (s, C_5H_5), 83.6 (s, C_5H_5), 94.2 [s, S(O)CH], 94.3 [s, S(O)CH]. − ^{31}P NMR (162 MHz, C_6D_6, 20°C), major helimer: δ = 78.0 [d, ^3J(P,P) = 31 Hz], 87.8 [d, ^3J(P,P) = 32 Hz]; minor helimer: 74.2 [d, ^3J(P,P) = 37 Hz], 86.7 [d, ^3J(P,P) = 37 Hz]. − $C_{54}H_{52}OP_2RuS$ (912.1)calcd. C 71.11, H 5.75, S 3.52; found C 68.91, H 6.42, S 3.42.

5e: Yield 70 mg (74%), m.p. 75°C (dec). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), both helimers: δ = 1.20 [d, ^3J(H,H) = 6.9 Hz, 3 H, CH_3], 1.22 [d, ^3J(H,H) = 7.0 Hz, 3 H, CH_3], 1.30 [d, ^3J(H,H) = 6.9 Hz, 3 H, CH_3], 1.34 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 1.37 [d, ^3J(H,H) = 6.9 Hz, 3 H, CH_3], 1.44 [d, ^3J(H,H) = 6.9 Hz, 3 H, CH_3], 1.54 [d, ^3J(H,H) = 6.7 Hz, 3 H, CH_3], 1.58 [d, ^3J(H,H) = 6.6 Hz, 3 H, CH_3], 2.79 [q, ^3J(H,H) = 6.8 Hz, 1 H, CH], 3.22 [q, ^3J(H,H) = 6.8 Hz, 1 H, CH], 3.38 [q, ^3J(H,H) = 6.8 Hz, 1 H, CH], 3.58 [q, ^3J(H,H) = 6.8 Hz, 1 H, CH], 4.13 [s, 1 H, S(O)CH], 4.85

(s, 5 H, C_5H_5), 4.88 (s, 5 H, C_5H_5), 5.36 [d, ^4J(P,H) = 1.1 Hz, 1 H, S(O)CH]. − ^{13}C NMR (100 MHz, C_6D_6, 20°C), both helimers: δ = 20.4 (s, CH_3), 24.1 (s, CH_3), 24.3 (s, CH_3), 24.5 (s, CH_3), 31.1 (s, CH), 32.4 (s, CH), 34.6 (s, CH), 34.8 (s, CH), 82.5 (s, C_5H_5), 83.4 (s, C_5H_5). − ^{31}P NMR (162 MHz, C_6D_6, 20°C), major helimer: δ = 79.4 [d, ^3J(P,P) = 31 Hz], 87.9 [d, ^3J(P,P) = 31 Hz]; minor helimer: 73.9 [d, ^3J(P,P) = 38 Hz], 86.3 [d, ^3J(P,P) = 38 Hz]. − $C_{56}H_{56}OP_2RuS$ (940.15) calcd. C 71.54, H 6.00, S 3.41; found C 70.14, H 6.16, S 3.32.

5f: Yield 72 mg (74%), m.p. 110°C (dec). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), both helimers: δ = 1.29 (s, 9 H, CH_3), 1.31 (s, 9 H, CH_3), 1.39 (s, 9 H, CH_3), 1.46 (s, 9 H, CH_3), 4.04 [s, 1 H, S(O)CH], 4.78 (s, 5 H, C_5H_5), 4.80 (s, 5 H, C_5H_5), 5.19 [s, 1 H, S(O)CH]. − ^{13}C NMR (100 MHz, C_6D_6, 20°C): δ = 31.5 (s, CH_3), 31.5 (s, CH_3), 33.1 (s, CH_3), 33.2 (s, CH_3), 34.8 [s, C(*t*Bu)], 38.7 [s, C(*t*Bu)], 39.1 [s, C(*t*Bu)], 82.8 (s, C_5H_5), 83.4 (s, C_5H_5). − ^{31}P NMR (162 MHz, C_6D_6, 20°C): δ = 74.1 [d, ^3J(P,P) = 37 Hz], 78.6 [d, ^3J(P,P) = 32 Hz], 86.2 [d, ^3J(P,P) = 37 Hz], 87.8 [d, ^3J(P,P) = 32 Hz]. − $C_{58}H_{60}OP_2RuS$ (968.20) calcd. C 71.95, H 6.25, S 3.31; found C 69.94, H 6.55, S 3.31.

Synthesis of the Thioaldehyde Complexes 6a−f: To a solution of the lactolate complex (0.10 mmol) in acetone (15 mL) was added an excess of NH_4BF_4, which caused an immediate color change to deep purple. After 1 h the product and the excess of NH_4BF_4 were precipitated by adding pentane. Compounds **6b−f** were purified by chromatography over silica gel with dichloromethane/acetone 10:1 as eluent. Compound **6a** reverted back to **5a** upon chromatography and could be separated only incompletely from the excess ammonium salt. After crystallization from dichloromethane/pentane the products were obtained as deep purple crystalline powders.

6a: Yield 100 mg (ca. 95%), contaminated with NH_4BF_4. − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C), both helimers: δ = 4.48 (s, 5 H, C_5H_5), 4.58 (s, 5 H, C_5H_5), 6.92 (br, 1 H, OH), 9.77 [d, ^4J(P,H) = 1.6 Hz, 1 H, HC=S], 9.96 (br, 1 H, HC=S). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C), both helimers: δ = 85.7 (s, C_5H_5), 86.0 (s, C_5H_5), 213.3 (br, HC=S), 216.5 [t, ^3J(P,C) = 7 Hz, HC=S]. − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C), both helimers: δ = 76.0 [d, ^3J(P,P) = 38 Hz], 76.2 [d, ^3J(P,P) = 37 Hz], 83.9 [d, ^3J(P,P) = 37 Hz], 84.1 [d, ^3J(P,P) = 38 Hz].

6b: Yield 75 mg (75%). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C), both helimers: δ = 2.85 (s, 3 H, OCH_3), 3.13 (s, 3 H, OCH_3), 3.25 (s, 3 H, OCH_3), 3.57 (s, 3 H, OCH_3), 4.27 (s, 5 H, C_5H_5), 4.31 (s, 5 H, C_5H_5), 6.50 (br, 1 H, OH), 9.75 (br, 1 H, HC=S), 9.79 (br, 1 H, HC=S). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C), both helimers: δ = 55.5 (s, OCH_3), 55.7 (s, OCH_3), 55.8 (s, OCH_3), 85.7 (s, C_5H_5), 215.6 (m, br, HC=S). − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C), major helimer: δ = 75.3 [d, ^3J(P,P) = 38 Hz], 83.9 [d, ^3J(P,P) = 38 Hz]; minor helimer: δ = 76.6 [d, ^3J(P,P) = 37 Hz], 83.9 [d, ^3J(P,P) = 37 Hz]. − $C_{52}H_{49}BF_4O_3P_2RuS$ (1003.85) calcd. C 62.22, H 4.92, S 3.19; found C 61.95, H 5.09, S 3.00.

6c: Yield 70 mg (72%), m.p. 147°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C), major helimer: δ = 1.41 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 4.54 (s, 5 H, C_5H_5), 6.24 (s, 1 H, OH), 9.81 [d, ^4J(P,H) = 1.6 Hz, 1 H, HC=S]; minor helimer: δ = 1.34 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 4.32 (s, 5 H, C_5H_5), 6.19 (s, 1 H, OH), 10.04 [d, ^4J(P,H) = 1.6 Hz, 1 H, HC=S]. − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C), both helimers: δ = 19.8 (s, CH_3), 20.2 (s, CH_3), 21.3 (s, CH_3), 21.4 (s, CH_3), 86.1 (s, C_5H_5), 86.4 (s, C_5H_5), 210.7 (br, HC=S), 214.8 [t, ^3J(P,C) = 5.6 Hz, HC=S]. − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C), major helimer: δ = 75.7 [d, ^3J(P,P) = 38 Hz], 88.7 [d, ^3J(P,P) = 38 Hz]; minor helimer: δ = 77.8 [d, ^3J(P,P) = 36 Hz], 82.9 [d, ^3J(P,P) = 36 Hz]. − $C_{52}H_{49}BF_4OP_2RuS$ (971.85) calcd. C 64.27, H 5.08, S 3.30; found C 63.52, H 5.69, S 3.27.

6d: Yield 70 mg (70%), m.p. 106°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C), major helimer: δ = 0.57 [t, ^3J(H,H) = 7.6 Hz, 3 H, CH_3], 1.20 [t, ^3J(H,H) = 7.6 Hz, 3 H, CH_3], 1.62−1.78 (m, 2 H, CH_2), 2.60 [q, ^3J(H,H) = 7.6 Hz, 2 H, CH_2], 4.35 (s, 5 H, C_5H_5), 6.24 (s, 1 H, OH), 10.06 (s, 1 H, HC=S); minor helimer: δ = 0.68 [t, ^3J(H,H) = 7.6 Hz, 3 H, CH_3], 1.17 [t, ^3J(H,H) = 7.6 Hz, 3 H, CH_3], 1.62−1.78 (m, 2 H, CH_2), 2.55 [q, ^3J(H,H) = 7.6 Hz, 2 H, CH_2], 4.48 (s, 5 H, C_5H_5), 5.93 (s, 1 H, OH), 9.93 (s, 1 H, HC=S). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C), both helimers: δ = 14.6 (s, CH_3), 14.7 (s, CH_3), 15.5 (s, CH_3), 15.7 (s, CH_3), 26.2 (s, CH_2), 26.7 (s, CH_2), 28.8 (s, CH_2), 28.9 (s, CH_2), 86.2 (s, C_5H_5), 86.4 (s, C_5H_5), 211.0 [t, ^3J(P,C) = 6.0 Hz, HC=S], 213.8 [t, ^3J(P,C) = 6.0 Hz, HC=S]. − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C), major helimer: δ = 75.4 [d, ^3J(P,P) = 38 Hz], 83.5 [d, ^3J(P,P) = 38 Hz]; minor helimer: δ = 77.5 [d, ^3J(P,P) = 37 Hz], 82.9 [d, ^3J(P,P) = 37 Hz]. − $C_{54}H_{53}BF_4OP_2RuS$ (999.90) calcd. C 64.87, H 5.34, S 3.21; found C 63.88, H 5.14, S 2.82.

6e: Yield 74 mg (72%), m.p. 120°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C), major helimer: δ = 0.55 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 0.88 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 2.03 [sept, ^3J(H,H) = 6.8 Hz, 1 H, CH], 2.88 [sept, ^3J(H,H) = 6.8 Hz, 1 H, CH], 4.37 (s, 5 H, C_5H_5), 6.00 (s, 1 H, OH), 10.28 (s, 1 H, HC=S); minor helimer: δ = 0.74 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 0.90 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 2.88 [sept, ^3J(H,H) = 6.8 Hz, 1 H, CH], 2.91 [sept, ^3J(H,H) = 6.8 Hz, 1 H, CH], 4.43 (s, 5 H, C_5H_5), 5.70 (s, 1 H, OH), 10.24 (s, 1 H, HC=S). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C): δ = 23.4 (s, CH_3), 23.5 (s, CH_3), 24.0 (s, CH_3), 24.1 (s, CH_3), 24.1 (s, CH_3), 24.2 (s, CH_3), 24.6 (s, CH_3),29.7 (s, CH_3), 30.5 (s, CH), 30.5 (s, CH), 34.3 (s, CH), 34.4 (s, CH), 86.5 (s, C_5H_5), 86.6 (s, C_5H_5), 211.9 [t, ^3J(P,C) = 6.3 Hz, HC=S], 212.7 [t, ^3J(P,C) = 6.1 Hz, HC=S]. − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C), major helimer: δ = 75.7 [d, ^3J(P,P) = 39 Hz], 83.3 [d, ^3J(P,P) = 39 Hz], minor helimer: δ = 76.0 [d, ^3J(P,P) = 39 Hz], 83.1 [d, ^3J(P,P) = 39 Hz]. − $C_{56}H_{57}BF_4OP_2RuS$ (1027.96) calcd. C 65.43, H 5.59, S 3.12; found C 64.78, H 5.68, S 3.10.

6f: Yield 65 mg (62%). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C), both helimers: δ = 0.69 (s, 9 H, CH_3), 0.79 (s, 9 H, CH_3), 1.30 (s, 9 H, CH_3), 1.33 (s, 9 H, CH_3), 4.34 (s, 5 H, C_5H_5), 4.44 (s, 5 H, C_5H_5), 5.22 (s, br, 1 H, OH), 5.43 (s, br, 1 H, OH), 10.22 (s, 1 H, HC=S), 10.28 (s, 1 H, HC=S). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C), both helimers: δ = 31.4 (s, CH_3), 31.4 (s, CH_3), 32.5 (s, CH_3), 32.7 (s, CH_3), 35.0 [s, C(*t*Bu)], 35.0 [s, C(*t*Bu)], 37.1 [s, C(*t*Bu)], 37.2 [s, C(*t*Bu)], 86.6(s, C_5H_5), 86.8 (s, C_5H_5), 210.3 [t, HC=S, ^3J(P,C) = 7 Hz], 212.2 (br, HC=S). − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C): δ = 75.6 [d, ^3J(P,P) = 48 Hz], 75.9 [d, ^3J(P,P) = 48 Hz], 82.7 [d, ^3J(P,P) = 39 Hz], 82.7 [d, ^3J(P,P) = 39 Hz]. − $C_{58}H_{61}BF_4OP_2RuS$ (1056.01) calcd. C 65.97, H 5.82, S 3.04; found C 64.78, H 5.68, S 3.10.

2-(Methylthio)benzonaphthopyran 7a: A solution of **5a** (50 mg, 0.06 mmol) and methyl iodide (0.5 mL, 8.03 mmol) in toluene was stored for 7 d at − 6°C. The mixture was then evaporated to dryness and the residue chromatographed over silica gel with toluene/acetone 10:1 as an eluent. The first yellow fraction contained the iodo complex **8**.[12] Compound **7a** was isolated from the second yellow band as a pale yellow oil, which was characterized spectroscopically. Yield 7 mg (45%). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ = 2.21 (s, 3 H, SCH_3), 6.56 [s, 1 H, S(O)CH], 7.18 [d, ^3J(H,H) = 8.0 Hz, 1 H, aryl], 7.25 [d, ^3J(H,H) = 7.6 Hz, 1 H, aryl], 7.36 [d, ^3J(H,H) = 7.9 Hz, 1 H, aryl], 7.38 [d, ^3J(H,H) = 8.4 Hz, 1 H, aryl], 7.54 [d, ^3J(H,H) = 8.2 Hz, 1 H, aryl], 7.57 [d, ^3J(H,H) =

8.0 Hz, 1 H, aryl], 7.81 [d, ^3J(H,H) = 8.2 Hz, 1 H, aryl], 7.90 [d, ^3J(H,H) = 7.8 Hz, 1 H, aryl], 8.10 [d, ^3J(H,H) = 7.7 Hz, 1 H, aryl], 8.61 [d, ^3J(H,H) = 7.9 Hz, 1 H, aryl].

Synthesis of the Thiolate Complexes 9a−f: To a solution of the thiolactone complex (0.20 mmol) in THF (10 mL) was added $LiAlH_4$ (20 mg, 0.50 mmol) at −70°C. Within a few minutes the color of the solution changed from deep purple to yellow. After allowing the mixture to warm to 20°C the solvent was removed under vacuum and the residue extracted with benzene (8 mL). After filtration over Celite the mixture was evaporated to dryness, the residue dissolved in dichloromethane and chromatographed over silica gel. The fraction containing the yellow band was evaporated to dryness and the product crystallized from benzene/pentane and was isolated as a yellow crystalline powder.

9a: Yield 117 mg (68%), m.p. 121°C (dec). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), major helimer: δ = 2.85 [d, ^2J(H,H) = 9.8 Hz, 1 H, SCH_2], 3.22 [d, ^2J(H,H) = 9.8 Hz, 1 H, SCH_2], 4.22 (s, 5 H, C_5H_5), 8.88 (s, 1 H, OH); minor helimer: δ = 1.78 [d, ^2J(H,H) = 9.9 Hz, 1 H, SCH_2], 3.01 [d, ^2J(H,H) = 9.9 Hz, 1 H, SCH_2], 4.30 (s, 5 H, C_5H_5), 9.19 (s, 1 H, OH). − ^{13}C NMR (100 MHz, C_6D_6, 20°C), major helimer: δ = 40.5 [dd, ^3J(P,C) = 6 Hz, ^3J(P,C) = 2 Hz, SCH_2], 84.6 (s, C_5H_5); minor helimer: δ = 36.8 [d, ^3J(P,C) = 5 Hz, SCH_2], 82.1 (s, C_5H_5). − ^{31}P NMR (161 MHz, C_6D_6, 20°C), major helimer: δ = 67.5 [d, ^3J(P,P) = 42 Hz], 90.5 [d, ^3J(P,P) = 42 Hz]; minor helimer: δ = 75.3 [d, ^3J(P,P) = 36 Hz], 86.1 [d, ^3J(P,P) = 36 Hz]. − $C_{50}H_{46}OP_2RuS$ (858.0) calcd. C 69.99, H 5.40; found C 69.76, H 5.76.

9b: Yield 130 mg (71%), m.p. 120°C (dec). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), major helimer: δ = 2.92 (s, OCH_3), 2.93 [d, ^2J(H,H) = 9.9 Hz, 1 H, SCH_2], 3.41 [d, ^2J(H,H) = 9.9 Hz, 1 H, SCH_2], 3.54 (s, OCH_3), 4.38 (s, 5 H, C_5H_5), 9.33 (s, 1 H, OH); minor helimer: δ = 1.79 [d, ^2J(H,H) = 9.8 Hz, 1 H, SCH_2], 2.98 (s, OCH_3), 3.17 [d, ^2J(H,H) = 9.8 Hz, 1 H, SCH_2], 3.47 (s, OCH_3), 4.32 (s, 5 H, C_5H_5), 9.10 (s, 1 H, OH). − ^{13}C NMR (100 MHz, C_6D_6, 20°C), both helimers: δ = 37.1 [d, ^3J(P,C) = 6 Hz, SCH_2], 41.0 [d, ^3J(P,C) = 6 Hz, SCH_2], 54.9 (s, OCH_3), 55.0 (s, OCH_3), 55.0 (s, OCH_3), 55.1 (s, OCH_3), 83.6 (s, C_5H_5), 84.7 (s, C_5H_5). − ^{31}P NMR (161 MHz, C_6D_6, 20°C), major helimer: δ = 66.5 [d, ^3J(P,P) = 42 Hz], 90.8 [d, ^3J(P,P) = 42 Hz]; minor helimer: δ = 74.8 [d, ^3J(P,P) = 36 Hz], 86.1 [d, ^3J(P,P) = 36 Hz]. − $C_{52}H_{50}O_3P_2RuS$ (918.0) calcd. C 68.03, H 5.49; found C 67.80, H 5.49.

9c: Yield 119 mg (67%), m.p. 124°C (dec). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), major helimer: δ = 1.80 (s, CH_3), 2.27 (s, CH_3), 2.93 [d, ^2J(H,H) = 9.8 Hz, 1 H, SCH_2], 3.13 [d, ^2J(H,H) = 9.8 Hz, 1 H, SCH_2], 4.24 (s, 5 H, C_5H_5), 8.32 (s, 1 H, OH); minor helimer: δ = 1.71 (s, CH_3), 2.02 [d, ^2J(H,H) = 10.0 Hz, 1 H, SCH_2], 2.34 (s, CH_3), 2.95 [d, ^2J(H,H) = 10.0 Hz, 1 H, SCH_2], 4.29 (s, 5 H, C_5H_5), 8.60 (s, 1 H, OH). − ^{13}C NMR (100 MHz, C_6D_6, 20°C), major helimer: δ = 20.3 (s, CH_3), 21.4 (s, CH_3), 40.3 [dd, ^3J(P,C) = 6 Hz, ^3J(P,C) = 2 Hz, SCH_2], 84.7 (s, C_5H_5); minor helimer: δ = 19.8 (s, CH_3), 20.2 (s, CH_3), SCH_2 signal superimposed by major helimer, 83.6 (s, C_5H_5) − ^{31}P NMR (161 MHz, C_6D_6, 20°C), major helimer: δ = 67.0 [d, ^3J(P,P) = 41 Hz], 90.4 [d, ^3J(P,P) = 41 Hz]; minor helimer: δ = 75.5 [d, ^3J(P,P) = 36 Hz], 85.9 [d, ^3J(P,P) = 36 Hz]. − $C_{52}H_{50}OP_2RuS$ (886.0) calcd. C 70.49, H 5.69; found C 70.97, H 5.64.

9d: Yield 124 mg (68%). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), major helimer: δ = 0.86 [t, ^3J(H,H) = 7.6 Hz, 3 H, CH_3], 1.26 [t, ^3J(H,H) = 7.6 Hz, 3 H, CH_3], 2.15 [q, ^3J(H,H) = 7.6 Hz, 1 H, CH_2], 2.17 [q, ^3J(H,H) = 7.6 Hz, 1 H, CH_2], 2.63 [q, ^3J(H,H) = 7.6 Hz, 2 H, CH_2], 2.91 [d, ^2J(H,H) = 10.0 Hz, 1 H, SCH_2], 3.16 [d, ^2J(H,H) = 10.0 Hz, 1 H, SCH_2], 4.22 (s, 5 H, C_5H_5); minor helimer: δ = 0.80 [t, ^3J(H,H) = 7.6 Hz, 3 H, CH_3], 1.31 [t, ^3J(H,H) = 7.6 Hz, 3 H, CH_3], 1.79 [d, ^2J(H,H) = 9.6 Hz, 1 H, SCH_2], 2.09 [q, ^3J(H,H) = 7.6 Hz, 1 H, CH_2], 2.10 [q, ^3J(H,H) = 7.6 Hz, 1 H, CH_2], 2.68 [q, ^3J(H,H) = 7.6 Hz, 2 H, CH_2], 2.96 [d, ^2J(H,H) = 9.6 Hz, 1 H, SCH_2], 4.27 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, C_6D_6, 20°C), major helimer: δ = 15.1 (s, CH_3), 16.3 (s, CH_3), 26.9 (s, CH_2), 29.3 (s, CH_2), 40.3 (br, SCH_2), 84.6 (s, C_5H_5); minor helimer: δ = 15.1 (s, CH_3), 16.4 (s, CH_3), 26.9 (s, CH_2), 29.4 (s, CH_2), 37.2 (br, SCH_2), 83.6 (s, C_5H_5). − ^{31}P NMR (161 MHz, C_6D_6, 20°C), major helimer: δ = 67.0 [d, ^3J(P,P) = 41 Hz]. 90.4 [d, ^3J(P,P) = 41 Hz]; minor helimer: δ = 75.7 [d, ^3J(P,P) = 36 Hz], 85.9 [d, ^3J(P,P) = 36 Hz]. − $C_{54}H_{54}OP_2RuS$ (914.1) calcd. C 70.95, H 5.95, S 3.51; found C 70.61, H 5.82, S 3.21.

9e: Yield 124 mg (66%). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), major helimer: δ = 0.95 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 1.05 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 1.32 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 1.32 [d, ^3J(H,H) = 6.8 Hz, 3 H, CH_3], 2.45 [sept, ^3J(H,H) = 6.8 Hz, 1 H, CH], 2.46 [sept, ^3J(H,H) = 6.8 Hz, 1 H, CH], 2.92 [d, ^2J(H,H) = 10.0 Hz, 1 H, SCH_2], 3.19 [d, ^2J(H,H) = 10.0 Hz, 1 H, SCH_2], 4.17 (s, 5 H, C_5H_5); minor helimer: δ = 0.95 [d, ^3J(H,H) = 6.8 Hz, 6 H, CH_3], 1.79 [d, ^2J(H,H) = 9.6 Hz, 1 H, SCH_2], 2.58−2.72 (m, 2 H, CH), 2.96 [d, ^2J(H,H) = 9.6 Hz, 1 H, SCH_2], 3.36 [d, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 3.38 [d, ^3J(H,H) = 7.2 Hz, 3 H, CH_3], 4.26 (s, 5 H, C_5H_5); − ^{13}C NMR (100 MHz, C_6D_6, 20°C), major helimer: δ = 24.2 (s, CH_3), 24.5 (s, CH_3), 24.7 (s, CH_3), 24.9 (s, CH_3), 30.8 (s, CH), 34.7 (s, CH), 40.7 (br, SCH_2), 84.6 (s, C_5H_5); minor helimer: δ = 24.1 (s, CH_3), 24.5 (s, CH_3), 24.5 (s, CH_3), 24.7 (s, CH_3), 30.8 (s, CH), 34.8 (s, CH), 37.5 [d, ^3J(P,C) = 6 Hz, SCH_2], 83.7 (s, C_5H_5). − ^{31}P NMR (161 MHz, C_6D_6, 20°C), major helimer: δ = 66.9 [d, ^3J(P,P) = 42 Hz], 90.3 [d, ^3J(P,P) = 42 Hz]; minor helimer: δ = 75.8 [d, ^3J(P,P) = 36 Hz], 85.8 [d, ^3J(P,P) = 36 Hz]. − $C_{56}H_{58}OP_2RuS$ (942.2) calcd. C 71.39, H 6.21, S 3.40; found C 71.11, H 6.42, S 3.10.

9f: Yield 167 mg (86%). − ^{1}H NMR (400 MHz, C_6D_6, 20°C), both helimers: δ = 1.06 (s, 9 H, CH_3), 1.07 (s, 9 H, CH_3), 1.40 (s, 9 H, CH_3), 1.45 (s, 9 H, CH_3), 1.77 [d, ^2J(H,H) = 9.9 Hz, 1 H, SCH_2], 2.92 [d, ^2J(H,H) = 9.7 Hz, 1 H, SCH_2], 3.00 [d, ^2J(H,H) = 9.7 Hz, 1 H, SCH_2], 3.23 [d, ^2J(H,H) = 9.9 Hz, 1 H, SCH_2], 4.15 (s, 5 H, C_5H_5),4.24 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, C_6D_6, 20°C), both helimers: δ = 31.8 (s, CH_3), 31.9 (s, CH_3), 32.7 (s, CH_3), 32.9 (s, CH_3), 34.8 [s, C(*t*Bu)], 34.9 [s, C(*t*Bu)], 37.4 [s, C(*t*Bu)], 37.5 [s, C(*t*Bu)], 41.3 [dd, ^3J(P,C) = 7 Hz, ^3J(P,C) = 2 Hz, SCH_2], 83.7 (s, C_5H_5), 84.5 (s, C_5H_5). − ^{31}P NMR (161 MHz, C_6D_6, 20°C), both helimers: δ = 67.2 [d, ^3J(P,P) = 42 Hz], 76.3 [d, ^3J(P,P) = 36 Hz], 85.7 [d, ^3J(P,P) = 36 Hz], 90.0 [d, ^3J(P,P) = 42 Hz]. − $C_{58}H_{62}OP_2RuS$ (970.2) calcd. C 71.80, H 6.44, S 3.30; found C 70.08, H 6.14, S 2.98.

Hydride Reduction of 5c: To a solution of **5c** (80 mg, 0.09 mmol) in THF (5 mL) was added at −70°C an excess (0.25 mmol) of either $LiBEt_3H$ or $LiAlH_4$. After 1 h the mixture was allowed to warm to 20°C. The solvent was then removed under vacuum and the dry residue extracted with benzene. After filtration over Celite and drying under vacuum **9c** was obtained as a yellow powder. Yields and diastereoisomer ratios are given in Equation 7.

Zirconium-assisted Hydride Reduction of 5a: To a solution of **5a** (100 mg, 0.12 mmol) in THF (15 mL) was added $[ZrCl_4(THF)_2]$ (200 mg, 0.53 mmol) at −70°C whereupon the color slowly changed to purple. After 8 h at this temperature the mixture was treated with $LiAlH_4$ (20 mg, 0.50 mmol), which caused an immediate color change to yellow. A few droplets of water were added to quench the excess hydride reagent, and then the mixture was

warmed to 20°C and evaporated under vacuum. The dry residue was extracted with benzene (8 mL), filtered over Celite, and the product isolated by freeze-drying. Yield 67 mg (65%), yellow crystalline powder, identified by ^{1}H and ^{31}P NMR as a mixture of both helimers of **9a** with inverted diastereoisomer ratio.

Alkylation of the Thiolate Complexes 9a−c: To a solution of the thiolate complex (0.10 mmol) in acetone (10 mL) was added methyl iodide (0.05 mL, 0.80 mmol) at 20°C. After 10 min the mixture was evaporated to 1 mL and the product precipitated by adding diethyl ether and pentane. After repeated washings with pentane and drying under vacuum the product was isolated as a pale yellow crystalline powder.

10a: Yield 98 mg (98%), m.p. 87°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C), major helimer: δ = 0.99 (s, 3 H, SCH_3), 4.23 (s, 5 H, C_5H_5), SCH_2 and OH signals obscured by phosphane ligand; minor helimer: δ = 4.19 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C), both helimers: δ = 25.0 (s, SCH_3), 47.2 (m, br, SCH_2), 85.1 (s, C_5H_5), 85.2 (s, C_5H_5). − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C), major helimer: δ = 65.9 [d, ^3J(P,P) = 39 Hz], 82.7 [d, ^3J(P,P) = 39 Hz]; minor helimer: δ = 64.9 [d, br, ^3J(P,P) = 40 Hz], 83.0 [d, ^3J(P,P) = 40 Hz]. − $C_{51}H_{49}IOP_2RuS$ (1000.0) calcd. C 61.26, H 4.94, S 3.21; found C 61.06, H 4.88, S 3.20.

10b: Yield 104 mg (98%), m.p. 91°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C), major helimer: δ = 1.04 (s, 3 H, SCH_3), 3.39 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 4.30 (s, 5 H, C_5H_5), SCH_2 and OH signals obscured by phosphane ligand; minor helimer: δ = 1.04 (s, 3 H, SCH_3), 3.36 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 4.25 (s, 5 H, C_5H_5). − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C), both helimers: δ = 24.3 (s, SCH_3), 25.1 (s, SCH_3), 46.9 (m, br, SCH_2), 47.2 (m, br, SCH_2), 55.3 (s, OCH_3), 55.7 (s, OCH_3), 85.0 (s, C_5H_5). − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C), major helimer: δ = 66.2 [d, ^3J(P,P) = 40 Hz], 83.1 [d, ^3J(P,P) = 40 Hz]; minor helimer: δ = 64.9 [d, br, ^3J(P,P) = 40 Hz], 82.6 [d, ^3J(P,P) = 40 Hz]. − $C_{53}H_{53}IO_3P_2RuS$ (1060.0) calcd. C 60.06, H 5.04, S 3.02; found C 59.69, H 4.94, S 2.96.

10c: Yield 102 mg (99%), m.p. 73°C (dec). − ^{1}H NMR (400 MHz, $CDCl_3$, 20°C), both helimers: δ = 1.03 (s, 3 H, SCH_3), 1.47 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 4.27 (s, 5 H, C_5H_5), 4.30 (s, 5 H, C_5H_5), SCH_2 and OH signals obscured by phosphane ligand. − ^{13}C NMR (100 MHz, $CDCl_3$, 20°C), both helimers: δ = 19.7 (s, CH_3), 21.0 (s, CH_3), 25.0 (s, br, SCH_3), 47.2 (m, br, SCH_2), 84.8 (s, C_5H_5). − ^{31}P NMR (161 MHz, $CDCl_3$, 20°C), major helimer: δ = 67.0 [d, ^3J(P,P) = 40 Hz], 83.1 [d, ^3J(P,P) = 40 Hz]; minor helimer: δ = 65.5 [d, br, ^3J(P,P) = 40 Hz], 83.5 [d, ^3J(P,P) = 40 Hz]. − $C_{53}H_{53}IOP_2RuS$ (1028.0) calcd. C 61.92, H 5.20; found C 61.79, H 5.43.

Detachment of the Methyl Thioethers 11a−c: A suspension of the thioether complex (0.1 mmol) in benzene (2 mL) was heated under reflux for 12 h. The mixture was worked up as described for **7a** leaving **11a−c** as pale yellow oils which were characterized by ^{1}H NMR.

11a: − ^{1}H NMR (400 MHz, C_6D_6, 20°C): δ = 1.60 (s, 3 H, SCH_3), 3.47, 3.48 (AB system, ^2J(H,H) = 15.0 Hz, 2 H, SCH_2), 4.59 (s, 1 H, OH), 6.85−8.30 (m, 10 H, aryl).

11b: − ^{1}H NMR (400 MHz, C_6D_6, 20°C): δ = 1.71 (s, 3 H, SCH_3), 3.00 (s, 3 H, OCH_3), 3.39 (s, 3 H, OCH_3), 3.68 (s, 2 H, SCH_2), 4.78 (s, 1 H, OH), 6.22−8.31 (m, 8 H, aryl).

11c: − ^{1}H NMR (400 MHz, C_6D_6, 20°C): δ = 1.65 (s, 3 H, SCH_3), 1.78 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 3.50 (s, 2 H, SCH_2), 4.60 (s, 1 H, OH), 6.66−8.30 (m, 8 H, aryl).

X-ray Structure Determination of [CpRu{(*S,S*)-CHIRAPHOS}-($SC_{19}H_{14}O$)]BF_4 (4c): Black-purple crystals suitable for an X-ray structure determination were obtained by diffusion of hexane into a dichloromethane solution of **4c**. Twenty-five centered reflections from a crystal of the dimensions given in Table 1 gave a rhombohedric unit cell. Data were collected from one fourth of the reflection sphere in the range 2° < Θ < 26° (Enraf−Nonius CAD 4 diffractometer, Mo-K_α radiation, graphite monochromator, filter factor 16.4). No absorption correction was applied (minimum

Table 1. Details of the structure determinations of [CpRu{(*S,S*)-CHIRAPHOS}($SC_{19}H_{14}O$)]BF_4 (**4c**) and [CpRu{(*S,S*)-CHIRAPHOS}($SC_{17}H_{11}O$)] (**5a**)

Compound	**4c**	**5a**
Empirical formula	$C_{52}H_{47}BF_4OP_2RuS{\cdot}CH_2Cl_2$	$C_{50}H_{44}OP_2RuS{\cdot}1.5\ C_6D_6$
Mol. mass	1054.70	982.21
Color	black-purple	orange
Crystal size (mm)	0.18×0.15×0.10	0.18×0.18×0.12
Temperature (K)	293(2)	293(2)
λ (Å)	0.70930	0.70930
Space group	*R*3 (No. 146)	$P22_12_1$ (No. 18)
a (Å)	18.869(2)	9.951(2)
b (Å)	18.869(2)	19.835(4)
c (Å)	36.705(9)	24.803(4)
V (Å^3)	11318(3)	4869(2)
Z	9	4
ρ (calc) (mg mm^{-3})	1.393	1.333
μ (Mo−K_α) (cm^{-1})	5.70	1.73
Θ Range (°)	2.15−25.92	2.04−29.90
Index range *h*	0, 20	0, 13
k	0, 20	0, 27
l	−45, 45	0, 34
Measured reflections	5408	7821
Independent reflections	5408	7821
Observed reflections	3999	3901
Parameters	586	583
R[a]	0.0452	0.0600
wR_2[a]	0.0938	0.0698

[a] $I_o > 2\ \sigma\ (I_o)$.

transmission 97.84%). The structure was solved by Patterson methods (program SHELXS 86)[28] in the space group R3 (Nr. 146). A CH_2Cl_2 molecule was found in the asymmetric unit and refined anisotropically. H atoms were included in idealized positions, coupled to their carbon atoms. The BF_4^- anion was found distributed over three special positions, one of which was slightly disordered. Twenty restraints were introduced to preserve the geometries of BF_4 and CH_2Cl_2. Least-squares cycles of the SHELXL 93 program package[29] led to the R values given in Table 1. The five highest maxima of the final difference Fourier map were all below 0.520 e $Å^{-3}$. Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 408734.

X-ray Structure Determination of [CpRu{(*S,S*)-CHIRAPHOS}($SC_{17}H_{11}O$)] (5a): Clear orange crystals suitable for an X-ray structure determination grew out of a C_6D_6 solution. Twenty-five centered reflections from a crystal of the dimensions given in Table 1 gave an orthorhombic unit cell. Data were collected from one eighth of the reflection sphere in the range $2° < \Theta < 30°$ (Enraf−Nonius CAD 4 diffractometer, Mo-K_α radiation, graphite monochromator, filter factor 16.4). An empirical absorption correction based on the counts of nine reflections was applied (min. transmission 97.80%). The structure was solved by Patterson methods (program SHELXS 86)[28] in the space group $P22_12_1$ (Nr. 18). The 1.5 molecules of C_6D_6 found in the asymmetric unit were refined anisotropically. H atoms were included in idealized positions, coupled to their carbon atoms. Least-squares cycles of the SHELXL 93 program package[29] led to the R values given in Table 1. The five highest maxima of the final difference Fourier map were below 0.503 e $Å^{-3}$. Further details of the structure determination may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 408735.

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