

**CIRCULAR DICHROISM, XCIII<sup>1</sup>**  
**DETERMINATION OF THE ABSOLUTE CONFIGURATION OF ALCOHOLS,  
OLEFINS, EPOXIDES, AND ETHERS FROM THE CD OF THEIR  
"IN SITU" COMPLEXES WITH [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>].**

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**ABSTRACT** - A new, very convenient and sensitive "in situ" method has been developed for the determination of the absolute configuration of chiral compounds, which can bind to the axial position of [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>] (**5**) and induce circular dichroism within its electronic absorption bands. The CD spectra of the "in situ" complexes of chiral alcohols, ethers (including epoxides), olefins, and ketones with **5** show up to 5 Cotton effects (A - E) in the 600 - 300 nm range. This method works well for chiral secondary alcohols and monoolefins. For these compounds tentative rules are proposed, which correlate the absolute stereochemistry with the sign of certain Cotton effects of their complexes. A rule for the sign of band E for alcohols and a quadrant rule for the sign of band C for olefins can be applied. Olefins induce unexpected strong Cotton effects in presence of **5** giving evidence for a relatively stable  $\pi$ -bond between olefin and rhodium atom.

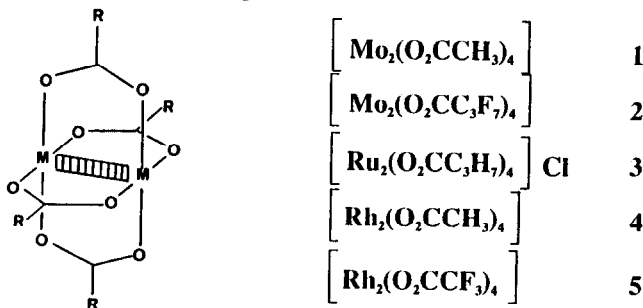
## 1. INTRODUCTION

Until now for many classes of chiral molecules reliable methods for the determination of absolute configuration are still missing. Especially for chiral monoalcohols, ethers, and olefins new or additional techniques are needed. For example, besides chemical correlations and X-ray diffractions of suitable derivatives no direct method is known for ethers. Chiroptical methods like *optical rotatory dispersion* (ORD) or *circular dichroism* (CD) are such direct methods which can differentiate between two enantiomers.<sup>2</sup> Nowadays the latter one is used most frequently.

For alcohols Nakanishi and Dillon have already proposed to make use of the induced CD with the perfluorinated copper complex [Cu(hfac)<sub>2</sub>], (hfac = hexafluoroacetylacetonate) to correlate the sign of the CD band at ca. 330 nm with the absolute configuration of the corresponding alcohol.<sup>3</sup> One disadvantage of this method is the band position, which is at short wavelength, so that in some cases additional chromophoric systems in the chiral ligand could have their absorptions in the same wavelength region.

Olefins have been examined by ORD of their osmate ester adducts with different kinds of pyridines, but long preparation time (1 - 2 d) including synthesis and purification of the adducts make it an uncomfortable method.<sup>4</sup> During the completion of this paper Kato reported a new direct method using the chirality recognition ability of an inherently chiral binaphthyl phosphoryl chloride [(BNP)Cl] for the determination of the absolute configuration of chiral carbinols.<sup>5</sup> But again, time-consuming preparation, purification and crystallization procedures are necessary to get suitable derivatives for CD measurements.

The purpose of this work was to develop a new method for the quick determination of the absolute configuration of the compounds mentioned above using easily available reagents. Within the last few years we have developed a very reliable method for the determination of the absolute configuration with the help of "in situ" complexes of nonabsorbing substances which can act as ligands for bi- or trinuclear transition metal complexes.<sup>6</sup> E.g. complexes of type  $[M_2(O_2CR)_4]$  ( $M = Mo, Rh, Ru$  etc.)<sup>7</sup> form cottonogenic derivatives either instantaneously or after heating in a suitable solvent with many different ligands, and do, therefore, not necessitate the preparation, isolation, and purification as in case of most other cottonogenic derivatives.



Depending on the nature of metal and the potential ligand these acylates differ in their applicability. For instance, dimolybdenum(II)tetraacetate (1) gives strong Cotton effects with chiral *bidentate* ligands such as diols, aminols, diamines or carboxylic acids by exchange of one or more acylate ligands.

On the other hand monoalcohols or other *unidentate* ligands usually do not induce Cotton effects for 1 although they could coordinate through the axial site of the cluster. A few examples such as the very unhindered  $\alpha$ -phenylethyl amine are known to form "in situ" complexes, but the CD spectra show only several small bands.<sup>6a</sup> This might be due to the fact that 1 shows only weak attraction for axial ligands.<sup>7,8</sup>

The rhodium and ruthenium carboxylates 3 and 4 have more affinity for such ligation.<sup>7,9</sup> Many crystallographical studies of such complexes have revealed structures in which the axial sites are occupied by a donor like a solvent molecule or a ligand, and recently we have shown that 3 and 4 give strong Cotton effects in presence of chiral amines or phosphanes as axial unidentate ligands.<sup>6d,e</sup> No Cotton effect could, however, be obtained for monoalcohols in presence of 3 or 4.

For 4 this result is very surprising in view of the existence of a methanol adduct with a relatively strong Rh-O<sub>axial</sub> bond ( $d_{Rh-O} = 2.286 \text{ \AA}$ ).<sup>10</sup> In spite of the existence of even single-crystals of the green, air-sensitive THF adduct  $[Rh_2(O_2CCH_3)_4(THF)_2]$ <sup>11</sup> no Cotton effects of chiral alcohols or ethers in presence of 4 could be observed. One could explain this behavior by either assuming a very low kinetic stability of those complexes, or by the presence of a relatively long Rh-L bond in solution, which allows for practically unhindered rotation around this axial bond.

Therefore we were looking for complexes which can bind alcohols stronger or more selectively and we found two crystal structures, done by Cotton and Felthouse ( $[Rh_2(O_2CCH_3)_4(Me_2SO)_2]$  and  $[Rh_2(O_2CCF_3)_4(Me_2SO)_2]$ ), from which the ambidentate nature of the dimethyl sulfoxide molecule was inferred.<sup>12</sup> With  $[Rh_2(O_2CCH_3)_4]$  (4) the DMSO molecules are coordinated through the sulfur, whereas with  $[Rh_2(O_2CCF_3)_4]$  (5) the strongly electron-withdrawing CF<sub>3</sub>-groups induce bonding via the oxygen atom. The fluorinated bridges of the cluster harden the rhodium centers and cause an enhancement of the Lewis acidity at the axial site in such a way that even weak bases like nitroxide radicals form adducts with 5.<sup>13</sup> Nakanishi and Dillon have reported already about the successful usage of a perfluorinated copper complex

([Cu(hfac)<sub>2</sub>], hfac = hexafluoroacetylacetonate) in CD-spectroscopy which was expected to be a better Lewis acid and hence alcohol acceptor.<sup>3</sup>

This prompted us to test the applicability of perfluorinated rhodium carboxylates for the determination of the absolute configuration of monoalcohols. Our choice of the perfluoroacetate **5** was suggested by the fact that the complex without axial ligands is easy to prepare and much less hygroscopic than the very moisture-sensitive perfluorobutyrate [Rh<sub>2</sub>(O<sub>2</sub>CC<sub>3</sub>F<sub>7</sub>)<sub>4</sub>]. Indeed the fluorinated complex **5** acted in the expected manner giving rise to induced Cotton effects with chiral monoalcohols. To our surprise even epoxides and other aliphatic ethers as well as ketones ligate to **5** and can, therefore, be investigated by this general CD-method.

Furthermore, in some recent papers olefin coordination with **5** was proposed to explain changes of the electronic absorption and NMR spectra.<sup>14</sup> Before this, olefin-coordination had been regarded as impossible<sup>15</sup> although many reactions of alkenes catalyzed by rhodium(II)carboxylates are known. These applications include for example the cyclopropanation of olefins by diazo compounds<sup>16</sup>, their auto-oxidation<sup>17</sup>, or their hydrogenation<sup>18</sup>.

For the latter reaction a mechanism was proposed according to which the olefin is bound to the axial site of the rhodium cluster.<sup>19</sup> Since the extensive studies of the thermodynamic and spectroscopic behavior of rhodium(II)carboxylates by Drago and coworkers the  $\pi$ -acceptor ability for this kind of compound is established.<sup>20</sup> In accordance with this, chiral olefins in presence of **5** give strong Cotton effects. Our results presented in this paper provide further evidence for such a relatively stable  $\pi$ -back-bonding.

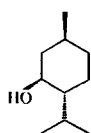
## 2. RESULTS AND DISCUSSION

### Electronic absorption spectra

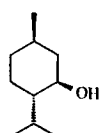
Typical spectra of **5** with alcohols in hexane show three major bands in the 750 - 250 nm region (Figure 1). At longest wavelengths, band I appears at 590 - 585 nm, band II is seen at 460 - 455 nm, and the strongest band V has its maximum at 260 nm. Two additional bands, III and IV, are visible as shoulders of band II at appr. 420 nm and of band V near 350 nm. Values for the position of pertinent absorption bands for [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>L<sub>n</sub>] are given in Table 1.

In case of epoxides, ethers, and olefins (except **31**, see below) the maximum of band I appears at somewhat longer wavelengths (600 - 590 nm). This shift is attributed to the sensitivity of band I to axial ligation of **5**, which has been described in many papers.<sup>20,21</sup> For very dilute solutions of **5** without axial ligands in hexane, band I is found at 610 nm. The magnitude of the shift resulting by axial ligation depends on the strength of the Rh-L bond. Alcohols cause a shift of appr. 20 nm, whereas with the more basic amines sometimes very large shifts ( $\geq 50$  nm) are observed. Band II is rather insensitive towards axial ligation.

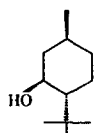
One explanation for this spectrochemical behavior is the interaction of electron lone pairs of the ligand with the  $\sigma_{\text{Rh-Rh}}^*$ (4a<sub>2u</sub>) orbital of the dirhodium cluster.<sup>20,21</sup> This interaction causes a destabilization of this orbital which is then at higher energy. Since the corresponding electronic transition for the electric dipole allowed absorption band I with x,y-polarization<sup>22</sup> has been assigned to the  $\pi_{\text{Rh-Rh}}^*$ (5e<sub>g</sub>)  $\rightarrow$   $\sigma_{\text{Rh-Rh}}^*$ (4a<sub>2u</sub>) electron excitation<sup>23,24</sup>, and the energy difference between  $\pi_{\text{Rh-Rh}}^*$  and  $\sigma_{\text{Rh-Rh}}^*$  has increased, band I must be shifted hypsochromically. The  $\pi_{\text{Rh-Rh}}^*$ (5e<sub>g</sub>)  $\rightarrow$   $\sigma_{\text{Rh-O}}^*$ (4b<sub>2u</sub>) transition, assigned to band II<sup>21,22</sup>, should not be influenced dramatically by axial ligands, because here most of the electron density is located



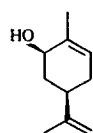
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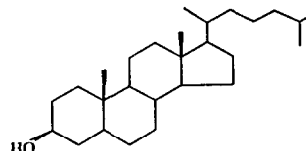
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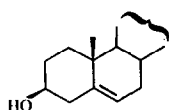
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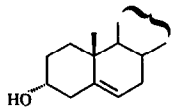
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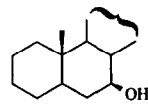
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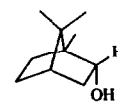
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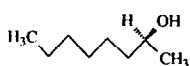
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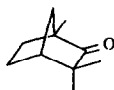
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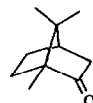
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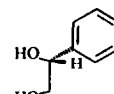
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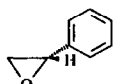
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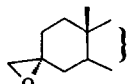
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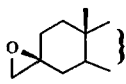
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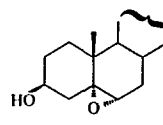
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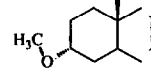
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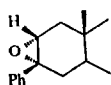
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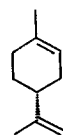
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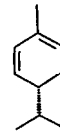
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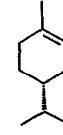
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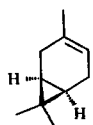
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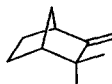
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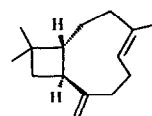
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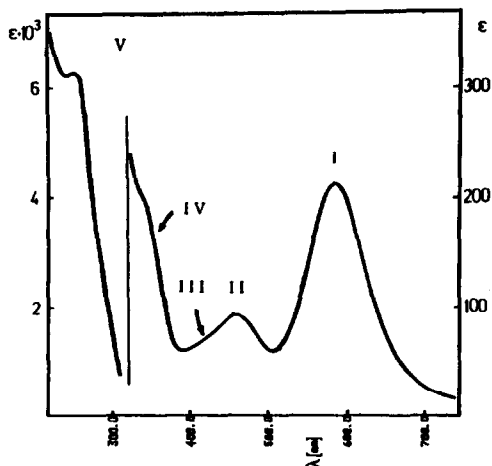


Figure 1: Typical absorption spectrum of  $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4\text{L}_2]$  ( $\text{L} = \text{sec. alcohol}$ ) in hexane.

Table 1: Position of bands I and II in the electronic absorption spectrum of  $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4\text{L}_n]$  in hexane if not stated otherwise (sh = shoulder, vs = very strong).

L, n = 2	No.	Band II Band I	
		$\lambda_{\text{max}}$ [nm]	
--	5	459	609
(-)-Menthol	7	459	587
	7 <sup>a)</sup>	457	597
(-)-cis-Carveol	9	462	582
5 $\alpha$ -Cholestan-3 $\beta$ -ol	10	454	590
Cholest-5-en-3 $\alpha$ -ol	12	456	590
5 $\alpha$ -Cholestan-7 $\beta$ -ol	13	460	591
(-)-Borneol	14 <sup>a)</sup>	453	597
(+)-2-Octanol	15	459	589
(+)-Styrene oxide	19	453	589
	19 <sup>a)</sup>	447	602
5 $\alpha$ ,6 $\alpha$ -Epoxy-cholestan-3 $\beta$ -ol	22	461	597
3 $\alpha$ -Methoxy-5 $\alpha$ -cholestane	23	455	597
(+)-Fenchone	16	455	606
(+)-Camphor	17	454	587
<b>L, n = 1</b>			
(-)- $\beta$ -Pinene	25	365(vs)	594
(+)-Limonene	26	349(vs)	596
(-)- $\alpha$ -Phellandrene	27	365(sh)	427(vs) 590
(+)-p-Menth-1-ene	28	365(vs)	600
(+)-3-Carene	29	362(vs)	592
(-)-trans-Caryophyllene	31	369(vs)	405(vs) 556

<sup>a)</sup> in  $\text{CHCl}_3$ .

within the cluster. This shift of band I manifests itself in a change of color during complexation (cf. Experimental). Steric requirements of the ligand can also influence band positions and color. For example, one tertiary alcohol gave only weak complexes with **5** and the solution became bluish-green as in case of epoxides.

The fairly low value of 582 nm for *cis*-carveol (**9**) can be explained by the inductive effect of the neighboring  $\pi$ -system, which is an electron-donating group and should increase the basicity of the hydroxy group. By this the splitting of HOMO and LUMO will be enlarged, leading to this observed hypsochromic shift. The electronic absorption spectra of the complexes of ketones are similar to those of the epoxides in the presence of **5**.

Solutions of olefin complexes in hexane are green. The coordination of olefins to the rhodium cluster **5** leads to dramatic changes in the absorption spectra, since the number of observable bands has dropped to two. The intensity of band I hardly has changed, but band II disappeared and band IV, which is only seen as a shoulder on band V in the spectra of alcohol adducts, has become the dominating band in these spectra in the range of 700 - 290 nm.

Exceptions are  $\alpha$ -phellandrene (**27**) and *trans*-caryophyllene (**31**). Compound **27** has a conjugated  $\pi$ -electron system and shows its strongest band at 427 nm, resulting in a yellow solution instead of a green one. The shift of band I to 590 nm is also fairly large and its intensity has decreased. Untypical behaviors of conjugated olefins have already been described by Doyle and coworkers who have reported uncharacteristic changes of  $\lambda_{\text{max}}$  of band I compared to those observed for non-conjugated olefins during the subsequent addition of an olefin to the solution of  $[\text{Rh}_2(\text{pfb})_4]$  in  $\text{CH}_2\text{Cl}_2$  (pfb = perfluorobutyrate).<sup>14</sup> The development of a yellow color was attributed<sup>14</sup> to a reduction of rhodium(II) to rhodium (I). To throw new light on this fact we added a trace of ethanol to 10 ml of this yellow solution of  $\alpha$ -phellandrene (**27**) in presence of **5**. Immediately the intense blue color of the ethanol adduct of **5** and its typical UV/Vis curve was obtained. For compound **31** see below.

### CD spectra

#### a) Alcohols

The geometry of complexation will be determined by the bulkiness of the groups ["M" (medium) and "L" (large)] for a secondary alcohol, and this size of groups has no simple relation with preferences as defined in the CIP system. In the following we use, therefore, the descriptors "bR" and "bS" for the absolute arrangements as shown in Figure 2.

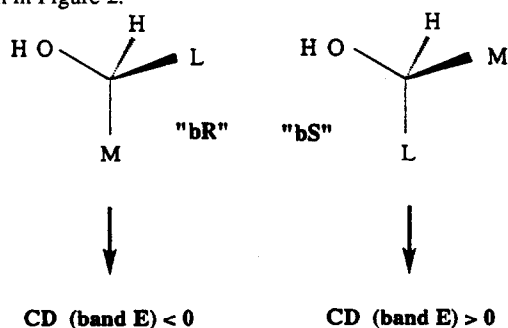


Figure 2: Definition of *bR*- and *bS*-configuration according to the size of the substituents. Empirical rule for the sign of the Cotton effect for band E in the CD spectrum of chiral secondary alcohols in presence of **5**.

Sometimes the assignment of a molecule to *bR* or *bS* is not trivial, so that models have to be constructed, which then (usually) give unequivocal answers about the steric environment of the bonding site in the ligand. The  $\Delta\epsilon$ -values given in Table 2 are calculated on the basis of concentration of the achiral stock complex **5**. Although the axial coordination of donor molecules to the rhodium cluster in solution is controlled by an equilibrium reaction,<sup>20</sup> we can safely assume total occupation of the free axial site of **5** by chiral ligands under our conditions. Some of the  $\Delta\epsilon$ -values are very small, but nevertheless the signal-to-noise ratio in each case was better than at least 10 : 1. The number of significant digits varies with the noise and is smaller at shorter wavelengths.

Chiral alcohols in presence of **5** show up to 5 Cotton effects (A-E) in the 700 - 300 nm region (Figures 3 and 4). Band A corresponds to band I of the isotropical absorption spectrum, band C to band II, D to III, and band E to the shoulder (band IV) of band V. Band B around 500 nm is seen only in CD, and must therefore correspond to a magnetically allowed transition. For most alcohol complexes the band at longest wavelengths (A) cannot be detected. Only **8** shows a very strong Cotton effect for the corresponding  $\pi^*_{\text{Rh-Rh}} \rightarrow \sigma^*_{\text{Rh-Rh}}$  transition.

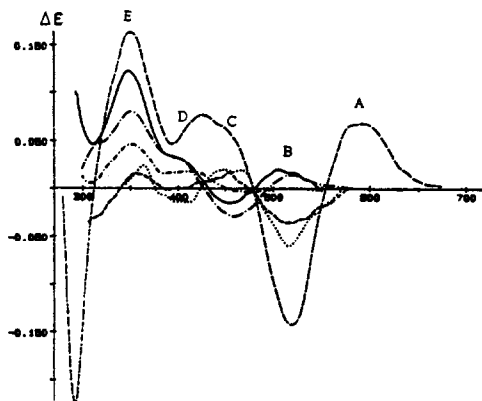


Figure 3 : CD of the chiral alcohols with "bS"-configuration in presence of the achiral stock complex **5** ( ———, [6] = 7.21 mM, [5] = 1.23 mM; ———, [8] = 3.58 mM, [5] = 1.25 mM; - - - - , [10] = 1.67 mM, [5] = 1.12 mM; . . . . , [11] = 2.38 mM, [5] = 1.13 mM; —•—•—, [13] = 2.95 mM, [5] = 1.4 mM; - - - - - , [15] = 8.12 mM, [5] = 1.13 mM). The CD curves for **10** and **11** are enlarged by the factors of 5 and 7, respectively.

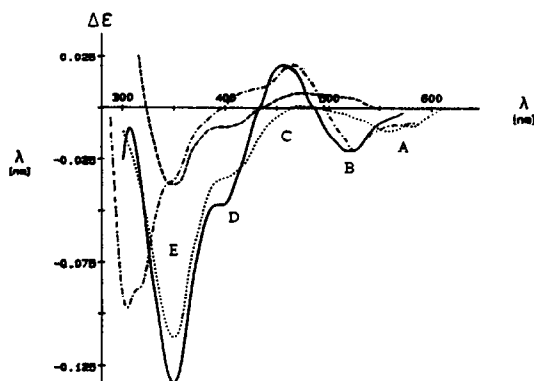


Figure 4 : CD of the chiral alcohols with "bR"-configuration in presence of **5** ( ———, [7] = 6.78 mM, [5] = 1.19 mM; . . . . , [14] = 6.5 mM, [5] = 1.35 mM; - - - - , [9] = 5.1 mM, [5] = 1.2 mM; - - - - - , [12] = 1.18 mM, [5] = 1.14 mM).

As can be read off Table 2 and Figures 3 and 4, only one single CD band can unequivocally be correlated with the absolute stereochemistry, viz. Cotton effect E around 350 nm. It is positive for alcohols with *bS* (Figure 3), and negative for those with *bR*-configuration (Figure 4). Also with this method difficulties may arise as mentioned for the  $[\text{Cu}(\text{hfac})_2]$  complex. Furthermore, in all but one case the Cotton effects B and C have opposite signs. Only for **9** both are positive, but in this case there exists another additional potential site of complexing (the methylene group), and one of these two CDs may come from a different mode of complexation. Such a complication is, however, only found when a very unhindered methylene group is present in the molecule; other double bonds, as in **11** and **12** do not compete with the alcohol grouping.

Table 2:  $\Delta\epsilon$ -values for the "in situ" complexes with  $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]$  in hexane (sh = shoulder).

Compound	No.	CD-bands	$\lambda_{\text{max}}^{\text{CD}} [\text{nm}]$		
			Band C	Band B	Band A
(+)-Menthol	6	348 +0.12	400 +0.033	454 -0.015	505 +0.020
(-)-Menthol	7	349 -0.13	397 -0.047	457 +0.02	519 -0.021
(-)-8-Phenyl- menthol	7 <sup>b)</sup>	349 -0.075	395 -0.019	450 +0.041	514 -0.022
(-)-8-Phenyl- menthol	8	350 +0.16	350 +0.068	426 +0.077	520 -0.14
(-)-cis-Carveol	9	349 -0.037	401 -0.009	477 +0.007	491 +0.006
5 $\alpha$ -Cholestan- 3 $\beta$ -ol	10	356 +0.003	356 +0.003	454 +0.003	519 -0.007
Cholesterol	11	364 +0.004	398 -0.002	467 +0.003	517 -0.009
Cholest-5-en- 3 $\alpha$ -ol	12	343(sh) -0.037	418 +0.007	465 +0.021	525 -0.021
5 $\alpha$ -Cholestan- 7 $\beta$ -ol	13	351 +0.080	398 +0.033	459 -0.029	521 +0.014
(-)-Borneol	14	350 -0.11	398 -0.035	472 +0.001	559 -0.011
(+)-2-Octanol	14 <sup>b)</sup>	352 -0.078	400 -0.025	486 +0.003	565 -0.007
(+)-Fenchone <sup>c)</sup>	15	352 +0.047	417 +0.018	475 -0.004	614 -0.005
(+)-Camphor <sup>c)</sup>	16	265 -0.98	302 +0.90	-----	515 -0.001
	17	264 +0.92	289 -0.94	-----	522 -0.004

Compound	No.	CD-bands	$\lambda_{\text{max}}^{\text{CD}} [\text{nm}]$		
			Band C	Band B	Band A
(-)-1-Phenyl- ethane-1,2-diol	18 <sup>b)</sup>	343 +0.12	398 +0.061	454 +0.041	509 +0.031
(+)-Styrene oxide	19	372 -0.050	411 -0.073	454 +0.010	480(sh) -0.018
(3R)-Epoxide <sup>d)</sup>	19 <sup>b)</sup>	339 +0.093	414 -0.019	454 +0.041	500 -0.017
(3S)-Epoxide <sup>d)</sup>	20	345(sh) -0.005	400(sh) +0.010	454 +0.041	509 -0.024
5 $\alpha,6\alpha$ -Epoxy- cholestan-3 $\beta$ -ol	21	355 +0.040	414 +0.025	450(sh) +0.012	502 -0.003
3 $\alpha$ -Methoxy- 5 $\alpha$ -cholestone	22	373 +0.048	402(sh) -0.007	455 -0.031	522 -0.021
(-)- $\beta$ -Pinene	23	370 +0.50	402(sh) -0.007	435(sh) -0.005	495 +0.017
(+)-Limonene	25	370 +0.50	402(sh) -0.007	467 +0.072	519 +0.081
(-)- $\alpha$ -Phellandrene	26	336 -2.18	424 +4.39	467 +0.047	535 -0.016
(+)-p-Menth-1-ene	27	339 -0.77	424 +4.39	467 +0.047	533 +0.37
(+)-3-Carene	28	371 -0.55	400 -0.17	463 +0.14	530 -0.10
(-)-trans-Caryo- pitylene	29	348 -0.49	383 +0.58	459 +0.31	530 -0.15
	31	364 -4.10	451 +0.31	525 -0.28	580 +0.035

a)  $\Delta\epsilon$  is based on the concentration of the stock complex 5. The concentrations of each compound and 5 are given in the corresponding figure.

b) in  $\text{CHCl}_3$ .

c) difference of CD of complexed and uncomplexed ketone. Not all bands are reported.

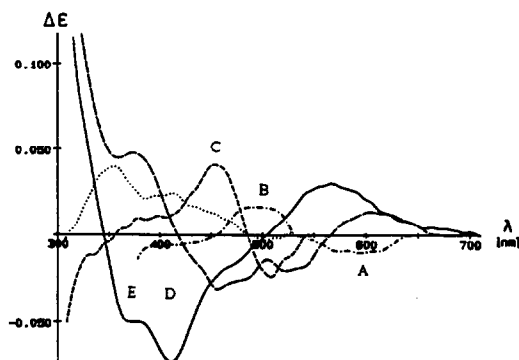
d) Epoxide = Spiro-(5 $\alpha$ -cholestone-3,2'-oxirane).



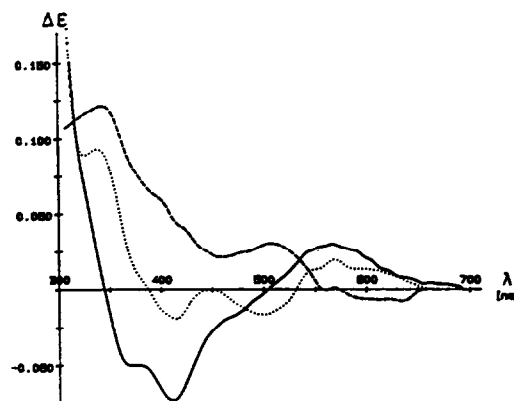
## b) Epoxides and ethers

Epoxides and ethers also complex easily with **5** acting as axial ligands. The CD-spectra of the bluish-green solutions are shown in Figure 5. Again up to five Cotton effects (A-E) are observed in the range of 700 - 300 nm. Although the Rh-O bond of ethers or epoxides should be weaker than the corresponding one of alcohols, electron-donating groups as e.g. the phenyl substituent in the styrene oxide (**19**) can increase the basicity of the oxygen atom and thus strengthen the Rh-O bond giving rise to stronger CD effects.

Even for **20** and **21**, in which the nearest chiral center is fairly far away at C-5 of the cholestane skeleton, significant Cotton effects are observed at 509 and 454 nm for **20**, and 414 and 355 nm for **21** in presence of **5**. Due to steric hindrance of the phenyl group at C-3, compound **24** does not ligate to the rhodium cluster and thus gives no CD with **5**. More examples are now under investigation in order to find a rule for the prediction of the absolute configuration of ethers and epoxides by this new method.



**Figure 5** : CD of the chiral epoxides **19** - **22** and of the chiral ether **23** in presence of **5** ( ———, [**19**] = 5.6 mM, [**5**] = 1.07 mM; - - -, [**20**] = 3.3 mM, [**5**] = 1.06 mM; . . . ., [**21**] = 3.01 mM, [**5**] = 1.05 mM; ———, [**22**] = 2.36 mM, [**5**] = 1.12 mM; - - - - - , [**23**] = 2.64 mM, [**5**] = 1.14 mM).



**Figure 6** : CD in presence of **5** of styrene oxide (**19**) ( ———, in hexane, [**19**] = 5.6 mM, [**5**] = 1.07 mM, [**5**] : [**19**] = 1 : 5.2), ( . . . . , in CHCl<sub>3</sub>, [**19**] = 6.65 mM, [**5**] = 0.95 mM, [**5**] : [**19**] = 1 : 7.0) and of the diol **18** ( - - - - , in CHCl<sub>3</sub>, [**18**] = 7.63 mM, [**5**] = 1.08 mM, [**5**] : [**18**] = 1 : 7.1) in presence of **5**. **18** and **19** have different configurations at C-1.

Although the epoxy alcohol **22** has two potential sites for coordination, we can formally assign it to the class of epoxides. Its CD spectrum with **5** shows ca. 10 times stronger Cotton effects compared to those of the corresponding alcohols **10** or **11**. Due to the C-19 methyl group, coordination through the epoxy oxygen on the rear side has preference over the ligation through the hydroxy oxygen at C-3. This behavior is also reflected in the large  $\Delta\epsilon$ -values of the "in situ" complex of the steroid **12**, whose site of ligation (3 $\alpha$ -OH group) is less hindered compared to that of **10** or **11** (3 $\beta$ -OH group), giving a stronger Rh-O bond.

That no diols are formed by ring cleavage of the epoxides during such measurements has been proved by thin layer chromatography of the "in situ" solutions at different times, and by examination of IR spectra of these solutions, which show no absorption bands for alcohols. Sometimes very strong Cotton effects of traces of an impurity *can* superpose the bands in the original spectrum. Although in our special case of "in situ" complexes very strong Cotton effects are improbable, we have measured the CD of the diol **18** in presence of **5** in  $\text{CHCl}_3$ . **18** was obtained from (-)-D-mandelic methylester by reduction with  $\text{LiAlH}_4$ <sup>25</sup> and has opposite absolute configuration at C-1 with respect to **19**. Comparison of their CD spectra in presence of **5** in  $\text{CHCl}_3$  revealed different shapes of the measured curves (Figure 6). The most significant difference is observed in the 400 - 300 nm region, in which the Cotton effects for **18** and **19** have different magnitudes but same sign despite the enantiomorphism of diol and epoxide.

### c) Olefins

In contrast to the CD of the complexes with chiral ligands described hitherto, the CD between **5** and olefins shows unusually strong Cotton effects (Figures 7,8 and 11). Especially for the conjugated olefin **27** and the caryophyllene **31** the Cotton effects in presence of **5** are amongst the largest ever recorded for such complexes (cf. Figure 11).

$\Delta\epsilon$ -values of ca. 4 are obtained for the CD band which corresponds to the strongest absorption band in the isotropic spectrum. Table 2 shows that the magnitude of even bands A and B of the olefin complexes is of same order as those of the strongest bands in the spectra of the complexes of alcohols.

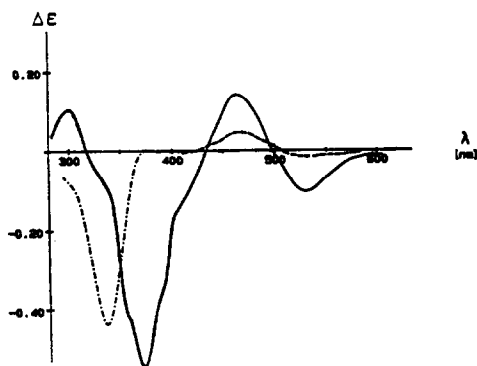


Figure 7 : CD of menthene (**28**) ( ——— ,  $[\text{28}] = 14.8$  mM ,  $[\text{5}] = 0.98$  mM ,  $l = 0.1$  cm) and of limonene (**26**) ( $[\text{26}] = 17.07$  mM ,  $[\text{5}] = 1.22$  mM; - - - ,  $l = 2$  cm ; - · - · - ,  $l = 0.05$  cm , multiplied by a factor of 0.2) in presence of **5**.

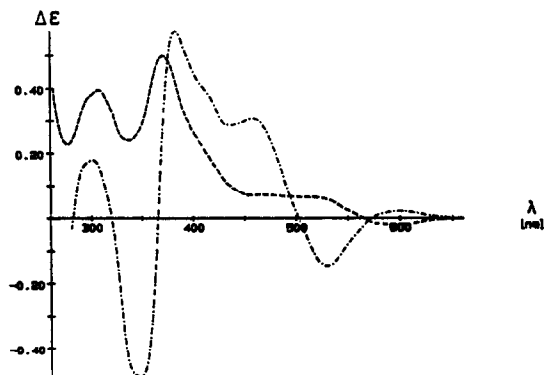
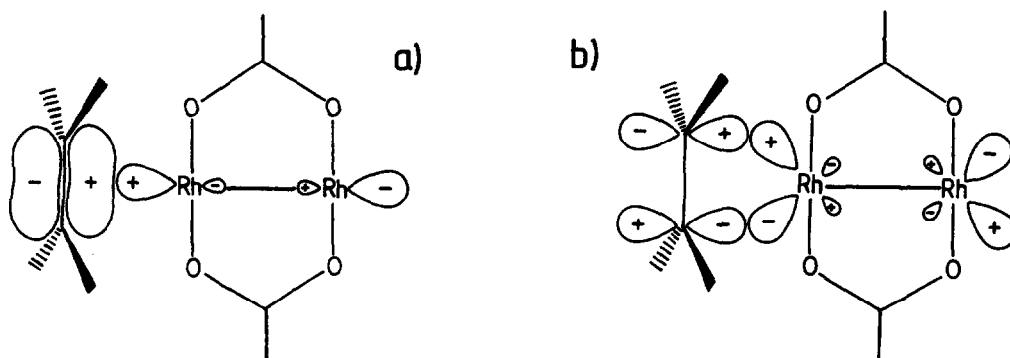


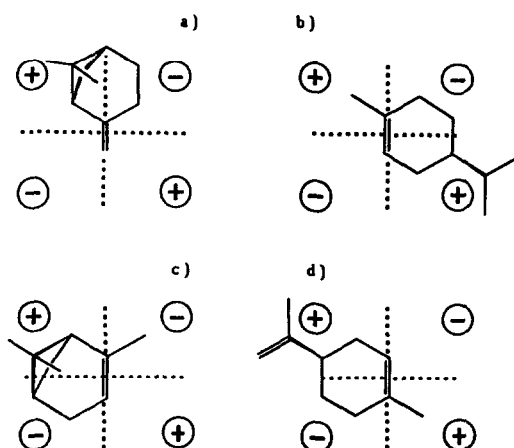
Figure 8 : CD of carene (**29**) ( $[\text{29}] = 7.21$  mM,  $[\text{5}] = 1.31$  mM; ——— ,  $l = 0.05$  cm) and of pinene (**25**) ( $[\text{25}] = 2.37$  mM,  $[\text{5}] = 0.94$  mM, - - - ,  $l = 0.2$  cm) in presence of **5**.

These facts imply, therefore, that the axial coordination of the olefin molecule results in a strong bonding and/or that the olefin molecule is rather fixed in one single conformation to the rhodium cluster. One reasonable explanation can be given by discussion of the bonding mode of olefins with the rhodium cluster **5** using Dewar's concept<sup>26</sup> of donation and back-bonding (Figure 9).



**Figure 9:** In a) overlap of filled  $\pi$ -orbitals of the olefin with unoccupied  $\sigma^*$ -orbitals ( $\sigma^*_{\text{Rh-Rh}}$ ) of the metal atom results in a donation of electrons from the olefin into acceptor orbitals of the rhodium atom. In b) back-bonding occurs from a filled metal  $d_{xz}$  or  $d_{yz}$  orbital ( $\pi^*_{\text{Rh-Rh}}$ ) into an empty  $\pi^*$ -orbital of the olefin. Both components a) and b) are involved in the total bonding and control the adduct formation. Once a  $\pi$ -bonding between the olefin and a  $\pi^*$ -MO on one rhodium has occurred, insufficient electron density in the  $\pi^*$ -orbitals of the other rhodium atom does not allow the formation of a second olefin-rhodium  $\pi$ -bond.<sup>27</sup>

As already mentioned at the beginning of this chapter, olefins in axial position can be readily exchanged by O-donor molecules, which indicates thus a weak Rh-olefin bond. Consequently, the reason for the strong Cotton effects must be the fixed conformation of the axially bound olefin as shown in Figure 9 b) and to the steric requirements of the four perfluoroacetate ligands. The olefin molecules must be arranged therefore in such a way that the double bond is perpendicular to the rhodium-rhodium bond, and that the more bulky olefin substituents point away from the cluster. Figure 10 shows that for all monoolefins (25, 26, 28, and 29) most of the atoms are positioned in one and the same sector. On the basis of their CD spectra a tentative rule can be proposed for the correlation of the signs of band C with the absolute configuration of an olefin, which is put forward in Figure 10.



**Figure 10:** Projection along the Rh-Rh bond. The dashed lines indicate the carboxylate planes or the nodal planes of the sector rule for the CD band C. The double-bond is orthogonal to the Rh-Rh bond and deliberately put vertically. The chiral ligand is arranged in such a way that the bulky groups are pointing away from the metal cluster and towards the observer. The sign of band C is then the same as the sign of the sector in which most carbon atoms are positioned: a) (-)- $\beta$ -pinene (25), b) (+)-p-menth-1-ene (27), c) (-)-3-carene (29), d) (+)-limonene (26). For all these compounds the sign of the CD band C is positive. This rule, which for all practical cases is a quadrant rule, can also be derived from a qualitative MO procedure (see forthcoming paper).

Compound **30** gives no detectable Cotton effects because the two methyl groups shield the exo-methylene group preventing by this the formation of an axial  $\pi$ -bond. For **26** the CD-sign within band C is the same as for the monoolefin **28**. Although two double bonds are present the CD-contribution of the isopropyl group is expected to be quite small since several torsional angles around the (C-4)-(C-8) bond may be adopted.

When a conjugated  $\pi$ -system is engaged in the coordination to the metal cluster the interaction becomes more complex and several different types of bonding are feasible (e.g.  $1,2-\eta^2$ -,  $3,4-\eta^2$ -mode). The unusual UV/Vis spectrum and the very strong Cotton effects (Figure 11) of the "in situ" complex of phellandrene (**27**) could be caused by a process of interconversion between these different types of bonding mode. But due to the fact that caryophyllene (**31**), which has a 1,5-diene-system, shows the same unusual effects, it seems that the two isolated  $\pi$ -systems of **31** are involved in a homoconjugation and the inductive effect of the uncoordinated  $\pi$ -bond strongly influences some electronic transitions of the metal cluster. More measurements with rhodium complexes and conjugated or homoconjugated olefins as axial ligands are now in progress to give a better understanding of the bonding mode.

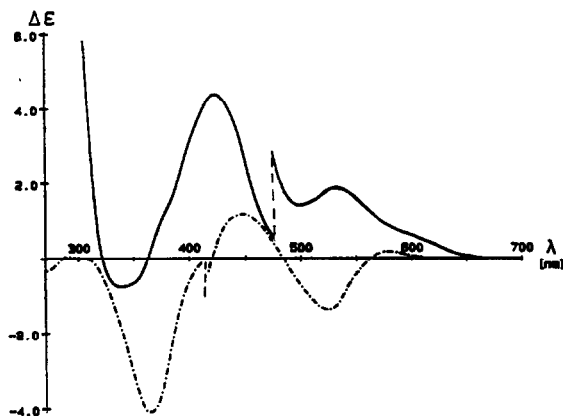


Figure 11: CD of phellandrene (**27**) (—,  $[27] = 13.62$  mM,  $[5] = 0.93$  mM) and of caryophyllene (**31**) (- · - · -,  $[31] = 4.42$  mM,  $[5] = 0.91$  mM) in presence of **5**. The parts of the curves at longer wavelengths are multiplied by a factor of 5, and were recorded using 1 cm cells. 0.05 cm cells were used for the high-energy range.

#### d) Ketones

Two structurally similar ketones (**16** and **17**) were measured in presence of **5**, and again strong Cotton effects in the high-energy range were observed. Figure 12 shows the difference spectra between the CD spectra of the ketone-rhodium complexes and those of the ketones before the addition of **5**, because the Cotton effects of the optically active complexes around 300 nm are superposed by those of the carbonyl chromophore of uncomplexed ketones.

For most induced Cotton effects their signs are opposite, and around 300 nm one would have to construct the CD of the complex more carefully. Since several good rules for different types of ketones are available we did not pursue this matter but wanted rather to show the principle applicability of **5** also for oxo-compounds.

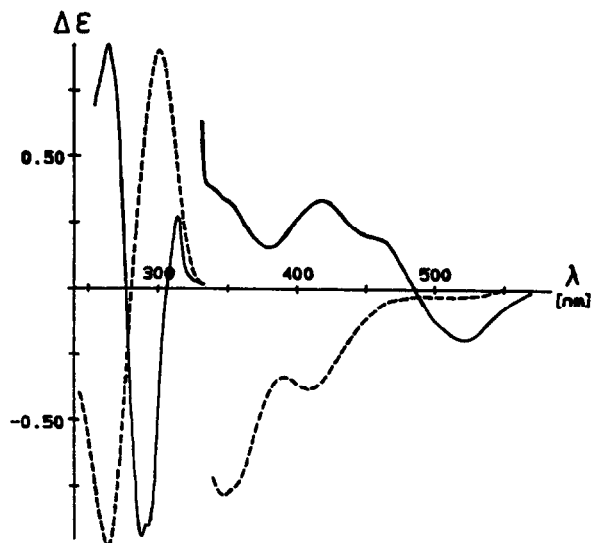


Figure 12: Difference curves between the "in situ" complexes and the uncomplexed ketones ( ---- , [16] = 5.1 mM, [S] = 1.0 mM; ——— , [17] = 5.7 mM, [S] = 1.0 mM). The parts of the curves at longer wavelengths are multiplied by a factor of 25.

The logical assumption that ketones coordinate in the same bidentate mode as olefins (B, Figure 13) is refuted by structural criteria of fenchone. The two methyl groups hinder an orthogonal orientation of the C–O bond to the axial site of the cluster. The same is valid for camphene (30) mentioned above, but fenchone (16), whose steric requirement is nearly identical with that of camphene (except one methyl group at the angular position), must have other possibilities for a coordination in axial position of 5. A parallel unidentate coordination (A, Figure 13) seems to be more probable. This is supported by the UV spectra of 16 and 17, which correspond more to those of the alcohol complexes than to the other olefin complexes.

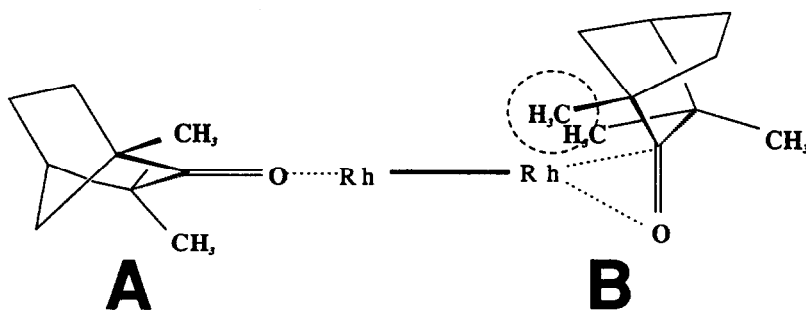


Figure 13: Two possible geometries of complexation of a ketone (A : "end-on", B : "side-on").

### e) Time- and solvent dependence of the CD spectra

Under an inert atmosphere at r.t. solutions of the complex are stable for a very long time. The CD spectra for alcohols and olefins measured after several days show even slightly stronger Cotton effects as those obtained immediately after preparation of the solutions. Only for epoxides small decreases of intensity are observed after several hours. For example, for the strongest band in the CD spectrum of styrene oxide (19) in presence of 5 the decrease of rotational strength after 12 h is 40 %, and after 3 weeks 65 %, but there is no change in shape or position of bands.

The CD spectra obtained of hexane solutions are only slightly different from those for  $\text{CHCl}_3$  solutions. For alcohols and olefins just differences in intensities of the CD bands can be observed. Usually the stronger Cotton effects for the "in situ" complexes result for hexane solutions. Shapes and positions of bands are the same, except for epoxides, for which slight shifts of some bands may occur (see also Figure 6).

### 3. SUMMARY

In the presence of the perfluorinated rhodium complex 5 chiral mono-ols, ethers (including epoxides), and olefins also show induced Cotton effects. Ketones give additional CD-bands in the range of 600 to 400 nm besides two around 300 and 270 nm. This behavior is due to the enhanced Lewis acidity of the axial site of the perfluorinated cluster as compared to the hitherto used tetraacetate 4. Also diols and enols show such induced CD-bands and we are testing at present whether their effects are additive or not.

A tentative rule could be proposed for the complexes of 5 with monoolefins and with monoalcohols. "Tailor-made" ligands are now prepared in order to support this rule, which should be reasonably explicable with the help of the qualitative MO-theory<sup>28</sup> as was possible for the complexes with chiral acids.<sup>29</sup>

Application of the new stock complex 5 has the following advantages over those complexes used hitherto:

- 1) In general less than 1 mg of the potential ligand can be used.
- 2) No tedious derivatisation is needed.
- 3) Since the formation of the chiral complexes is very fast the CD can be measured already a few minutes after dissolving the potential ligand in the solvent containing the stock complex.
- 4) The chiral complexes are stable over a long time and only slightly sensitive towards air.
- 5) The signs of the Cotton effects are neither depending on the concentration of 5 nor of the chiral ligand, provided that more than 2 equivalents of the latter are used.
- 6) The essential induced CD-bands are mostly in a wavelength range where other chromophores (e.g. aromatic or heterocyclic  $\pi$ -systems) do not absorb.
- 7) In contrast to the hitherto used complexes the axial ligands from those of 5 can easily be split off by addition of methanol. By chromatography on silica both, the chiral ligand as well as the stock complex, can be separated and regained in very good yield.

#### 4. EXPERIMENTAL

The optically active substances obtained commercially were used without further purification except 17, which was freed of borneol by column chromatography (6: HAARMANN & REIMER; 7: RIEDEL; 8, 19: MERCK; 16: EGA; 11, 15, 26: JANSSEN; 14, 17, 25, 27 - 31: FLUKA). The compounds 9<sup>30</sup>, 10<sup>31</sup>, 12<sup>32</sup>, 13<sup>33</sup>, 18<sup>25</sup>, 20 & 21<sup>34</sup>, 22<sup>35</sup>, 23<sup>36</sup> and 24<sup>35</sup> were prepared in our laboratory. Purity was checked in all cases by thin layer chromatography.

##### Preparation of the axial free [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>] (5)

The rhodium(II)trifluoroacetate complex was prepared by a modification of the literature method.<sup>37</sup>

1 g [Rh<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] (DEGUSSA) was refluxed in 10 ml trifluoroacetic acid under an inert atmosphere for about 4 h. After removal of the solvent under reduced pressure, the crude bluish-green product was purified by column chromatography through 50 g of neutral silica (140 - 270 mesh) contained in a 30 cm × 30 mm glass column. Elution with a petrol ether/ ether/ methanol mixture (4:2:1), evaporation of the solvents and drying of the blue methanol adduct in vacuo for 2 h at 1.0°C afforded in an almost quantitative yield (1.37 g, 99%) green, anhydrous [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>].

##### CD measurements

To ca. 6 - 8 mg [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>] and 3 - 6 equivalents (appr. 5 - 10 mg) of optically active substance 10 ml spectrograde hexane is added (good S / N -ratios are still obtained when only 1/10 of these weights are used). Exclusion of air is not necessary. Due to the insolubility of [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>] in hexane, any coloring of the hexane solvent indicates a spontaneous complexation between 5 and the substance. If necessary, the solution is shaken vigorously and may even be warmed with a stream of hot air for several minutes. Usually alcohols give at r.t. a blue, ethers or epoxides and ketones a bluish-green, and olefins a green color.<sup>38</sup> For sparingly soluble compounds ethanol-free CHCl<sub>3</sub> may also be used. This can be freed of ethanol by filtration over basic Al<sub>2</sub>O<sub>3</sub> (act. I).<sup>39</sup>

The CD spectra were recorded on a dichrograph MARK III (ISA-Jobin Yvon) or a JASCO J-600, which were connected to an AT-computer. Depending on the S / N -ratio the  $\lambda$ -scan speed was 0.2 or 0.5 nm/s. Curve smoothing was achieved by the Golay-Savitzky algorithm<sup>40</sup> and the  $\Delta\epsilon$ -values were calculated on the basis of the achiral stock complex.

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