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Dirhodium tetraacetate as an auxiliary chromophore in a circular dichroic study on *vic*-amino alcohols

Jadwiga Frelek,* Jarosław Jaźwiński, Marek Masnyk, Patrycja Ruśkowska and Rafał Szmigielski

Institute of Organic Chemistry of the Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw, Poland

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Abstract—The dirhodium method proposed herein, involves the in situ formation of chiral complexes of optically active *vic*-amino alcohols with the achiral dirhodium tetraacetate [$Rh_2(OAc)_4$] acting as an auxiliary chromophore. The resulting CD spectra are suitable for stereochemical studies, since the observed sign of Cotton effects arising within the d–d absorption bands of the metal core is determined by the chirality of the amino alcohol ligand. It has been demonstrated that in acetonitrile and chloroform solutions, chiral complexes are formed by axial ligation of the ligand to the metal atom(s) of the dirhodium core. This axial binding occurs through the nitrogen atom of the 1,2-amino alcohol unit independently of the ligand-to-metal molar ratio, as shown from the ^{15}N and low-temperature NMR experiments. In agreement with NMR results, ESI MS experiments indicate that in solution, a mixture of chiral complexes with ligand-to-metal molar ratios 1:1 and 2:1 is present. An empirically based rule correlating the sign of Cotton effect occurring above 600 nm with the stereochemistry of ligand has been formulated.

1. Introduction

Rhodium(II) dinuclear carboxylato-complexes of the [$Rh_2(OOCR)_4$] type have been the subject of intensive research due to their chemical reactivity,[1] potential applications as anticancer agents,[1,2] as well as high catalytic activity in many reactions. Highly enantioselective cyclopropanations, intramolecular carbon–hydrogen insertion reactions, and intermolecular addition reactions are among the reactions in which dirhodium tetracarboxylates and their derivatives are widely used as efficient catalysts of choice, for example, Doyle's, McKervey's, and Ikegami's catalysts.[3] Very recently, it has been found that a dirhodium complex with Mosher acid ligands can act as a solvating NMR auxiliary for chiral recognition of various monovalent ligands.[4]

The chiral coordination compounds can also be used to assign the absolute configuration to coordinating ligands by means of circular dichroism spectroscopy (CD). One of the available procedures for such an assignment consists of making chiral complexes in situ through mixing a solution of an achiral transition metal complex displaying adequate absorption characteristics with an optically active but nonabsorbing substance. Among the various transition metal complexes employed,[5] the dirhodium tetraacetate [$Rh_2(OAc)_4$] seems to be the most suitable candidate for this purpose since it can accept both mono- and bidentate ligands.[1] It can easily exchange in situ one or more of its acetate units with a different type of ligand or, alternatively, it can fix them by coordination to form chiral complexes of a bridging or a chelating structure. In both cases, the CD arising within the d–d absorption bands is determined by the chirality of the compound acting as ligand(s).

Among ligands coordinating easily to the dirhodium core are amines, diamines, amino- and hydroxy-acids as well as *vic*-amino alcohols.[6] Recently, we demonstrated that the dirhodium tetraacetate forms in situ complexes with optically active *vic*-amino alcohols in ethanol solution.[7] The CD spectra of such complexes are suitable for the determination of absolute configuration of ligands. The configurational assignment is based on the proposed helicity rule that links signs of the Cotton effects (CEs) appearing around 300, 380, and 440 nm with the sign of the N–C–C–O torsional angle.

* Corresponding author. Fax: +48 22 632 6681; e-mail: frelek@icho.edu.pl

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In addition, the bidentate bridging mode of binding of an amino alcohol to the Rh_2-core was assumed to be most probable for this solvent.[7]

However, if acetonitrile or chloroform are used as solvents, the shapes of the CD curves and the signs of the particular Cotton effects considerably differ in respect to those recorded in ethanol for the same compounds, as can be seen in Figure 1. This fact may suggest that the mode of binding of an amino alcohol molecule to the Rh_2-core differs depending on the solvent used. Acetonitrile can be categorized as a coordinating solvent whereas chloroform can be regarded as a noncoordinating one. Since dirhodium tetraacetate, besides its aptitude to exchange acetate ligand(s), possesses also pronounced ability to bind a wide variety of ligands in its axial positions (along the Rh–Rh bond),[1] a unidentate ligation of the chiral ligand or a similar ligation of the coordinating solvent molecule can take place in acetonitrile. In the case of chloroform, however, the axial site must remain unoccupied by a solvent molecule.

To contribute to the understanding of the observable differences in the CD spectra of dirhodium complexes with *vic*-amino alcohols recorded in various solvents, we decided to study their chiroptical properties in detail. We also hoped that our studies would shed some light on the mode of complexation of the dirhodium core by an amino alcohol.

Since amino alcohols represent an important group of organic compounds due to their significant biological activity and wide application in synthesis,[8,9] the unequivocal and reliable determination of the absolute configuration of this class of compounds is of appreciable importance. Therefore, the assignment of the absolute and relative configurations to the amino alcohols has been a topic of interest for a number of research groups applying CD and NMR spectroscopic techniques. Very recently, a transformation of *vic*-amino alcohols into the corresponding oxazolidinones to elucidate their relative configuration by NMR without chiral shifts reagents has been proposed.[10] Also methods based on CD induced by helix formation of a poly(4-carboxyphenyl)acetylene upon complexation with chiral amino alcohols[11] or by the formation of coordinated complexes between lanthanide tris-(β-diketonates) and amino alcohols[12] have been reported. The exciton-coupled circular dichroism (ECCD), based on the quantum mechanical theory of a coupled oscillator,[13] has also been applied successfully to the absolute stereochemical assignment of *vic*-amino alcohols in the form of their Cu(II) complexes[14] or macrocyclic host–guest complexes with a host porphyrin tweezer.[15] Very recently, new chromophoric systems applicable in the ECCD configurational analysis of various classes of compounds, including *vic*-amino alcohols, were summarized in review.[16] In contrast to rigid molecules, however, for flexible molecules a sign change of the couplet without a change of the absolute configuration may take place. This is due to the fact that in flexible molecules, an unequivocal assignment of the exciton absorption and CD bands (α and β transitions) is not always possible. Although attempts have been made to overcome this,[14,15b] a correct application of the exciton chirality method becomes difficult in some cases.[17,18] From this point of view, a development of alternative methods, which can be complementary to the methods used to date is advantageous. With this in mind, we decided to check whether the applicability of the helicity rule, previously proposed by us,[7] can be extended also to acetonitrile and chloroform solutions. The 620 nm CD band appearing in the spectra recorded in acetonitrile and chloroform (Fig. 1) seems to be especially useful for stereochemical assignment because of its location in the low-energy region, that is, far away from the own absorption of typical chromophores present in organic molecules. Herein, we report the utility of this Cotton effect (CE) for correlation between its sign and stereochemistry of an amino alcohol.

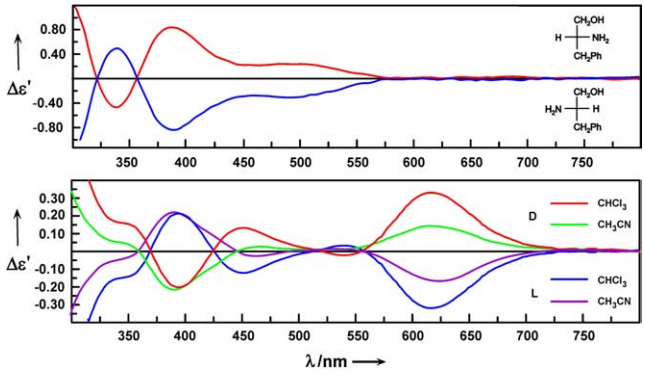

Figure 1. CD spectra of the D-phenylalaninol **5** and L-phenylalaninol **9** in the presence of $[Rh_2(OAc)_4]$ recorded in ethanol (top) and in acetonitrile and chloroform (bottom).

2. Results and discussion

We started our investigation by finding out the best experimental conditions for the formation of the chiral complex and by testing the stability of the complex in solution. Thus, a dependence of the CD spectra on the ligand-to-metal molar ratio and on time was examined. Herein, D-phenylalaninol, as a representative amino alcohol, was chosen.

2.1. The CD spectra dependence on ligand-to-stock complex molar ratio

Measurements were performed in both chloroform and acetonitrile in 0.5:1, 1:1, 1.5:1, 3:1, 5:1, 6.5:1, 8:1, and 10:1 ligand-to-metal ratios. In the case of acetonitrile, for the molar ratio range from 0.5:1 to 5:1, only very small differences in the shape of the CD curves were observed. In general, an increase in the ligand concentration resulted in a proportional increase of the band intensity only (Fig. 2, top). However, in the cases of 6.5:1, 8:1, and particularly in 10:1 ligand-to-metal molar ratios, a substantial increase of band intensity occurred in the high-energy region followed by decrease of band intensity in the 550–750 nm spectral range. Moreover, a small shift of the band positions, particularly in the

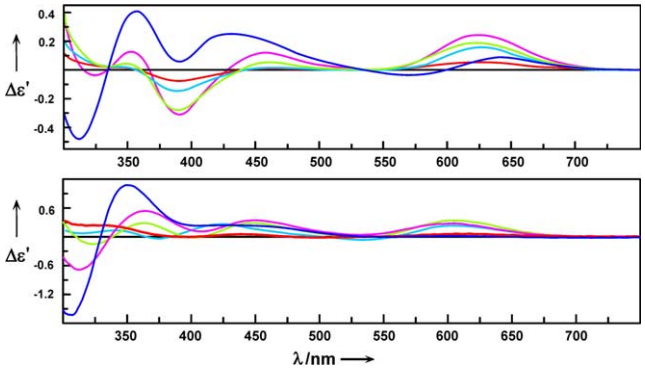

Figure 2. CD spectra dependence on selected ligand-to-metal molar ratio in acetonitrile (top) and chloroform (bottom): 1:1 (——), 1.5:1 (——), 3:1 (——), 5:1 (——), and 10:1 (——). Spectra recorded 24 h after mixing of components: D-phenylalaninol **9** and Rh-stock complex. CD spectrum for 10:1 molar ratio in chloroform is twofold diminished.

long wavelength spectral range, was observed (Fig. 2, top). A more complex picture was observed in the case of chloroform solution. There, in addition to the band intensity increase corresponding to the increase of the ligand concentration, some changes in the band positions were observed (Fig. 2, bottom). However, within the ligand-to-metal ratio range from 0.5:1 to 5:1 and in the 400–780 nm spectral range the shape of the CD curves remains generally unchanged. Thus, the CD spectra recorded in such a spectral range and in 0.5:1–5:1 ligand-to-metal ratio can be used for the stereochemical studies. This statement applies to both solvents studied.

2.2. The CD spectra dependence on time

Measurements over an extended period of time were carried out in both solvents. In general, we found that the signs of the Cotton effects were not time dependent. However, as is evident from Figure 3, the intensity of all CD bands increased with time. A maximum of band intensity in acetonitrile and chloroform was reached at approximately 24 h after the preparation of the chiral complex, independently of the ligand to the stock complex molar ratios, and then remained unchanged over the next 96 h.

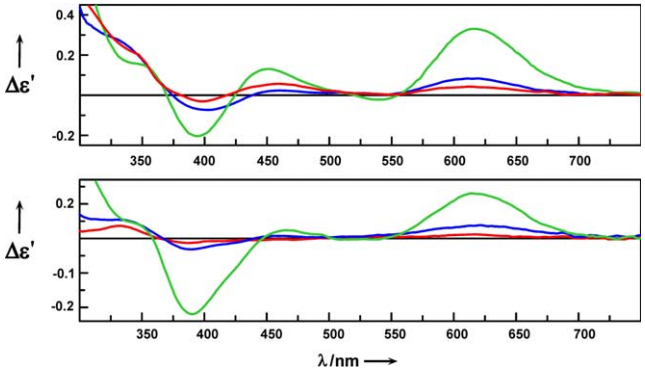

Figure 3. CD spectra of in situ formed Rh-complexes of D-phenylalaninol **5** in chloroform (top) and in acetonitrile (bottom) after: 0.5 h (——), 3 h (——), and 24 h (——). Chiral complexes recorded in the 1.5:1 ligand-to-metal ratio.

2.3. The CD spectra dependence on solvent

Amino alcohols **1**–**22**, representing both adrenaline and ephedrine types, were chosen as model compounds for a circular dichroic study in acetonitrile and chloroform (Fig. 4). On the basis of the results presented in Section 2.1, we regarded the 1.5:1 molar ratio of the constituents as the most convenient for our chiroptical study. Moreover, according to results from Section 2.2, we decided to record the CD spectra after 24 h from the moment of chiral complex formation (mixing of the stock solutions). The CD data for Rh-complexes of amino alcohols **1**–**22** recorded in acetonitrile and chloroform solutions under the above defined conditions are summarized in Table 1.

As can be seen from Table 1, the rhodium complexes formed in situ with *vic*-amino alcohols show two prominent CD bands around 380 and 620 nm in both solvents. In general, the first band is of an opposite sign to the latter one (Figs. 5 and 6). In chloroform, however, in addition to the bands at 380 and 620 nm, two other distinct CD bands occurring around 440 and 550 nm and of opposite signs to each other are present in the spectra (Fig. 6). The CD band occurring in both solvents around 620 nm seems to be the most suitable for the stereochemical assignment due to its location and high intensity.

The small differences observed in the magnitude of certain Cotton effects in spectra of respective enantiomers can be attributed to the fact that the exact concentration of chiral complex in each of the studied solutions is unknown. Therefore, the CD data are presented as the $\Delta\varepsilon'$ values calculated in the usual way as $\Delta\varepsilon' = \Delta A/c \times d$, where c is the molar concentration of the Rh complex, assuming 100% complexation.

Although the general shapes of CD curves are quite similar in both solvents (Figs. 5 and 6), some differences between them can be observed. The data collected in Table 1 demonstrates that, in general, the intensity of particular Cotton effects is stronger if chloroform is used as a solvent. Moreover, the Cotton effects around 620 nm are present in all 22 amino alcohols measured in chloroform whereas in acetonitrile, this Cotton effect is absent in amino alcohols of adrenaline type (compounds **19**–**22**) and, with the exception of an enantiomeric pair formed by compounds **14** and **16**, in ephedrine drugs **13**, **15**, and **17**.

Based on the data shown in Figures 5 and 6, it could be assumed that for the D-series of amino alcohols the CD band around 620 nm is positive, while it is negative for the respective L-series. This regularity, however, holds only for amino alcohols **1**–**12**, as can be seen from Table 1. Therefore, a common rule for the correlation between CD and the absolute configuration that would obey all compounds in question should be found. For this purpose, the structure of the chiral complexes formed in

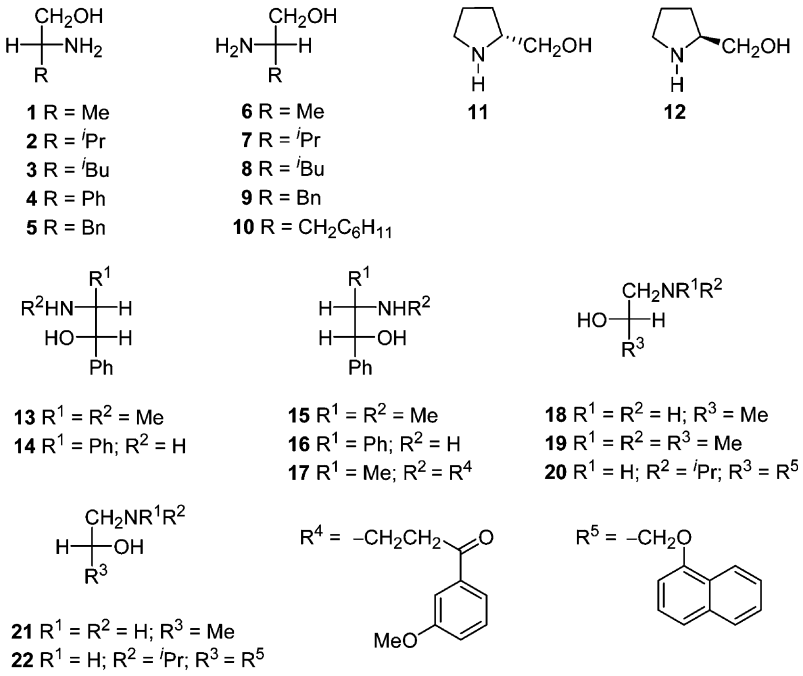

Figure 4. Investigated *vic*-amino alcohols **1**–**22**.

solution can be helpful. However, despite many attempts, we were not able to obtain single crystals of the chiral complex suitable for X-ray analysis. Therefore, to resolve the problem of structure identification of the chiral complex formed in situ, we decided to use other spectroscopic methods.

2.4. Electronic absorption spectra in the visible region

A simple method that is particularly useful for differentiating the type of complex formed is the analysis of its electronic absorption.[19] In general, the electronic spectra of dirhodium tetracarboxylates consist of two principal bands in the visible region, band I around 600 nm and band II near 450 nm (Fig. 7).[1,7,19] Two stronger bands occur in the UV range, namely band III near 250 nm (shoulder) and band IV at around 220 nm. Band I, attributed to the π^*(Rh–Rh)→σ^*(Rh–Rh) transition,[1,20] is strongly influenced by the changes in the axial ligands and is shifted to the lower wavelength depending on the nature of ligands. In contrast, band II, assigned as an electronically allowed component of the π(Rh–O)→σ^*(Rh–O) excitation,[1,20] is more sensitive to the change of the equatorial binding ligands.[19]

In the rhodium complex with D-phenylalaninol in chloroform, band I is blue shifted for about 25 nm compared to the stock complex. Only a very small shift (ca. 2 nm) was observed for the band I position for the same chiral complex in acetonitrile. The results are in agreement with the literature data indicating that the low energy band in the visible spectrum increases in energy depending on the nature of the axial ligand.[19,20] Thus, the data prove the initial axial coordination of the amino alcohol to the Rh_2-core in both solvents. In addition, only a very small difference in the positions of bands I and II were observed over a long period of time (Fig. 8A). This suggests the stability of the chiral dirhodium complex in both solvents. Furthermore, the fact that no time changes in the absorption band positions were observed, indicates that the amino alcohol molecules occupy the axial coordination sites predominantly.

According to the literature data,[21] the position of absorption band I in acetonitrile (ca. 550 nm) suggests that in the adduct formed in situ, both axial coordination sites are occupied by either two D-phenylalaninol molecules or by one chiral ligand and one solvent molecule. In the case of the chloroform solution, the different positions of the same absorption band (ca. 580 nm) may point out to an adduct with only one D-phenylalaninol molecule coordinated to the axial position of the Rh_2-core.[22] A possible reason for this difference may be the insolubility of the dirhodium tetraacetate in chloroform, which can hinder the coordination process. According to the literature data,[21] however, entities of the type $Rh_2(O_2CR)_4L$ have a strong tendency to associate in pairs by sharing carboxylate oxygen atoms. In addition, formation of the complex in which an amino alcohol molecule coordinates with its two binding sites to the axial positions of two Rh_2-units to form a one-dimensional zigzag chain has to be also taken into consideration.[23] Moreover, a shift of band I position in noncoordinating solvents to higher energy reported for dirhodium carboxylates indicate that there must be some axial interaction of the stock complex with the solvent.[21]

It can be assumed that in both solvents studied amino alcohol ligands bind at the axial position/s to form chiral complexes with Rh_2-core. Most likely a mixture of 1:1 and 2:1 chiral complexes is present in the solutions. Figure 8B shows the CD and electronic spectra of

Table 1. CD data of in situ-formed Rh-complexes of compounds **1**–**22** recorded in chloroform and acetonitrile 24 h after dissolving

Compound	Solvent	CD {$\Delta\varepsilon'$ (nm)}				
1	$CHCl_3$	+0.07 (359.5)	−0.07 (397.5)	+0.11 (451.5)	−0.07 (549.5)	+0.18 (627.0)
	Me_3CN	+0.06 (359.0)		+0.04 (465.0)	−0.01 (553.5)	+0.09 (628.0)
2	$CHCl_3$	+0.21 (348.5)	−0.31 (388.5)	+0.21 (449.0)	−0.02 (539.0)	+0.47 (616.5)
	Me_3CN	+0.06 (349.5)	−0.10 (387.0)	+0.02 (462.5)		+0.10 (621.5)
3	$CHCl_3$	+0.06 (351.0)	−0.28 (388.5)	+0.15 (451.5)	−0.04 (547.5)	+0.35 (621.5)
	Me_3CN	+0.03 (346.0)	−0.12 (384.0)			+0.11 (622.0)
4	$CHCl_3$	+0.11 (360.0)	−0.09 (406.5)	+0.07 (470.5)	−0.04 (554.5)	+0.16 (630.5)
	Me_3CN	+0.02 (364.0)	−0.01 (431.0)	+0.01 (494.0)		+0.03 (628.0)
5	$CHCl_3$	+0.15 (350.0)	−0.20 (394.0)	+0.13 (452.0)	−0.02 (539.0)	+0.33 (615.5)
	Me_3CN	+0.05 (342.0)	−0.22 (390.0)	+0.03 (465.0)		+0.15 (618.0)
6	$CHCl_3$	−0.05 (358.0)	+0.06 (390.5)	−0.10 (452.0)	+0.06 (558.0)	−0.19 (629.0)
	Me_3CN	−0.13 (360.0)		−0.08 (463.0)	+0.01 (554.5)	−0.14 (625.0)
7	$CHCl_3$	−0.10 (348.0)	+0.33 (388.0)	−0.16 (436.5)	+0.02 (546.5)	−0.41 (619.0)
	Me_3CN	−0.02 (347.5)	+0.16 (384.5)	−0.02 (462.0)		−0.12 (620.0)
8	$CHCl_3$	−0.03 (351.5)	+0.21 (386.0)	−0.19 (447.5)	+0.05 (548.5)	−0.33 (622.5)
	Me_3CN	−0.05 (348.5)	+0.18 (386.0)			−0.20 (620.5)
9	$CHCl_3$	−0.13 (353.0)	+0.19 (396.0)	−0.12 (452.5)	+0.02 (540.0)	−0.31 (617.0)
	Me_3CN	−0.03 (344.5)	+0.20 (389.5)	−0.02 (462.8)		−0.12 (620.0)
10	$CHCl_3$	−0.13 (350.5)	+0.20 (408.0)	−0.07 (479.0)	+0.05 (553.5)	−0.28 (636.5)
	Me_3CN	−0.05 (352.5)	+0.03 (439.0)		+0.02 (560.0)	−0.06 (646.5)
11	$CHCl_3$	+0.15 (345.5)	−0.44 (408.5)	+0.06 (487.0)		+0.39 (602.0)
	Me_3CN		+0.12 (396.0)			+0.06 (608.0)
12	$CHCl_3$	−0.15 (345.0)	+0.50 (410.0)	−0.06 (485.0)		−0.46 (604.0)
	Me_3CN		−0.12 (392.0)			−0.06 (606.5)
13	$CHCl_3$	+0.32 (333.0)	−0.48 (392.5)			−0.24 (612.5)
	Me_3CN			No CD		
14	$CHCl_3$	−0.20 (331.0)	−0.11 (383.5)	+0.06 (455.5)		−0.06 (617.0)
	Me_3CN			+0.05 (424.5)		−0.03 (598.5)
15	$CHCl_3$	−0.31 (332.5)	+0.46 (390.5)			+0.23 (614.0)
	Me_3CN			No CD		
16	$CHCl_3$	+0.21 (328.5)	+0.10 (382.0)	−0.07 (451.5)		+0.05 (615.5)
	Me_3CN			−0.06 (421.5)		+0.03 (600.0)
17	$CHCl_3$		+0.22 (373.0)	−0.31 (440.5)	+0.03 (502.0)	+0.17 (625.5)
	Me_3CN			No CD		
18	$CHCl_3$	−0.11 (380.0)	−0.14 (408.5)		+0.07 (573.5)	−0.02 (642.5)
	Me_3CN		−0.31 (412.0)		+0.12 (590.0)	
19	$CHCl_3$	−0.07 (370.0)	+0.06 (406.0)	−0.14 (461.5)		−0.03 (622.5)
	Me_3CN			No CD		
20	$CHCl_3$		−0.08 (382.5)	+0.03 (480.0)	−0.05 (536.5)	−0.05 (644.0)
	Me_3CN			No CD		
21	$CHCl_3$	+0.17 (376.0)	+0.19 (403.5)		−0.09 (572.0)	+0.03 (645.0)
	Me_3CN		+0.32 (412.5)		−0.13 (584.5)	
22	$CHCl_3$		+0.10 (386.5)	−0.07 (474.5)	+0.04 (534.5)	+0.06 (645.0)
	Me_3CN			No CD		

Values are given as $\Delta\varepsilon'$ (nm).

Rh-complex with D-phenylalaninol in both solvents measured after 24 h from the moment of complex formation.

2.5. ^1H, ^{13}C, ^{15}N, and low temperature NMR studies

As a model compound for NMR study, D-phenylalaninol **5** was chosen. Analogously as in the case of CD and EA visible spectra, no significant differences in resonances in ^1H and ^{13}C NMR spectra were observed as a function of time. In the case of chloroform solution, the most diagnostic signal both in the proton and carbon spectra is the singlet at ca. 1.9 and 24 ppm, respectively (Fig. 9). This singlet is attributed to all methyl groups of the dirhodium core and unequivocally indicates their

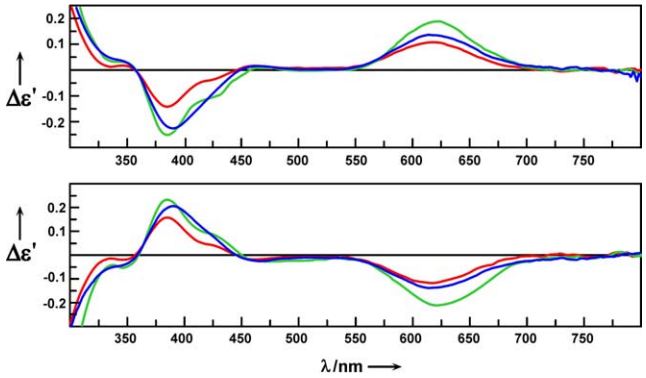

Figure 5. CD spectra of in situ formed Rh-complexes of amino alcohols **2** (——), **3** (——), **5** (——) (top), and **7** (——), **8** (——), **9** (——) (bottom) recorded in acetonitrile 24 h after dissolution of the constituents.

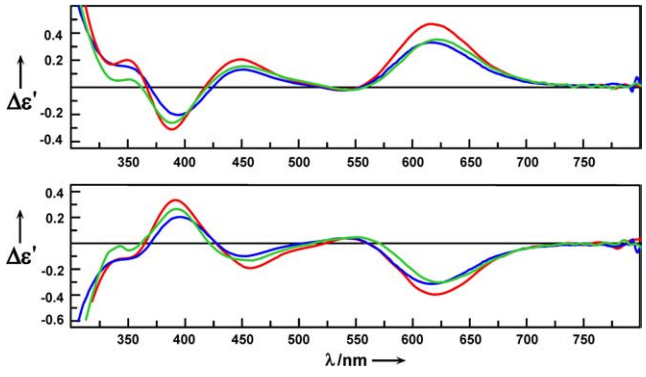

Figure 6. CD spectra of in situ formed Rh-complexes of amino alcohols **2** (——), **3** (——), **5** (——) (top), and **7** (——), **8** (——), **9** (——) (bottom) recorded in chloroform 24 h after dissolution of the constituents.

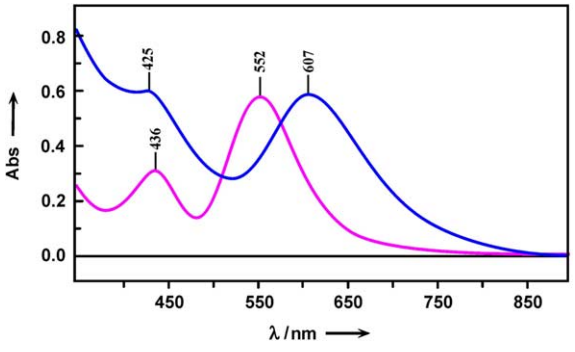

Figure 7. Electronic spectra of $[Rh_2(OAc)_4]$ in acetonitrile (——) and chloroform (——).

equivalence. On this basis it can be assumed that in chloroform a chiral complex, with the amino alcohol ligand(s), bound in the axial site(s) of the dirhodium core (collinear with the Rh–Rh bond) is formed.

A very similar situation is present in acetonitrile. In this case, again, the resonance signal attributed to the methyl groups of the dirhodium core was found in both ^{1}H and ^{13}C NMR spectra as a singlet at ca. 1.7 and 24 ppm, respectively (Fig. 10). This confirmed the assumption that also in acetonitrile an axially bounded chiral complex is formed.

To gain more information about the structure of the chiral complex, for example, to establish the stoichiometry of the chiral complex and to answer the question whether the ligation occurs through the nitrogen or oxygen atoms of an amino alcohol unit, low-temperature NMR experiments in $CDCl_3$ and CD_3CN were performed. The results of an NMR titration experiment in $CDCl_3$ solution are shown in Figure 11. Due to the low solubility of $[Rh_2(OAc)_4]$ in $CDCl_3$, a mixture of dirhodium tetraacetate, D-phenylalaninol ligand and solvent was placed on an ultrasonic bath for a few minutes. Then, after decantation of an insoluble material, the sample solution was used to record the spectrum.

In the low-temperature (243 K) spectrum of sample with a ligand-to-metal 2:1 ratio the signals within range from 4.02 to 3.10 ppm have been identified by the application of one-bond $^{13}C,^{1}H$ HSQC correlation, and assigned to the five nonequivalent protons of the CH and CH_2 groups (Table 2). Peaks at 4.53, 4.37, and 4.15 ppm were assigned as the signals of two nonequivalent protons of NH_2 and OH groups, respectively. The lack of free ligand signals in the 2:1 mixture spectrum suggests that the D-phenylalaninol is completely bound by the rhodium core and, consequently, only the 2:1 adduct exists in the solution. The signals of free ligand appear in the spectrum of a 2.5:1 mixture, where an excess of ligand is present in the solution.

The noncomplexed D-phenylalaninol **5** ^{15}N atom resonates at −348.5 ppm (Table 2), while in the complex this signal is shifted by −16.3 ppm. In order to acquire the reference data, the spectrum of α-methylbenzylamine–Rh_2-core system has been recorded under the analogous conditions. Similarly to the D-phenylalaninol **5**, a change of ^{15}N chemical shift of −15.2 ppm was found. Since only one mode of binding, via a nitrogen atom, is possible for this amine, the similarity of shift values observed for both α-methylbenzylamine and D-phenylalaninol **5** leads us to the conclusion that the binding of rhodium core also occurs via the nitrogen atom of D-phenylalaninol.

$^{15}N,^{1}H$ HSQC one-bond correlation spectrum indicates that the signals at 4.53 and 4.37 ppm correlate with the ^{15}N signal at −364.8 ppm and form two anti-phase doublets with $^{1}J(^{15}N–^{1}H)$ of ca. 64 Hz (Fig. 12). The observation of different chemical shifts for the two NH_2 protons validates the assumption that complexation occurs through the nitrogen since the presence of rhodium atom would prevent the rapid inversion of configuration on the nitrogen.

The spectrum of a 1:1 mixture (Fig. 11), revealing four signals in the range from 4.4 to 5.2 ppm and, additionally, few signals of CH_3 groups, suggests the presence of at least two species in the solution, presumably 1:1 and 1:2 adducts. However, the signal integration reveals

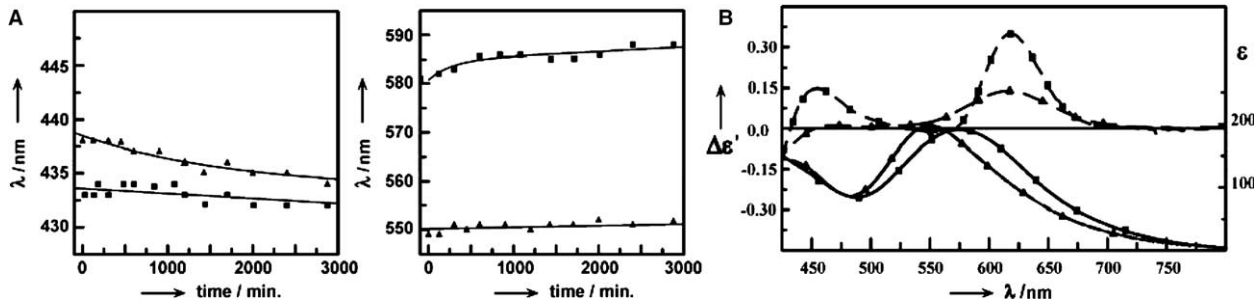

Figure 8. Time-dependence of the long-wavelength absorption bands I and II in the Rh-complex with D-phenylalaninol **5** in acetonitrile (–▲–) and chloroform (–■–) solutions (A) and comparison of the CD (–■–) and vis (–▲–) spectra of the Rh-complex with D-phenylalaninol **5** (1.5:1 ligand-to-metal molar ratio) measured after 24 h at room temperature in acetonitrile (–▲–) and chloroform (–■–) (B).

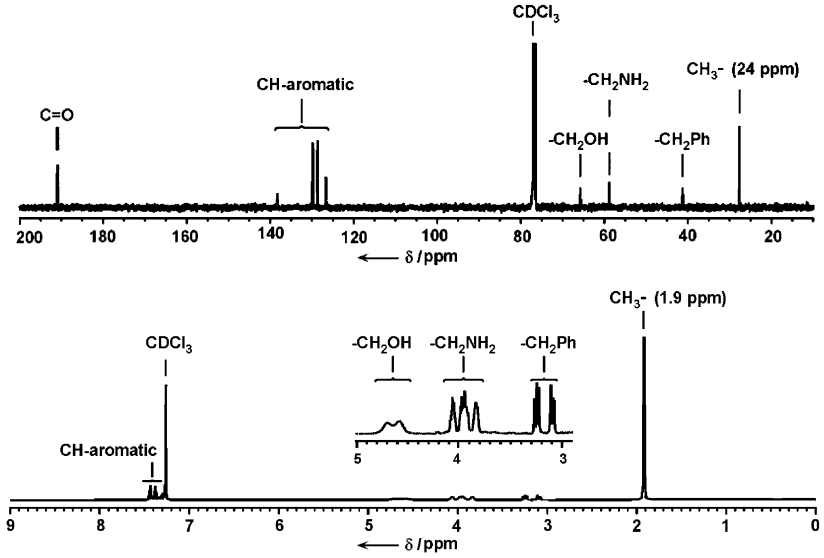

Figure 9. ^{1}H (bottom) and ^{13}C (top) NMR spectra of the in situ formed chiral complex of the D-phenylalaninol **5** coordinated to the dirhodium tetraacetate measured in $CDCl_3$.

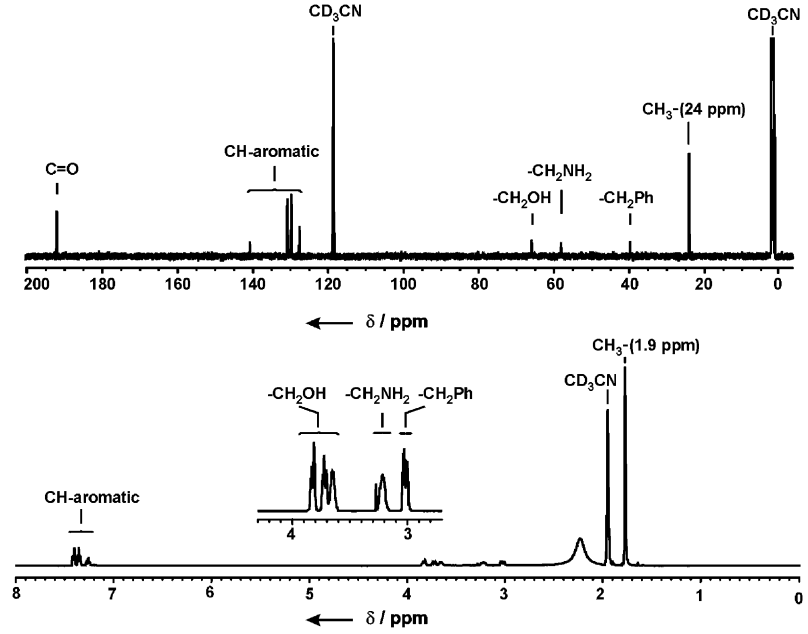

Figure 10. ^{1}H (bottom) and ^{13}C NMR (top) spectra of the in situ-formed chiral complex of the D-phenylalaninol coordinated to the dirhodium tetraacetate (1.5:1 molar ratio) measured in CD_3CN.

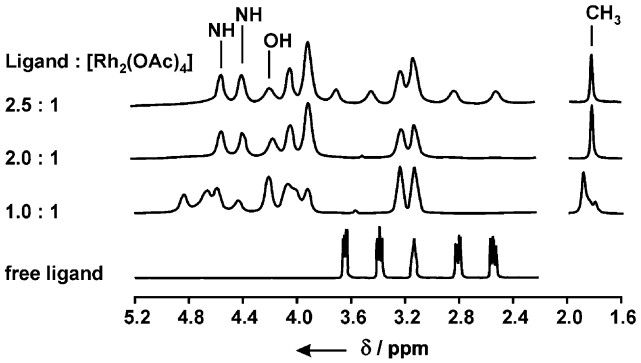

Figure 11. ^{1}H NMR titration of $[Rh_2(O_2CCH_3)_4]$ with the D-phenylalaninol in $CDCl_3$ solution at 243 K.

Table 2. ^{1}H, ^{13}C (parentheses), and ^{15}N NMR (square brackets) chemical shifts for D-phenylalaninol **5** and its 2:1 adduct with dirhodium tetraacetate in $CDCl_3$ at 243 K

Atoms	**5** δ (ppm)	Adduct δ (ppm)
CH_2	3.68; 3.42; (66.0)	4.02; 3.88[a]; (64.7)
CH_2	2.80; 2.48; (40.5)	3.19; 3.10; (39.2)
CH	3.12; (54.1)	3.88[a]; (36.5)
Ph(*i*)	(138.7)	NM
Ph(*o*)	7.19; (129.0)	7.44; (129.6)
Ph(*m*)	7.31; (128.5)	7.37; (127.9)
Ph(*p*)	7.23; (126.4)	7.29; (126.1)
NH_2	Ca. 1.8[b] [−348.5]	4.53; 4.37 [−364.8][c]
OH	Ca. 1.8[b]	4.15
$Rh_2(CO_2CH_3)_4$	NM	1.88 (24.0)

[a] Overlapped signals.
[b] Broad signal.
[c] $^{1}J(^{15}N–^{1}H)$ = 64 Hz; NM—not measured.

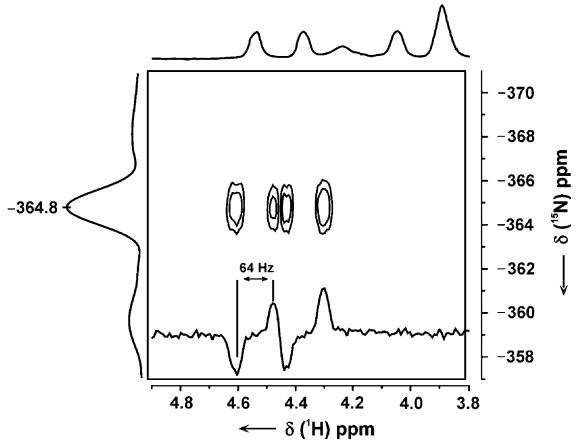

Figure 12. ^{15}N–^{1}H HSQC spectrum of 1:1 adduct between the D-phenylalaninol and Rh_2-core in $CDCl_3$ at 243 K. Intersections were taken at −364.8 ppm (horizontal trace, F2 domain) and 4.6 ppm (vertical trace, F1 domain).

a 1:1 ratio of the ligand to Rh_2-core. Thus, only a 1:1 adduct should be present in solution, since the $[Rh_2(OAc)_4]$ is practically insoluble in $CDCl_3$. This result can be explained assuming that, in chloroform solution, in addition to the above discussed 1:1 Rh_2–N type adducts, the polymeric arrays can also be formed by the complexation through oxygen atom of the hydroxy group (Rh_2-core–NH_2CHR–OH–Rh_2-core–NH_2CHR–OH, etc.). The ability of the $[Rh_2(OAc)_4]$ to form chain structure complexes in which Rh_2-cores are linked by axial ligands with at least two binding sites, for example, 2,6-diaminopyridine or 2-anilinopyridinate, is well known in the literature.[23] The NMR results are in agreement with the electronic absorption data discussed in Section 2.4.

The results of the NMR titration experiment in CD_3CN solution are shown in Figure 13 and Table 3. In contrast to $CDCl_3$, all reagents, Rh_2-core, and D-phenylalaninol **5**, are soluble in CD_3CN. However, due to the coordinating nature of the solvent molecule, the stock complex exists in the solution as an adduct with acetonitrile.[1] For this reason, the D-phenylalaninol **5** has to compete with solvent molecules for the complexation site.

In contrast to the experiments in $CDCl_3$ solution, the spectrum of the 0.5:1 mixture of Rh_2-core and phenylalaninol **5** in CD_3CN solution contains the relatively narrow signals of one adduct only. The different behavior of the ligand in CD_3CN solution can be explained by the influence of the solvent, which competes with the ligand and prevents its complexation via the oxygen atom. The five signals within the range from 2.8 to 4 ppm are assigned to the CH and CH_2 hydrogen atoms. The two multiplets at 4.50 and 4.32 ppm are assigned to

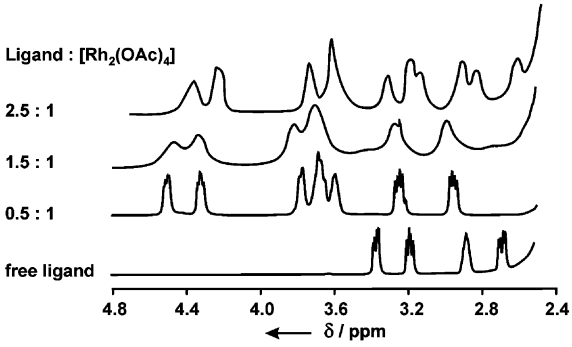

Figure 13. ^{1}H NMR titration of $[Rh_2(OAc)_4]$ with D-phenylalaninol in CD_3CN solution at 243 K.

Table 3. ^{1}H NMR chemical shifts for D-phenylalaninol **5** and its adduct with dirhodium tetraacetate in CD_3CN at 243 K

Atoms	**5** δ (ppm)	Adduct δ (ppm)
CH_2	NO[a]; 2.67	3.24; 2.95
CH_2	3.36; 3.18	3.78; 3.59
CH	2.87	3.67
Ph(*o*)	7.18[b]	7.38
Ph(*m*)	7.27	7.33
Ph(*p*)	7.18[b]	7.24
NH_2	NO[c]	4.50[d]; 4.32[e]
OH	NO[c]	NO[c]
$Rh_2(CO_2CH_3)_4$		1.74

[a] Not observed; overlapping with H_2O signal.
[b] Broad signals.
[c] Not observed.
[d] $^{2}J(^{1}H–^{1}H)$ = 10.5 Hz; $^{3}J(^{1}H–^{1}H)$ = 4.8 Hz.
[e] $^{2}J(^{1}H–^{1}H)$ = 10.5 Hz; $^{3}J(^{1}H–^{1}H)$ = 6.2 Hz.

the non-equivalent hydrogen atoms of NH_2 group. The coupling constant of 10.5 Hz can be assigned as $^2J(^1H–^1H)$ geminal coupling and couplings of 4.8 and 6.2 Hz can be attributed to the ^3J(NH–CH) couplings.

An excess of the stock complex in a 0.5:1 mixture assures the presence of a 1:1 adduct only. An addition of further quantity of ligand to the mixture to form complexes of 1.5:1 and 2.5:1 molar ratios resulted in the broadening of resonance signals. The signals of free phenylalaninol even appear in the 1.5:1 mixture.

Our NMR experiments in CD_3CN did not allow us to establish whether the 1:1 or 2:1 adduct is formed in solution in presence of ligand excess. However, it is obvious that, in CD_3CN solution, some sort of equilibrium exists between the free ligand and adducts, even in the 1.5:1 mixture. This observation also points to a different behavior of a given ligand in $CDCl_3$ solution.

From the above it can be concluded that:

(i) The low-temperature NMR experiments allow for the observation of resonance signals of the free ligand and Rh-adducts separately, including the signals of the OH group and of two nonequivalent hydrogen atoms in NH_2. In contrast, the spectrum taken at room temperature (303 K) consists of only one set of averaged signals.
(i) The D-phenylalaninol **5** generally tends to form successively either 1:1 or 2:1 adducts with Rh_2-core (Fig. 14).
(i) The ^{15}N NMR complexation chemical shift $\Delta\delta$, as well as the nonequivalency of hydrogen atoms in NH_2 group suggest that the phenylalaninol is binding via the nitrogen atom.

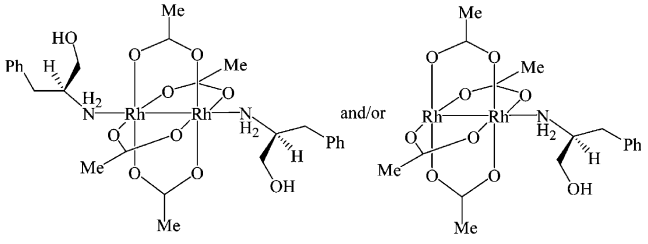

Figure 14. Postulated structures of the chiral complex of amino-alcohol with $[Rh_2(OAc)_4]$ formed in situ: 2:1 (left) and 1:1 (right) ligand-to-metal core.

2.6. Electrospray ionization mass spectrometry

Electrospray mass spectrometry is a helpful method for probing complexation processes between organic molecules.[24] ESI mass spectra recorded for two various solutions, each prepared by dissolving dirhodium acetate and phenylalaninol **5** in 1.5:1 ligand-to-metal molar ratio in acetonitrile and chloroform diluted by small amount of acetonitrile due to technical reason (5–6% acetonitrile in chloroform—for details, see Section 4), showed the presence of two common peaks at *m*/*z* 745 and 594 Th in each spectrum (Fig. 15). High resolution mass measurements revealed that the former corresponds to the ion of the composition $C_{26}H_{39}N_2O_{10}Rh_2$, whereas the latter to the ion of the composition $C_{17}H_{26}NO_9Rh_2$. These data suggest that in both cases the formation of protonated dirhodium-type complex ions, differing in the number of coordinated ligands, occurred. The 745 Th ion corresponds to the formation of a complex between phenylalaninol and dirhodium acetate in a 2:1 rate, whereas the 594 Th ion to the complex of 1:1 stoichiometry (ligand-to-metal). Mass spectra presented in Figure 15 also displayed two common peaks at 685 and 534 Th. Fragmentation analysis confirms that both arise from the dissociation processes of ions at 745 and 594 Th, respectively, in the course of acetate radical loss. Moreover, the data obtained from the cone voltage experiments revealed that ion at 594 Th cannot be formed from the 745 Th ion.

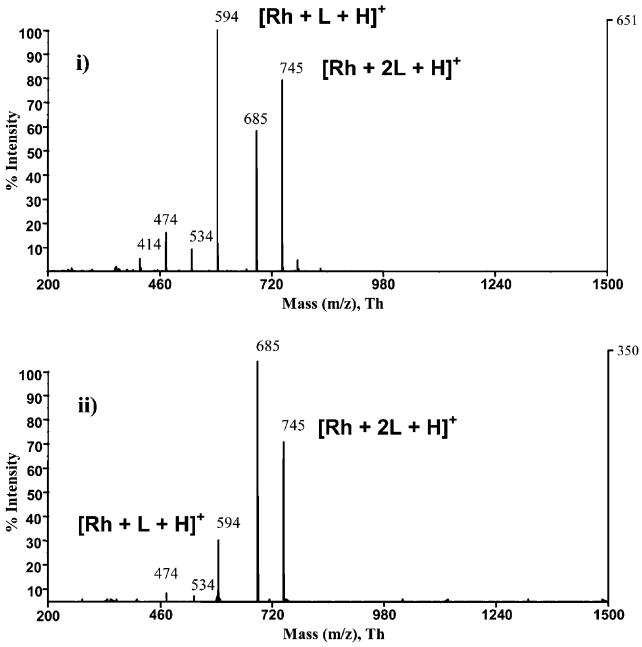

Figure 15. Electrospray mass spectra of the solution containing dirhodium tetraacetate and D-phenylalaninol **5** in a 1.5:1 ligand-to-metal molar ratio recorded in (i) CH_3CN and (ii) $CHCl_3$ (diluted by CH_3CN). L = D-phenylalaninol **5**; Rh = $[Rh_2(O_2CCH_3)_4]$.

On the basis of the results obtained, it can be concluded that the extent of complexation of amino alcohol to the dirhodium core is the same regardless of the solvent applied. It is worth mentioning that the above conclusion is in common with data obtained previously for chlorotetrabutyratiodiruthenium(II,III)-phenylalaninol system.[25]

2.7. Sector rule for correlation of the CD data with structure

The results presented above enable us to conclude that in both solvents, that is, chloroform and acetonitrile, and regardless of the ligand-to-metal molar ratios, the *vic*-amino alcohols coordinate to the Rh_2-core axially through the amino group to form 1:1 and/or 2:1 chiral complexes, predominately. Thus, amino alcohol molecules act as the unidentate ligands and some similarity between their CD spectra and those of amines can be

expected. This is indeed the case, as can be seen in Figure 16 where CD spectra of D-phenylalaninol **9** and D-phenylethylamine are presented.

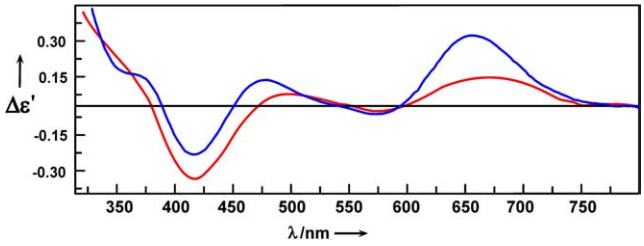

Figure 16. CD spectra of in situ formed Rh-complexes of D-phenylalaninol **9** (——) and D-phenylethylamine (——) recorded in chloroform.

The results allow further conclusion, namely, that due to the different structures of chiral complexes formed in ethanol versus acetonitrile and chloroform, the helicity rule developed for ethanol solution is not applicable in the case of the two latter solvents. It was previously stated that in the ethanol solution, a bridging type of ligation of a 1,2-amino alcohol to the Rh_2-core takes place.[7] Therefore, the achiral chromophore is incorporated into a chiral ring, which implies that the CD is mainly governed by a helicity rule. In the case of axial coordination, regardless of whether the chiral complexes are of 1:1 or 1:2 stoichiometry, a sector rule should correlate the CD data and structure.

Upon axial coordination of an amino alcohol (alcohols) the original D_{4h}-symmetry of the Rh_2-core remains for 2:1 complexes, and for 1:1 complexes it becomes slightly reduced to C_{4v}. In both cases, the chromophoric system formed includes Rh–N bond(s). According to Schellman and Ruch, an octant rule should be valid as the symmetry-determined simplest sector rule.[26,27] However, a more useful and simple sector rule for the CD band arising around 620 nm, shown in Figure 17, can be successfully used as a working tool. To apply the rule, the projection should be made along the metal–metal axis, that is, from the nitrogen toward the metal atom, with the longest chain of bonds of antiperiplanar conformation arranged upwards in the vertical plane. The existence of the antiperiplanar conformation adopted by

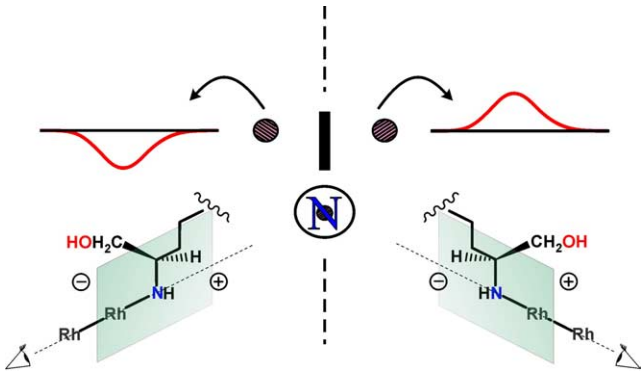

Figure 17. Empirical sector rule for correlation between stereochemistry of a 1,2-amino-alcohol and CD band above 600 nm.

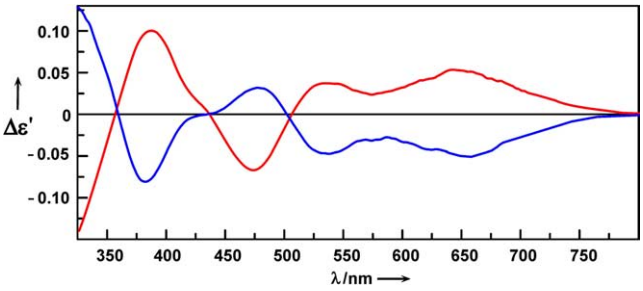

Figure 18. CD spectra of Rh-complexes of propranolols **20** (——) and **22** (——) recorded in chloroform.

the longest carbon–carbon chain connected to the N-atom is assumed to be preferable for steric reasons. Then, the group positioned 'right up back' shows the schematically drawn positive Cotton effect around 620 nm and the group positioned 'left up back' demonstrates a negative CE at the same wavelength.

The rule works for both acetonitrile and chloroform solutions. However, chloroform seems to be the solvent of choice for the purpose of stereochemical assignment because Cotton effects above 600 nm are present in the CD spectra of all amino alcohols investigated. In the case of acetonitrile no Cotton effects were observed in adrenaline type amino alcohols (compounds **19**–**22**) and sterically hindered ephedrine drugs **13**, **15** and **17**. The presence of a band around 550 nm observed in their absorption spectra indicates that in these cases solely adducts with solvent molecules were formed.

Due to the location of the CD band under consideration in the low-energy spectral region, which lies far away from the absorption region of common chromophores, the method can be also widely applied for compounds possessing an additional chromophoric system in the molecule. As an example, propranolols **20** and **22**, representing adrenergic drugs, can be mentioned. Their naphthalene chromophore absorbs more than enough to observe well-developed Cotton effects above 600 nm (Table 1, Fig. 18).

3. Conclusion

The in situ dirhodium method can be regarded as a straightforward and versatile method for the determination of the absolute configuration of *vic*-amino alcohols, supplementary to other methods, for example, exciton chirality method.[14–16] In comparison to the ECCD, the fact that no quantitative values were obtained could be regarded as a disadvantage of the proposed method. However, for the purposes of determining the absolute configuration, only the signs and the relative magnitudes of the Cotton effects are important, not their absolute values. On the other hand, this disadvantage is compensated for by the fact that there is no need to synthesize, isolate and purify any derivatives before obtaining the CD spectrum. It is worthwhile considering that, in general, less than 1 mg of the potential ligand is sufficient for obtaining a very good and reproducible CD spectrum.

The empirical rule correlating a sign of the Cotton effect above 600 nm in chiral dirhodium complexes is suitable for the absolute configurational assignment of a broad variety of *vic*-amino alcohols of adrenaline and ephedrine types. For this purpose, chloroform seems to be the solvent of choice because Cotton effects above 600 nm are present in the CD spectra of all amino alcohols studied and because this particular CE is relatively strong. In many cases, it was the strongest one observed.

4. Experimental

UV–vis spectra were measured on a Cary 100 spectrophotometer in acetonitrile and chloroform. CD spectra were recorded in the 250–800 nm range, at room temperature, with a Jasco 715 spectropolarimeter using acetonitrile and chloroform solutions in cells of 2, 10, or 20 mm path length (spectral band with 2 nm, sensitivity 10×10^{-6} or 20×10^{-6} ΔA-unit/nm). Depending on the S/N ratio, the λ-scan speed was 0.2 or 0.5 nm/s.

For CD standard measurements the solid chiral amino alcohol (1–5 mg, ca. 0.003 M/L) was dissolved in a stock solution of dirhodium tetraacetate (6–7 mg, ca. 0.002 M/L) in acetonitrile and chloroform so that the molar ratio of the stock complex to ligand was about 1:1.5, in general. In special cases, for example, concentration-dependent CD measurements, other metal-to-ligand ratios were used (see text). Some of the $\Delta\varepsilon'$-values were very small, but nevertheless the signal-to-noise ratio in all cases was better then at least 10:1.

All NMR measurements were conducted on a Bruker DRX-500 spectrometer equipped with 5 mm triple broadband inverse probe with *z*-gradient coil. ^{1}H NMR, ^{13}C NMR, ^{13}C,^{1}H HMQS, ^{15}N,^{1}H HMBC, and ^{15}N,^{1}H HSQC experiments were performed using standard Bruker software (XWIN NMR operating system). Typically, the sample contained ca. 7 mg of $[Rh_2(OAc)_4]$ in 0.7 mL of solvent (ca. 22 mM solution). Variable temperature spectra were recorded with a BVT 3000 temperature unit. Temperatures were read from the instrument panel; no additional temperature correction was performed.

The signals (ppm) were referred to solvent peaks ($CDCl_3$ ^{1}H residual peak, 7.26 ppm; $CHCl_3$ ^{13}C peak, 77.2 ppm, CD_3CN residual peak 1.93 ppm). ^{15}N chemical shifts are given with respect to CH_3NO_2 ^{15}N peak (0 ppm).

Typically, a 100×1024 (1024×1024) matrix was used for ^{13}C,^{1}H correlation experiments (HSQC and HMBC), with parameters acquisition time 0.13 s, relaxation delay 1.2 s, sweep width 159 ppm (20,000 Hz) in F1 (^{13}C) domain and 2–4 scans per experiment. A 40×512 (512×1024) matrix was used for ^{15}N,^{1}H HSQC correlation experiment, with parameters acquisition time 0.26 s, relaxation delay 1.5 s, sweep width 30 ppm (1517 Hz) and 32 scans per experiment. ^{1}H NMR spectra were recorded using the spectral resolution of ca. 0.2 Hz per point.

Mass spectrometry experiments were carried out with electrospray ionization time-of-flight mass spectrometer Mariner (Perseptive). Each measurement was performed after 2 h from the preparation of the corresponding solutions and additionally repeated after 24 h. The *m*/*z* values in the mass spectra were given in Th (Thomson) units according to the literature suggestion.[28] For technical reasons, mainly to make the ionization process the most effective, prior to acquiring the mass spectrum in chloroform, the analyte was diluted by a small amount of acetonitrile (5–6% acetonitrile in chloroform).

Source of compounds: compounds **1**–**22** were purchased from Fluka and/or Aldrich and used without further purification. Dirhodium tetraacetate as well as acetonitrile and chloroform (both Uvasol purity), were purchased from Aldrich and Merck, respectively. Acetonitrile was used without further purification, whereas traces of ethanol were removed from chloroform according to the common procedure.[29]

Acknowledgements

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