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Chiral Recognition of Olefins by ^{1}H NMR Spectroscopy in the Presence of a Chiral Dirhodium Complex[1]

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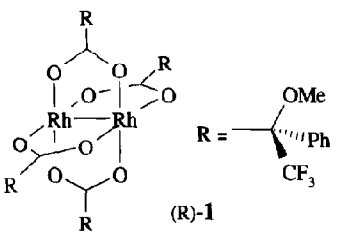
Abstract: A new NMR method using **1** for chiral recognition of olefins is presented and compared with Mannschreck's method using Yb(hfc)$_3$/Ag(fod). It was found that the spectroscopic results are comparable but the new rhodium reagent is much easier to handle and can readily be recovered.



(R)-**1**

INTRODUCTION

Asymmetric synthesis is one of the most important fields in modern organic chemistry. Therefore it is indispensable to have efficient methods for chiral recognition, i.e. for the determination of enantiomeric ratios. Here, NMR spectroscopy in the presence of chiral auxiliaries [mostly chiral alcohols and amines[2] or lanthanide complexes with chiral ligands (CLSR)[3]] has been applied successfully over many years. However, a number of functionalities like olefinic and aromatic hydrocarbons require the addition of a silver salt as a second auxiliary.[4,5] Recently, some binuclear metal complexes have been introduced as additives in CD spectroscopy,[6,7,8] and dirhodium tetraacetate has proved to be suitable for NMR investigations of olefins.[9] Since this complex is diamagnetic we were interested in further exploring its potential in NMR application. However, in contrast to CD, NMR spectroscopy is an achiral method so that we had to introduce chirality into the rhodium complex. So, we exchanged the acetate groups by enantiomerically pure Mosher's acid (MTPA)[10] to produce $Rh_2(MTPA)_4$ (1).

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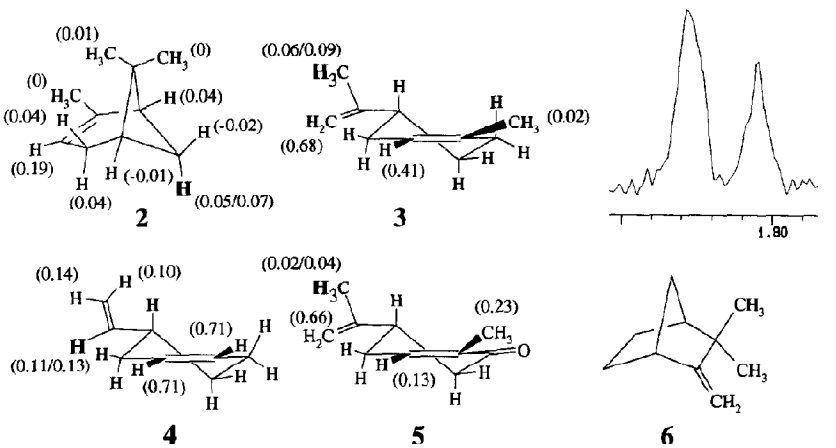
RESULTS AND DISCUSSION

In this preliminary communication we report our ^{1}H NMR results in the investigation of mixtures of both enantiomers of α-pinene (**2**), limonene (**3**), 4-vinyl-1-cyclohexene (**4**) and carvone (**5**). Many of the ^{1}H signals are shifted (Δδ, in ppm) to different extents on addition of **1** and few show splittings (Δ, in Hz) due to enantiomeric differentiation. Figure 1 shows all detectable Δδ-values (in parentheses) for an equimolar ratio of **1** and the respective olefin **2** - **5**. It is striking that in the dienes **3** and **5** the ^{1}H signals of the exocyclic double bond show larger shifts than those of the endocyclic double bond whereas in **4** the sequence is opposite. We assume that in each case the double bond with the larger Δδ-values is the binding site. Signal splittings Δ occur less frequently and not necessarily at signals with large shifts. Such data are collected in Table 1 for the olefins **2** - **5**.

Fig. 1: Structures of the olefins **2** - **5** (only one enantiomer despicted) and signals shifts (Δδ, in ppm, values in parentheses)[a] observed after addition of an equimolar amount of (R)-**1**; inserted spectrum shows the signal of the highlighted protons of **3** (resolution-enhanced).



[a] Hydrogens without numbers in parentheses: Δδ could not be determined due to signal overlap.

Table 1: Chemical shifts (δ, in ppm) and enantiomeric splittings (Δ, in Hz) of highlighted ^{1}H signals in **2** to **5** on addition of (R)-**1**

	2	**3**	**4**	**5**
δ [in ppm][a]	1.22/1.24	1.80/1.83	5.96/5.98	1.73/1.75
Δ [in Hz]	3.0	4.0	3.3[b]	2.7

[a] First value corresponds to the major [(+)**2**, (-)-**3**, (+)-**5**], the second to the minor enantiomer; **4** was a racemate so that an assignment is not possible.

[b] In this example the 3.3 Hz splitting was visible already at a molar ration of 0.33 (**1** : **4**).

In each instance there was one signal at which the enantiomeric purity of the olefins could be monitored because it was split according to the enantiomeric ratio of the olefins. The inverse experiment using (S)-**1** gave inverse results as expected.

In its spectroscopic results this new method seems to be equivalent to that proposed by Offermann and Mannschreck[4]. It might be inferior if there is severe steric crowding at the double bond. For example, camphene (**6**) with the two methyl groups in α-position to the double bond did not provide satisfactory signal shifts and splittings whereas Mannschreck's method works well with **6**. However, the use of **1** has - to our opinion - a number of advantages:

(a) The complex **1** is diamagnetic so that line broadening effects as observed in CLSR experiments, especially at higher concentrations, do not appear.

(b) It is a simple two-component-experiment whereas Mannschreck's method uses three and the selection of the three concentrations is often critical.

(c) Complex **1** is a stable and non-hygroscopic solid so that it can be synthesized, purified and handled without any special precautions. A $CDCl_3$ solution of **1** with a calibrated concentration can be used for many experiments over a long period of time.

(d) In contrast to the reagents used by Mannschreck's method, the dirhodium complex **1** can be recovered without significant loss by simply adding methanol to the mixture followed by a chromatographic separation with a mixture of petrol ether/diethyl ether/methanol (4 : 2 : 1).

(e) In general, ^1H signal shifts ($\Delta\delta$) are clearly smaller than in a CLSR experiment, especially when high CLSR molar ratios are needed. So, it is easier to identify the individual signals in the mixture, and the danger of signal overlapping is less severe.

Currently, we are investigating the scope and limits of the use of **1** for further olefins, and we are extending our study to other functionalities where Mannschreck's method fails and the classical CLSR application is difficult.

According to current catalogue prizes the total cost of **1** is approximately twice as much as for the CLSR/Ag(fod)-mixture calibrated to equivalent NMR experiments. However, the great stability of **1** and the possibility to recover it overcompensates the higher costs of the precursors.

EXPERIMENTAL

Dirhodium tetra-(R)-α-methoxy-α-(trifluormethyl)-phenylacetate (**1**) is prepared as follows:[11] 500 mg of commercially available $Rh_2(OCOCH_3)_4$ (1.13 mmol) were dissolved in 20 ml of an aqueous solution (2 M) sodium carbonate and heated to 80 °C for 20 min until a blue-purple colour appeared. After cooling and filtration the residue was washed with small portions of water, methanol and ether. Drying at 50 °C *in vacuo* afforded a light blue-purple crystal powder of rhodium carbonate sodium salt[10] in ca 90% yield.

100 mg of the rhodium carbonate sodium salt (0.18 mmol) and 350 mg R-MTPA (1.48 mmol, 8 molar equivalents, e.e.: 98.5%) were dissolved in 10 ml water under nitrogen atmosphere and heated to 90°C for 40 min until a blue-green sticky solid separated. After cooling the water was decanted, the residue dissolved in CH_2Cl_2 and the organic layer washed 3x with 2 M sodium carbonate solution and 2x with water to remove an excess of MPTA. Further chromatographic purification on silica gel with CH_2Cl_2/ethyl acetate (9 : 1) as eluents gave green crystals which decompose above 200°C.

$[\alpha]_D^{20}$ = -201±10 (c 0.0048, $CHCl_3$); IR (KBr, cm^{-1}) 3055, 3000, 2955, 1616, 1391, 1266, 1169, 816.

^{1}H NMR ($CDCl_3$, δ) 3.16 (s, 3H, OCH_3), 7.1-7.31 (m, 5H, Ph). ^{13}C NMR (CD_3OD, δ) 55.4 (OCH_3), 85.3 (C), 128.0 (CF_3), 130.2 (C-*para*), 129.0 and 128.8 (C-*ortho* and C-*meta*), 133.2 (C-*ipso*), 186.7 (C=O). FAB-MS (m/z) 1138 (M^+). Found: C, 42.6%; H, 3.02%. Calculated: C, 42.2%; H, 2.83%.

The syntheses of **1** with (S)-MTPA (e.e.: 98.5%) is analogous, and all physical and spectroscopic data are the same except $[\alpha]_D^{20}$ = +187±10 (c 0.0048, $CHCl_3$). The great experimental errors of the two $[\alpha]_D^{20}$-values are due to the low transparency of **1** and low rotation angles. Consequently, α-values had to be determined at very low concentrations in 1-cm-cuvettes and were not precise.

^{1}H NMR spectra were recorded on a Bruker WP-200 at 200 MHz in 5 mm probes. The olefins were added to ca 4 mmolar solutions of **1** in $CDCl_3$. Chemical shifts are referred to the $CHCl_3$ signal (δ = 7.26) for ^{1}H and to the central peak of CD_3OD (δ = 49.0) for ^{13}C. Resolution enhancement facilitates the determination of the enantiomeric purity. Typically, the number of accumulations was 128 resulting in ca 10 min recording time for each spectrum. ^{1}H signal assignments of the olefins were assured separately by ^{1}H-decoupling, NOE and COSY experiments.

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