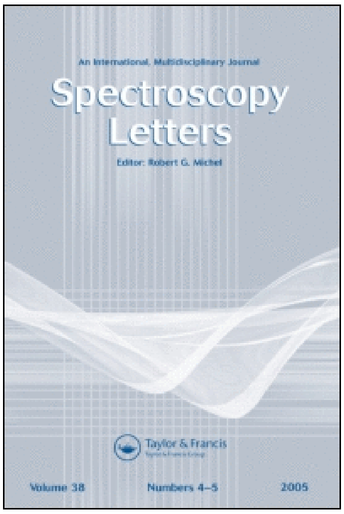

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# NMR Spectroscopic Study of Camphanic Acid, $Rh_2[Camphanate]_4$, and its Adducts with 1,4-Benzodiazepines

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# NMR SPECTROSCOPIC STUDY OF CAMPHANIC ACID, $Rh_2$[CAMPHANATE]$_4$, AND ITS ADDUCTS WITH 1,4-BENZODIAZEPINES

Key words: NMR study, Camphanic acid, Dirhodium tetracamphanate complex, 5-Pyrido-1,4-benzodiazepin-2-ones

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## ABSTRACT

The $^1$H and $^{13}$C NMR spectra of chiral camphanic acid, lactone of *(1S,3R)*-1-hydroxy-2,2,3-trimethyl-cyclopentan-1,3-dicarboxylic acid (**1**), and dirhodium tetracamphanate complex (**2**) were completely assigned on the basis of one- and two-dimensional NMR experiments. The NMR spectra of the adducts of dirhodium tetracamphanate **2** with 5-pyrido-1,4-benzodiazepin-2-ones **3** and **4**, complexes with catalytic activity, support the assignation and also revealed two different types of axial complexation of these nitrogen ligands.

## INTRODUCTION

Dirhodium tetracarboxylate complexes $Rh_2(OCOR)_4$ have attracted a considerable interest due to their catalytic and biological activity. These dimeric compounds form a rhodium-rhodium multiple bond, while four carboxylates bridge two rhodium atoms.[1] Two axial positions can be occupied by a variety of $\sigma$ and $\pi$ donor ligands.[1,2] Many examples of two nitrogen ligands bound in monodentate mode to axial positions yielding symmetric 2:1 adducts $R'_2NRh(OCOR)_4RhNR'_2$ are reported in the literature.[1] The ligands in the axial positions, unlike the equatorial carboxylate ligands, are labile and can easily be exchanged. The adducts of dirhodium tetracarboxylates with nitrogen bases are important complex species because of their biological activity[3] and catalytic properties.[4,5] Biological activity has stimulated an intense study of the chemistry of achiral dirhodium tetracarboxylates, mainly dirhodium tetraacetates with ligands of relevance in biology such as adenine and other nucleobases, or some model bisnitrogen ligands.[6-8]

Camphanic acid (**1**) is a well known chiral auxiliary agent, used for separation of racemates,[9,10] in the preparation of chiral phosphine ligands for Rh(I) complex catalysis,[11,12] and in structural studies.[13,14] However, there is no report on the full assignment of proton and carbon atoms in the $^1H$ and $^{13}C$ NMR spectra of camphanic acid or its complex salts.

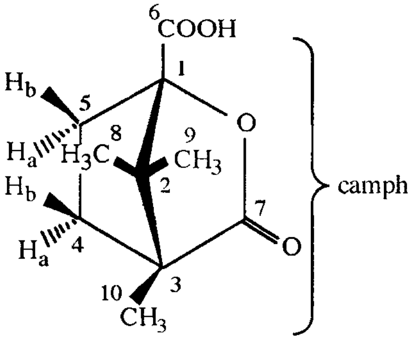
## EXPERIMENTAL

*NMR experiments.* The $^1H$ and $^{13}C$ NMR spectra were recorded at 25°C with a Varian-Gemini 300 spectrometer operating at 300.08 and 75.46 MHz, respectively. Each one-dimensional $^1H$ NMR spectrum was collected using a single 30° (5 ms) pulse, 1 s of relaxation delay time, the acquisition time of 2.0 s, and with total sweep width of 3000 Hz, sampled with 12K points. Data processing employed a Lorentz line broadening factor of 0.5 Hz. The spectra were referenced to the residual solvent signals [$(CD_3)_2CO$ $\delta = 2.04$, $C_5D_5N$ $\delta = 7.19$, and $CDCl_3$ $\delta = 7.26$ ppm]. The sweep width used for the $^{13}C$ NMR spectra were 18000 Hz, the pulse width was 4.5 ms (30°), the acquisition time was 1.25 s and the relaxation delay was 1 s. Chemical shifts were measured relative to internal solvent signals set at [$(CD_3)_2CO$ $\delta = 29.8$, $C_5H_5N$ $\delta = 123.5$, and $CDCl_3$ $\delta = 76.9$ ppm] downfield to tetramethylsilane.

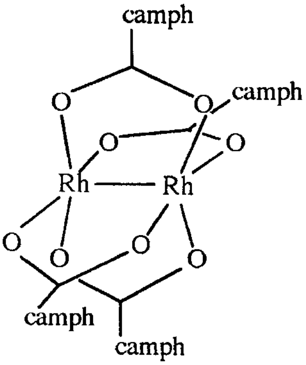
Two-dimensional experiments: homonuclear $^1H$-$^1H$ chemical shift correlation (COSY) spectra, NOESY and HETCOR were performed at 25±1°C using a standard sequence of the Varian Gemini software package. The COSY spectra were obtained in the magnitude mode, while the NOESY spectra were obtained in the phase-sensitive mode. The COSY and NOESY experiments had 1024 points in the F2- and 256 slices in Fl-dimensional, which were zero-filled to 1024 points. Each slice was obtained using 16 averages, the relaxation delay of 1 s and the spectral width of 3000 Hz. The resolutions in both domains were 6.0 Hz/point. The NOESY employed the mixing time of 700 ms.

The HETCOR experiment had 2048 points in F2- and 256 slices in Fl-dimension and they were zero-filled to 512 points. Each slice was obtained using 128 repetitions, the relaxation delay of 1 s and the spectral width of 13600 Hz in F2 and 2700 Hz in Fl domains, respectively. The resolution in F2 was 13.3 Hz/point and in Fl dimension it was 10.5 Hz/point. The protons were decoupled with Waltz 16 modulation.

The compounds **1-4** are prepared as already described.[14,15]



**1**



**2**

## RESULTS AND DISCUSSION

Preliminary assignation of the carbon atom resonances in **1** and **2** has been performed on the basis of one-dimensional $^{13}C$ NMR spectra, Table 1. Quarternary atoms C-2 and C-3 are magnetically very similar, and distinction was based on higher deshielding of the C-3 atom, $\alpha$- to the lactone carbonyl group, than of the C-2 atom in $\beta$-position to carbonyl and carboxyl groups. From this reason the resonance of C-10-methyl carbon appears at the highest field, while the difference in chemical shifts between resonances of C-8- and C-9-methyl carbons is less pronounced. The lactone carbonyl C-7 resonance in three solvents is found at 8.6, 9.6 and 5.52 ppm downfield from the carboxylic carbonyl C-6 resonance. Similar difference in deshielding effect is observed for C-4 and C-5.

The $^1H$ NMR spectrum of **1** is apparently simple in various solvents and consists of the three singlets for the methyl groups and four multiplets for four protons in the ethylenic subunit. Still, full assignment of the spin systems in **1** and **2** was possible only after detailed analysis of the COSY, HETCOR and NOESY spectra. The $^1H$ NMR chemical shift data in deuteroacetone, deuteropyridine and deuterochloroform are listed in Table 2. In the COSY spectra of **1**, the cross-peaks of the methylenic protons attached to C-4 and C-5 atoms have been observed. Each proton rises three cross-peaks, a characteristic pattern for two vicinal methylene groups with four nonequivalent protons. Distinction between protons bound to C-4 and C-5 was made on the basis of two-dimensional heteronuclear correlation (HETCOR) spectra, wherein two pairs of cross-peaks revealed the interaction between two methylene groups (Fig. 1).

The carbon atom resonance in the higher field (29.27 ppm in deuteroacetone) is connected to the proton resonances at 1.616 and 2.036 ppm, while the second carbon ($\delta = 31.23$ ppm) is attached to the protons rising signals at 1.981 and 2.475 ppm, respectively (Table 2). Camphanic acid **1** forms pyridinium salt, and in deuteropyridine carboxylic group deshields both protons on C-5 more than on C-4; *syn* ($H_b$) and *anti* ($H_a$) protons still remain undistinguishable.

**Table 1**. $^{13}C$ Chemical Shift Data ($\delta$ in ppm) of Camphanic Acid (**1**) and $Rh_2(camph)_4$ (**2**) in Deuteroacetone, Deuteropyridine and Deuterochloroform at 25°C.

| Carbon | **1** | | | **2** | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $(CD_3)_2CO$ | $C_5D_5N$ | $CDCl_3$ | $(CD_3)_2CO$ | $C_5D_5N$ | $CDCl_3$ | $\Delta_1^a$ | $\Delta_2^a$ | $\Delta_3^a$ |
| C-1 | 91.65 | 92.68 | 91.65 | 91.20 | 91.77 | 91.35 | -0.45 | -0.91 | -0.30 |
| C-2 | 54.33 | 54.20 | 54.82 | 53.74 | 54.12 | 53.96 | -0.59 | -0.08 | -0.86 |
| C-3 | 55.30 | 55.38 | 55.34 | 54.37 | 54.85 | 54.54 | -0.93 | -0.53 | -0.80 |
| C-4 | 29.27 | 29.65 | 29.24 | 28.76 | 29.21 | 28.77 | -0.51 | -0.44 | -0.47 |
| C-5 | 31.23 | 31.46 | 30.95 | 30.74 | 31.48 | 30.81 | -0.49 | -0.02 | -0.16 |
| C-6 | 168.88 | 170.95 | 172.71 | 186.52 | 187.71 | 186.45 | 17.64 | 16.76 | 13.74 |
| C-7 | 178.47 | 179.55 | 178.23 | 177.75 | 178.52 | 178.14 | -0.72 | -1.03 | -0.09 |
| C-8 | 16.96 | 17.28 | 16.96 | 16.68 | 17.20 | 17.27 | -0.28 | -0.08 | 0.31 |
| C-9 | 16.96 | 17.22 | 16.91 | 16.40 | 17.05 | 16.84 | -0.56 | -0.17 | -0.07 |
| C-10 | 9.97 | 10.22 | 9.93 | 9.32 | 10.00 | 9.68 | -0.65 | -0.22 | -0.25 |

[a] $\Delta_1 = \delta_2 - \delta_1$ of respective signals of **1** and **2** in $(CD_3)_2CO$; $\Delta_2 = \delta_2 - \delta_1$ of respective signals in $C_5D_5N$; $\Delta_3 = \delta_2 - \delta_1$ of respective signals in $CDCl_3$.

**Table 2.** $^1H$ Chemical Shift Data ($\delta$ in ppm) of Camphanic Acid (**1**) and $Rh_2(camph)_4$ (**2**) in Deuteroacetone, Deuteropyridine and Deuterochloroform at 25°C

| | **1** | | | **2** | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Proton | $(CD_3)_2CO$ | $C_5D_5N$ | $CDCl_3$ | $(CD_3)_2CO$ | $C_5D_5N$ | $CDCl_3$ | $\Delta_1{}^a$ | $\Delta_2{}^a$ | $\Delta_3{}^a$ |
| H-$4_a$ | 1.616 | 1.413 | 1.735 | 1.492 | 1.408 | 1.592 | -0.124 | -0.005 | -0.143 |
| H-$4_b$ | 2.036 | 1.671 | 2.101 | 1.914 | 1.662 | 1.877 | -0.122 | -0.009 | -0.224 |
| H-$5_a$ | 1.981 | 1.901 | 1.976 | 1.699 | 1.691 | 1.694 | -0.282 | -0.210 | -0.282 |
| H-$5_b$ | 2.475 | 2.397 | 2.473 | 2.347 | 2.284 | 2.349 | -0.128 | -0.113 | -0.124 |
| Me-8 | 1.100 | 0.915 | 1.141 | 0.917 | 0.825 | 0.987 | -0.183 | -0.080 | -0.154 |
| Me-9 | 0.947 | 0.842 | 1.025 | 0.685 | 0.711 | 0.740 | -0.262 | -0.131 | -0.285 |
| Me-10 | 1.069 | 0.904 | 1.106 | 0.978 | 0.889 | 1.051 | -0.091 | -0.015 | -0.055 |

[a] $\Delta_1 = \delta_2 - \delta_1$ of respective signals of **1** and **2** in $(CD_3)_2CO$; $\Delta_2 = \delta_2 - \delta_1$ of respective signals in $C_5D_5N$; $\Delta_3 = \delta_2 - \delta_1$ of respective signals in $CDCl_3$.

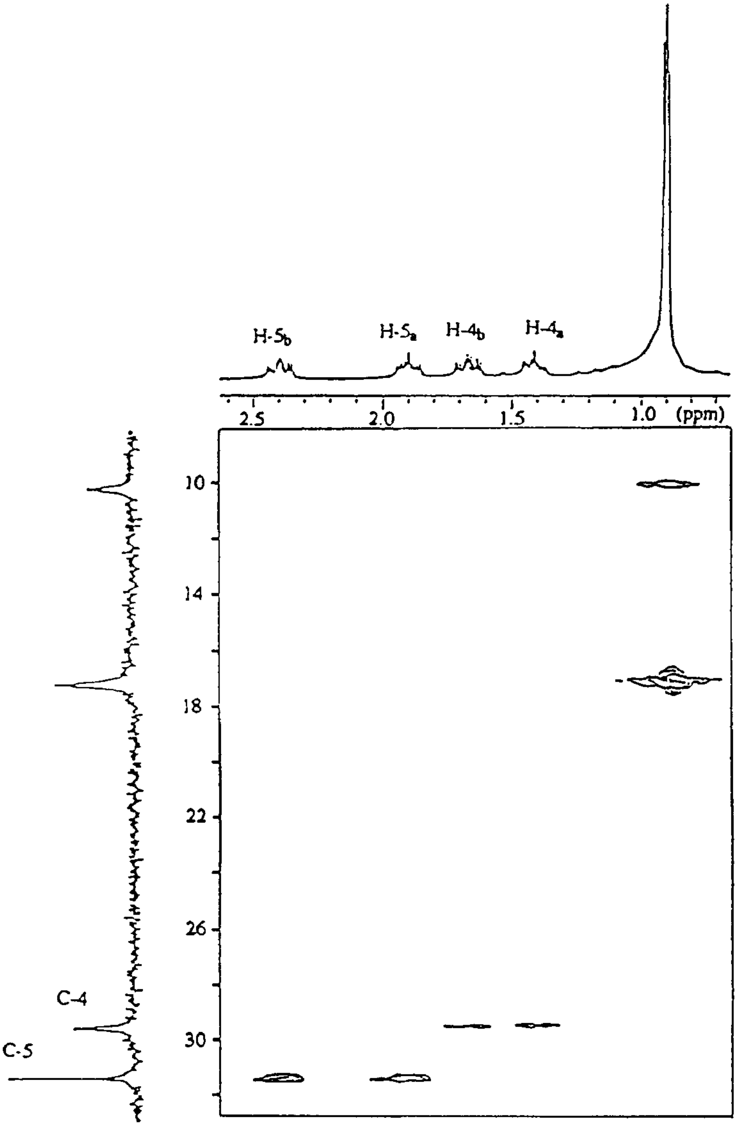


**Fig. 1.** $^1H$-$^{13}C$ heteronuclear correlation (HETCOR) spectrum of camphanic acid (**1**) in deuteropyridine, 25°C

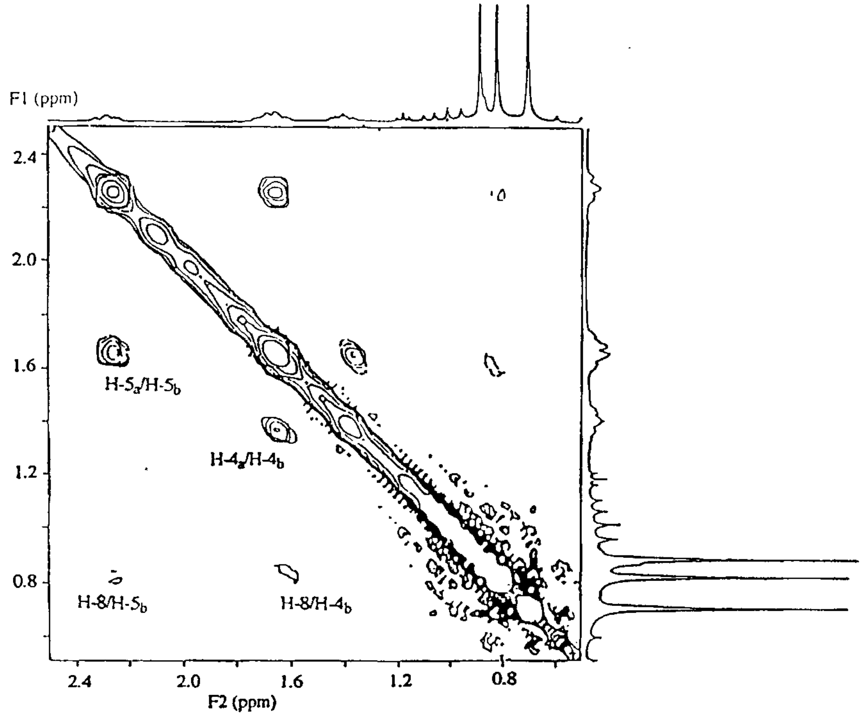


**Fig. 2.** NOESY spectrum of $Rh_2(camph)_4$ (**2**) in deuteropyridine, 25°C.

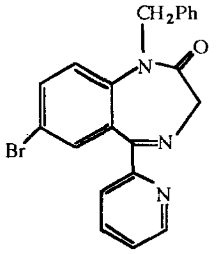
The intramolecular proton-proton connectivities observed in the NOESY spectrum (Fig. 2) provides additional piece of information which allow unambiguous assignation of the methylenic protons. Two cross-peaks between methylene and methyl regions were assigned to the *syn* protons ($H_b$) on C-4 and C-5, and C-8-methyl group, *i.e.* to the protons which are the closest through space. The chemical shift sequence of the proton signals of **1** in deuteroacetone and deuterochloroform is $\delta H\text{-}5_b > \delta H\text{-}4_b > \delta H\text{-}5_a > \delta H\text{-}4_a$, while in deuteropyridine it is $\delta H\text{-}5_b > \delta H\text{-}5_a > \delta H\text{-}4_b > \delta H\text{-}4_a$.

In dinuclear Rh(II) complex **2** all protons of **1** are shielded (Table 2), but the sequence of the methylenic proton resonances is not affected. The most shielded protons in deuteroacetone and deuterochloroform are closest to the carbonyl group, *i.e.* H-$5_a$ and Me-9 ($\Delta\delta$ is approx. 0.27 ppm). The most distant protons of Me-10 are least affected. Owing to the formation of pyridine adduct all protons in **2** are less shifted to higher field in deuteropyridine than in deuteroacetone.

In the complex **2** all carbon resonances of the ligand, except that of C-6, are shifted less than 1 ppm, as compared to the same resonances for **1**. It is interesting to note that the axial coordination of pyridine to **2**, which strongly influences its chromophoric system as demonstrated by UV and CD spectra,[14,16] does not significantly influence the $\delta$ values of carbons in **2** as compared to the values in the deuteroacetone and deuterochloroform (Table 1). A large effect in the corresponding proton spectrum might be attributed to the well-known aromatic solvent induced shift (ASIS) effect of pyridine.

In conclusion, the NMR data revealed strong electron transfer from the carboxylic group to the Rh(II) atoms in dinuclear complex **2**. The reactivity of the Rh(II) tetracarboxylates in catalytic cyclopropanation (coordination of electron-defficient carbene) presumably derives from this property.[17]

Coordination of 5-pyrido-1,4-benzodiazepin-2-ones **3** and **4** to **2** was then studied, since we notified that complexes of 1,4-benzodiazepines with Rh(OAc)$_4$ are catalysts in hydrogen transfer reactions.[5] Signals that belong to atoms near the coordination site are sometimes broad in the NMR spectra of such complexes, because of kinetic unstability of such organometallic species.[18]



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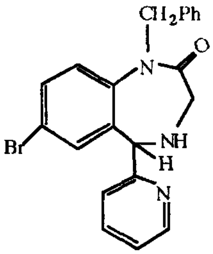
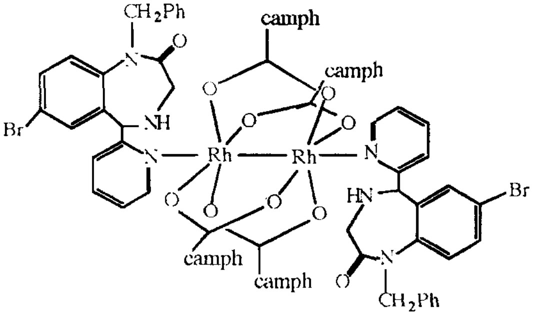


**4**

In the $^{13}$C NMR spectrum of dirhodium tetracamphanate **2** adduct with ligand **3** all signals are broadened, in particular those at $\delta$ 30.81, 53.96, 91.35 and 186.45 ppm, belonging to C-atoms near to coordination site; C-5, C-2, C-1 and C-6. $^{13}C$ NMR spectrum of the adduct with **4** exhibit similar feature, confirming the assignation of the signals for C-2 and C-3.

$^{1}H$ NMR spectra (Fig. 3), revealed that complexation of **2** with **3** or **4** originated a different types of adducts. The $^{1}H$ NMR of adduct from **2** and saturated ligand **4** is quite simple and shows only three singlets for three methyl groups in camphanic subunit. The final spectrum of the adduct reveals 1:2 ratio of **2**:**4**. This suggests that structural equivalence of all four camphane moieties is remained, and benzodiazepine is loosely bound (freely rotating) as monodentate ligand. The accumulated evidence indicates the structure **5** for **2**:**4** adduct, similar to that of dirhodium tetraacetate with pyridine.[1] Two molecules of 4,5-dihydro-ligand **4** are coordinated *via* pyridine nitrogen to both rhodium atoms of **2**. Since pyridine nitrogen disposes with better π-back donating properties than N-4, it is preferred for the coordination to the axial position of the Rh atom.[19]



**5**

On the other hand, $^{1}H$ NMR spectra of adduct **2**:**3** are a much more complex; a multiplicity of methyl signals appears in the final adduct, which exhibits 1:1 stoichometry. This suggest that complex has nonsymmetrical structure **6**, similar to the structure of dirhodium tetraacetate complex with bipyridine.[3] Its formation require the cleavage of Rh-O bond and displacing of one camphanic molecule to the second rhodium atom. Interaction of this type with adenine groups is of importance for the biological, carcinostatic activity of rhodium dinuclear complexes with achiral carboxylic acids.[6] Analogous binding

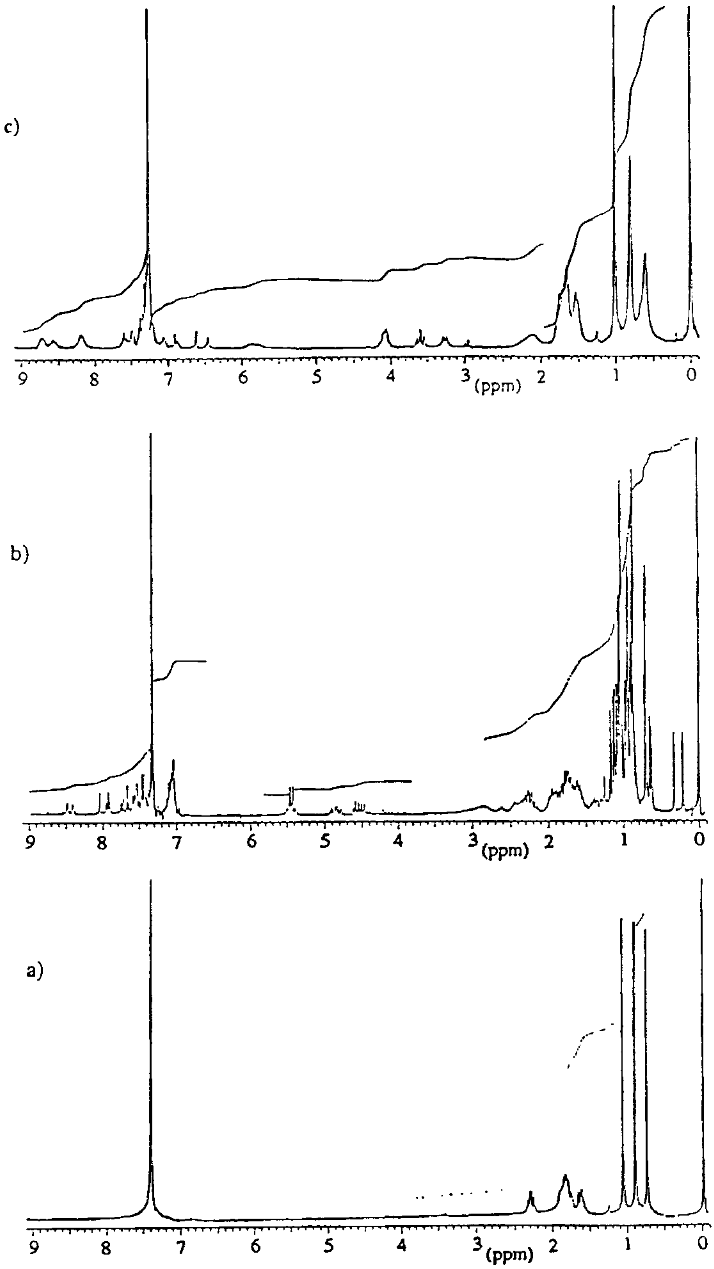
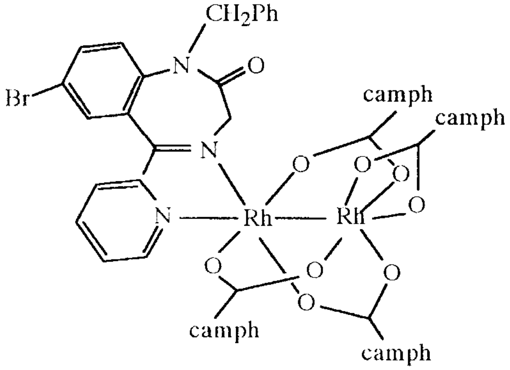


**Fig.** 3. The $^1$H NMR spectra in deuterochloroform of **a**) $Rh_2$[camphanate]$_4$ (**2**); **b**) adduct of $Rh_2$[camphanate]$_4$ with **3**; **c**) adduct of $Rh_2$[camphanate]$_4$ with **4**.

in **6** generates one specific coordination site on the second Rh atom, and renders the whole complex topologically well defined. Study of the enantioselectivity of chiral complexes **5** and **6** in some model reactions (hydrogen transfer, cyclopropanation) is envisaged.



**6**

## CONCLUSION

In conclusion we can state that combined NMR techniques, herein described, allowed complete assignment of $^{13}C$ and $^{1}H$ NMR spectra of camphanic acid, well known chiral auxiliary agent, and its Rh(II) dimeric salt. From the NMR data can be also concluded on the electron transfer from the carboxylic group to the Rh-atoms in dinuclear complex **2**. Reactivity of Rh(II) carboxylates in some catalytic reactions resides presumably in this property.

NMR spectra of the adducts of dirhodium tetracamphanate **2** with 5-pyrido-1,4-benzodiazepines **3** and **4**, *i.e.* **6** and **5**, confirmed the assignation, and revealed two different types of complexation in these adducts. Whereas the former ligand forms 1:1 adduct with bidentate bound pyridobenzodiazepine as the most stable, the latter is bound *via* pyridine nitrogen in the symmetric 2:1 adduct. Reported results are expected to contribute to general understanding of catalytic activity and enantioselectivity of this type of chiral complexes.

## ACKNOWLEDGMENTS

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