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Structure and Relative Stability of Dirhodium Tetracamphanate Adducts with 5-Pyrido-1,4-benzodiazepines and Their 4,5-Dihydro Congeners; First Representatives of Non-Symmetric Bidentate 1,4-Bisnitrogen Ligands

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^{1}H-NMR Spectra of dirhodium tetracamphanate adducts with 5-pyrido-1,4-benzodiazepin-2-ones **3–5** reveal different modes of complexation. Depending on the structure of the chelating pyridobenzodiazepine, two types of kinetic and dynamic profiles are observed. Ligands **3** and **4**, possessing a 1,4-bisnitrogen subunit with 4π electrons, behave as bidentate ligands and form the kinetically stable 1:1 adducts, non-symmetric diastereomers **6A, 7A**, which undergo fast isomerization into the thermodynamically more stable **6B, 7B**. Ligand **5** (4,5-dihydro derivative of **4**) behaves as a pyridine derivative, forming the kinetically stable, symmetric 2:1 aduct **8**, which very slowly isomerizes into non-symetric 1:1 aduct **9**. The relative stability of **8** is attributed to the hydrogen bonding N(4)-H-O(camphanyl), as well as to the low coordinating ability of the non-conjugated, pyramidal N(4) atom.

INTRODUCTION

The dirhodium tetracarboxylate complexes with nitrogen bases have attracted considerable interest due to their catalytic[1,2] and biological activity.[3–6] There is a whole variety of chelate binding modes for the complexes of dirhodium tetracarboxylates and bisnitrogen bases. The most detailed stud-

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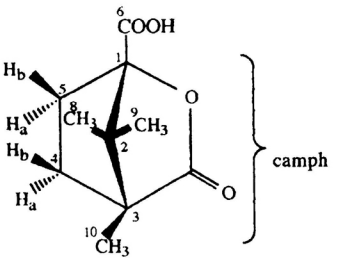

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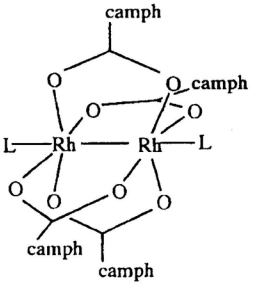
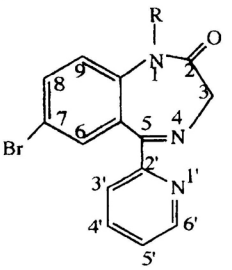
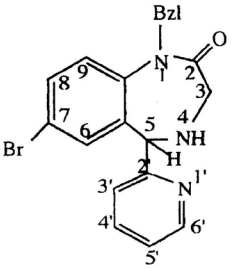


2 L=EtOH



3 R=H
4 R=Bzl



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ies of achiral tetracarboxylates have been reported by Cotton *et al.*[7,8] and Crawford *et al.*[3] These authors have determined the solid state and solution structure of the 2,2'-bipyridine adduct with $Rh_2(OCOCH_3)_4$. In the solid state, 2,2'-bipyridine is bound as a bidentate ligand to one Rh atom, and it shifts one acetate group to the second rhodium atom as 1,3-O,O'-bidentate ligand.[3a] In solution, various bipyridyl adducts with variable chelating modes are present.[3b] However, there is no report on the bidentate chelating of non-symmetric bisnitrogen ligands to one rhodium atom.

Two properties of chiral rhodium tetracarboxylate complexes govern their applications in homogeneous catalysis: the effective transfer of chiral information present either in the carboxylic acid subunit or in the nitrogen base, and the kinetic stability of the catalytically active complex formed on coordination of the substrate and reactant to the rhodium atom(s). So far, the chirality transfer in the dirhodium tetracarboxylate catalyzed reactions has been regularly derived from the chiral carboxylic acid subunit. It was usually introduced as a chiral carboxylate anion,[9,10] only recently Doyle *et al.*[11] have de-

scribed the efficient enantioselective cyclopropanation with the complexes of chiral 5-membered lactames as 1,3-bidentate ligands.

All these facts stimulated us to study the adducts obtained from dimeric rhodium tetracamphanate **2** and two structurally different types of 5-pyrido-1,4-benzodiazepines **3, 4** and their 4,5-dihydro congener **5**. Recently, we have determined the solid state structure of Rh_2(camphanate)$_4$ (**2**) and the UV/CD properties of adducts with MeOH and pyridine.[12] In order to interpret the NMR spectroscopic data for adducts **6–9**, obtained by the complexation of **2** with 5-pyrido-1,4-benzodiazepin-2-ones **3–5**, a need for complete assignement of the spectra of compounds **1** and **2** arose. In a recent communication,[13] we have reported fully assigned all proton and carbon atoms in the ^{1}H- and ^{13}C-NMR spectra of camphanic acid (lactone of (1*S*, 3*R*)-1-hydroxy-2,2,3-trimetehyl-cyclopentan-1,3-dicarboxylic acid, **1**) and dirhodium tetracamphanate complex **2** on the basis of one- and two-dimensional experiments in different solvents.

At this point, we became interested in getting more insight into the solution structure of the benzodiazepine adducts obtained by the complexation of **2** with 7-bromo-1,3-dihydro-5-(pyrid-2'-yl)-2H-1,4-benzodiazepin-2-one (**3**),[14,15] the corresponding 1-benzyl-derivative (**4**)[16] and its 4,5-dihydro congener (**5**),[17] where the benzodiazepines **3–5** are potential 1,4-bidentate ligands. Owing to their non-symmetry, a bidentate binding mode can give rise to diastereometric complexes. In principle, the larger number of catalytically active diastereomeric species in the cycle, the lower enantioselectivity of transformation of prochiral substrate is expected.[18] Therefore, a study of diastereomeric species present in solution is valuable for designing highly enantioselective catalysts based on adducts of dimeric rhodium tetracarboxylates.

RESULTS

*^{1}H-NMR Spectra Analysis of the Rh_2(camphanate)$_4$ Adducts with 5-pyrido-1,4-benzodiazepines **6–9***

*A. (Rh_2(camphanate)$_4$ × ((7-bromo-1,3-dihydro-5-(pyrid-2'-yl)-2H-1,4-benzodiazepin-2-one)) (**6**)*

The ^{1}H-NMR spectrum of the free ligand **3** shows a singlet for NH at δ = 9.23, a doublet at δ = 8.64 (J = 4.7 Hz) for H-6', a multiplet for the aromatic protons at δ = 6.94 – 8.06, and a sharp singlet at δ = 4.37 for the H-3 atoms (Table I).

Formation of complex **6** is observed at a molar ratio of **3:2** = 0.5:1 (Table I). Doublet for H-6' in **6** is shifted upfield to δ = 8.28. The sharp singlet for H-3 atoms of nitrogen ligand **3** is transformed into two doublets. One of them

TABLE I

Characteristic ^1H chemical shift data for ligands **3–5** and complexes **2** and **6–9** in $CDCl_3$ at R.T.

Compound	Molar ratio L:2 or time intervals	H-6' A	H-6' B	H-5 A	H-5 B	PhCHa,b		H-3a, H-3b A	H-3a, H-3b B	Me		
2										1.04	0.88	0.73
3		8.64		–		–		4.37				
4		8.64		–		5.01	5.26	4.97	3.97			
5		8.58		5.03		3.45	3.23	3.80				
6	0.5 : 1.0	8.28						5.30 (5.86)	4.39 (4.67)			
	1.0 : 1.0	8.29						5.33	4.38			
	1.5 : 1.0	8.29						5.33	4.38			
	2.0 : 1.0	8.29						5.33	4.38			
7	0.5 : 1.0	8.26				5.43	4.84	5.94, 4.58	5.56, 4.31			
	1.0 : 1.0	8.38	8.30			"		"				
	1.5 : 1.0	8.40	8.34			"		"				
	2.0 : 1.0	8.40	8.34			"		"				
7	0 hours	10.41, 10.36				5.43	4.84	5.94, 4.58	5.56, 4.31			
	3 hours		8.41, 8.34			5.40	4.82		5.40, 4.46			
	24 hours		8.41, 8.34			5.40	4.82		5.40, 4.46			
	14 days		8.41, 8.34			5.40	4.82		5.40, 4.46			
8	0.5 : 1.0	8.72, 8.63		5.93, 5.86		3.60	3.28	4.09		1.03	0.84	0.69
	1.0 : 1.0	"		5.89, 5.78		3.58	3.25	4.07		1.00	0.82	0.63
	1.5 : 1.0	"		5.86, 5.76		3.58	3.25	4.03		0.99	0.80	0.59
	2.0 : 1.0	"		5.80, 5.70		3.58	3.25	4.00		0.98	0.78	0.57
9	3 hours	9.48, 9.08	8.08, 7.94	5.88, 5.73		4.98	4.80	5.07, 4.54	5.30, 4.66			
	7 hours	9.45, 9.14	8.08, 7.92	5.88, 5.73		4.98	4.80	5.09, 4.53	5.27, 4.67			
	24 hours	9.50, 9.14	8.08, 7.86	5.90, 5.75		4.95	4.77	5.00, 4.49	5.23, 4.66			
	77 hours	9.51, 9.14	8.00, 7.86	5.88, 5.74		4.94	4.77	5.03, 4.48	5.23, 4.66			
	7 days	9.50, 9.14	8.00, 7.84	5.91, 5.76		4.95	4.78	5.04, 4.50	5.24, 4.66			
	14 days	9.51, 9.16	7.98, 7.84	5.90, 5.74		4.90	4.76	5.01, 4.48	5.22, 4.65			

remains at the same position and the other is influenced by complexation and shifted downfield to δ = 5.30. The H-3 atoms show two additional multiplets of low intensity centered at δ = 5.86 and 4.67. Their intensity, lineshape and, to a lesser extent, chemical shifts change on increasing the ratio of **3:2**. Three characteristic singlets due to the three methyl groups of camphanic residue in **2** at δ = 1.04, 0.88 and 0.73, respectively, give rise to a multiplet at a higher field and new singlets of lower intensity at δ = 0.25, 0.40 and 0.50. At the molar ratio of **3:2** = 1.5:1, the presence of the free ligand **3** can be observed.

*B. (Rh_2(comphanate)$_4$ × (1-benzyl-7-bromo-1,3-dihydro-5-(pyrid-2'-yl)-2H-1,4-benzodiazepin-2-one)) (**7**)*

The ^{1}H-NMR spectrum of the nitrogen ligand **4** exhibits a characteristic doublet at δ = 8.64 (J = 4.8 Hz) for H-6', two doublets for $PhCH_2$ (δ = 5.01 and 5.26, J = 15.8 Hz), and doublets at δ = 4.97 (J = 10.2 Hz) for H-3a, and at δ = 3.97 (J = 10.2 Hz) for H-3b (Table I, Figure 1a), along with several signals in the aromatic region.

At a molar ratio of **4:2** = 0.5:1, H-6' is shifted downfield affording two multiplets centered at δ = 10.41 and 10.36 (Figure 3b), while at a molar ratio 1:1, two doublets at δ = 8.38 and 8.30 are observed (Figure 1c). By further addition of ligand **4**, the H-6' doublet of the free ligand appears along with the latter two doublets (Figure 1d). At a molar ratio **4:2** = 0.5:1, the two doublets for the diastereotopic H-3 atoms are shifted downfield, producing four multiplets: two of higher intensity centered at δ = 5.94 and 4.31 and two of low intensity centered at δ = 5.56 and 4.58 (Figures 1b and 3b). The intensity of the signal at δ = 4.58 ppm increases with the increase of the molar ratio **4:2**, while the signal at δ = 5.56 becomes superimposed by the multiplet of benzylic signals centered at δ = 5.40 (Figures 1c and 1d). Two doublets of benzylic methylene AB system are shifted in the opposite directions, giving two multiplets centered at δ = 5.43 and 4.84. The unambigous distinction between the resonances for diastereotopic H-3 and benzylic methylene-protons was made on the basis of the COSY spectra (Figure 2). At a molar ratio **4:2** = 0.5:1, besides methyl groups arising from the free Rh_2(camphanate)$_4$, a multiplet appears at δ = 0.95, which belongs to the methyl groups of complex **7**. Some additional signals for methyl groups at a higher field can be observed, as well. Two AB systems, arising from 2H-3 and $PhCH_2$ of the free ligand, can be observed at the molar ratios **4:2** = 1.5:1 and 2:1.

The ^{1}H-NMR spectrum of the sample containing **4:2** in the molar ratio 0.5:1 was repeatedly recorded (Figures 3b–d). The spectra unambigously show that soon after dissolution of the components, the isomer formed initially is transformed into another, more stable isomer, which remains unchanged even after 14 days.

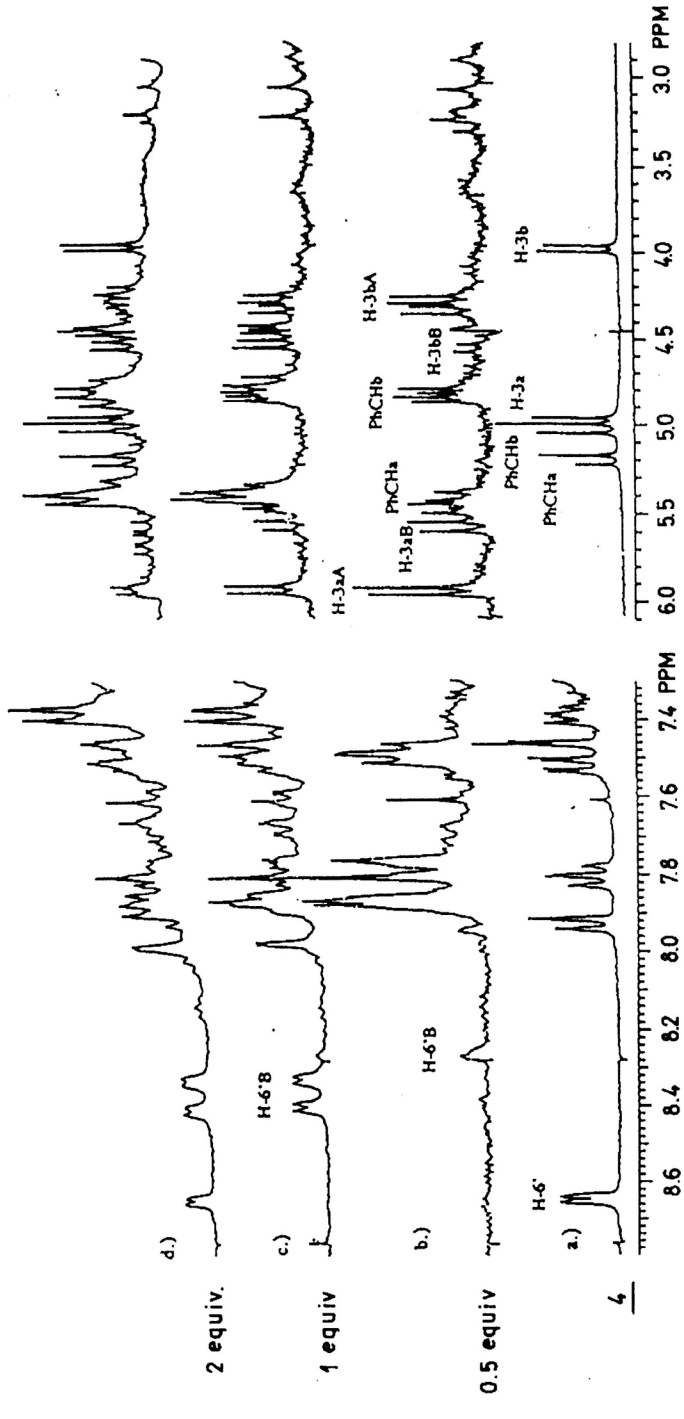


Figure 1. 300 MHz ^{1}H-NMR spectra of **7** obtained by titration of 1.0 eq. **2** with ligand **4** in deuterochloroform: a) ligand **4**; b) 0.5 eq. **4**; c) 1.0 eq. **4**; d) 2.0 eq. **4**.

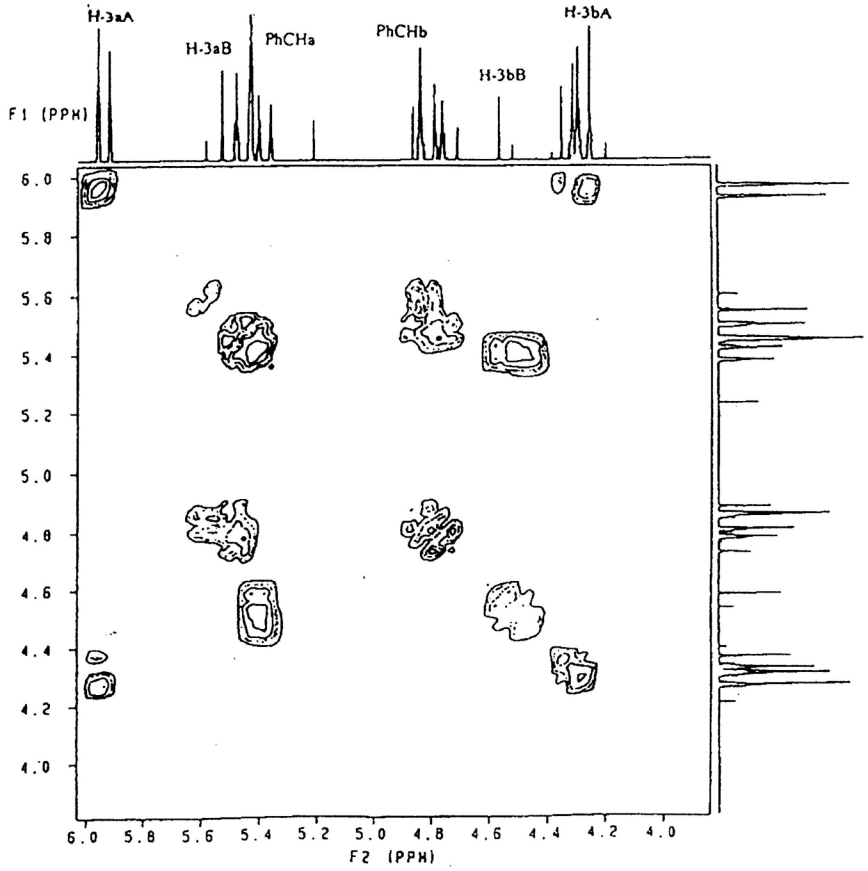


Figure 2. COSY spectrum of **7** obtained by titration of 1.0 eq. **2** with 0.5 eq. **4** in deuterochloroform.

*C. (Rh_2(camphanate)$_4$ × 2(1-benzyl-7-bromo-1,3,4,5-tetrahydro-5-(pyrid-2'-yl)-2H-1,4-benzodiazepin-2-one)) (**8**)*

The ^{1}H-NMR spectrum of the free nitrogen ligand **5** shows the following characteristic signals: a doublet at δ = 8.58 (J = 4.6 Hz) for H-6', a broad singlet at δ = 8.50 for N4-H, a singlet at δ = 5.03 for H-5, a sharp singlet at δ = 3.80 for 2H-3, and doublets at δ = 3.45 (J = 14.2 Hz) and δ = 3.23 (J = 14.2 Hz) for $PhCH_2$ (Table I).

Gradual addition of ligand **5** to the solution of **2** in $CDCl_3$ generates large changes for the resonances of H-5 and four pyridinic protons (Figure 4). The doublet at δ = 8.58 belonging to H-6' is shifted downfield and is split into two

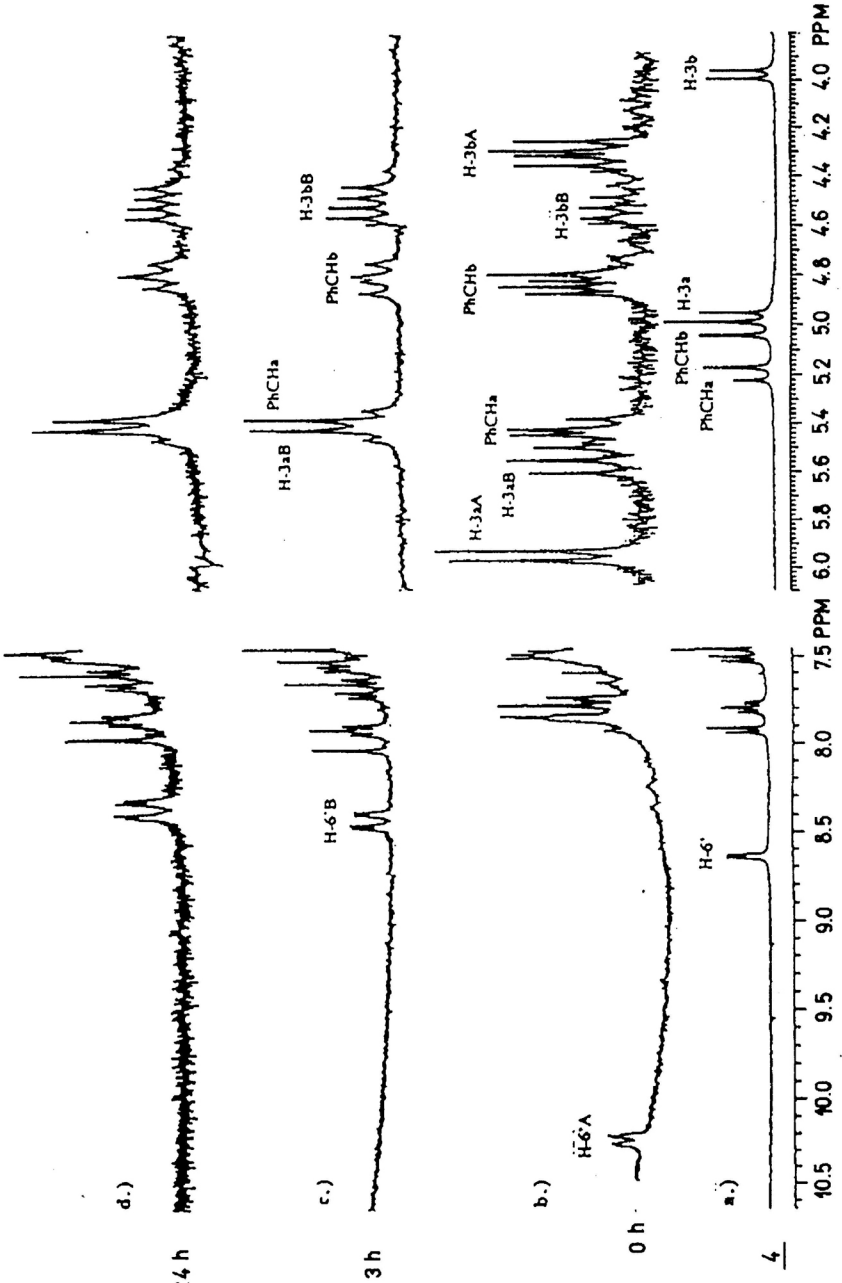


Figure 3. 300 MHz ^{1}H-NMR spectra of **4** : **2** = 0.5 : 1.0 in deuterochloroform recorded at time intervals: a) ligand **4**; b) 0 h; c) 3 hrs; d) 24 hrs.

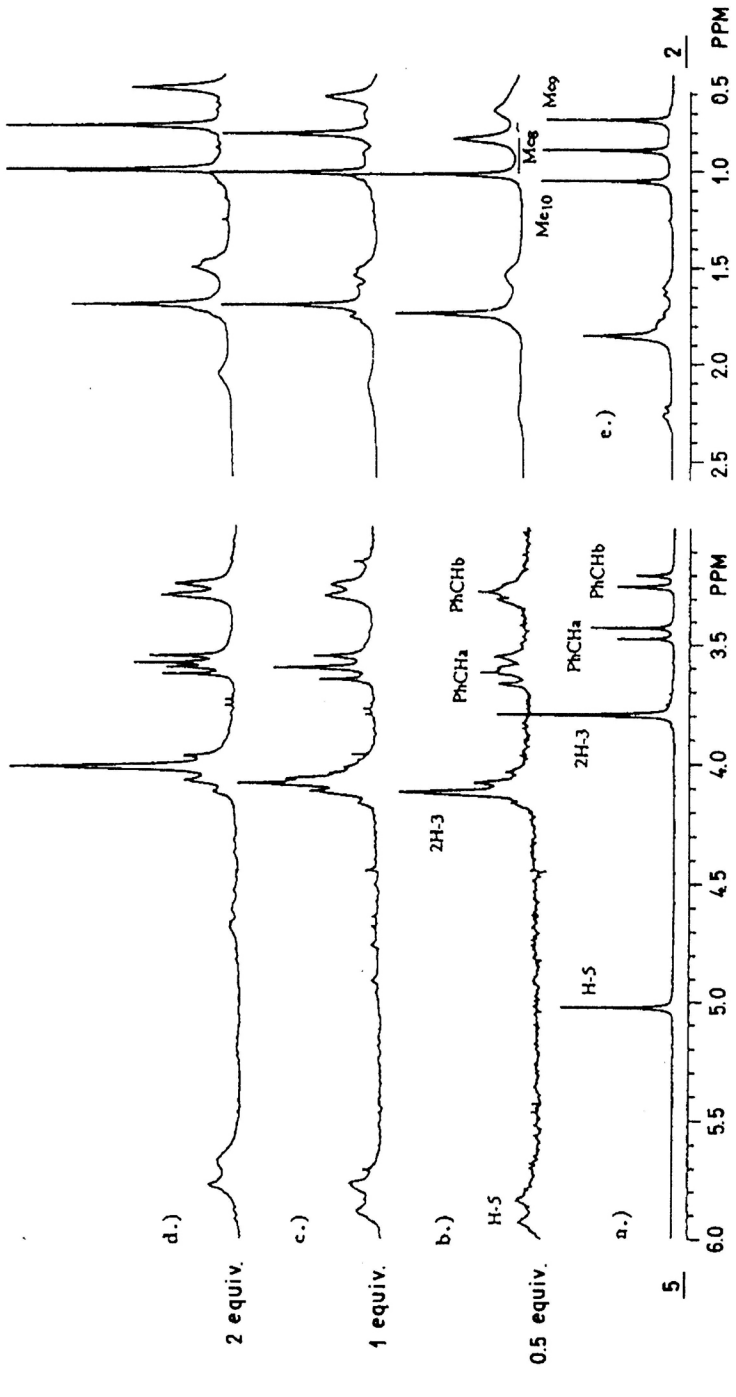


Figure 4. 300 MHz ^{1}H-NMR spectra of **8** obtained by titration of 1.0 eq. **2** with ligand **5** in deuterochloroform: a) ligand **5**; b) 0.5 eq. **5**; c) 1.0 eq. **5**; d) 2.0 eq. **5**; e) Rh_2(camph)$_4$ **2**.

doublets at δ = 8.72 and 8.63. The sharp singlet for H-5 is transformed into a broad doublet, shifted downfield from δ = 5.03 to δ = 5.86 (Δδ = –0.83 ppm). The sharp singlet for 2H-3 is slightly broadened and shifted to δ = 4.09 (Δδ = –0.29 ppm). The two doublets for $PhCH_2$ are transformed into two multiplets at δ = 3.60 and 3.28, respectively. The three methyl groups of the camphanic unit are shifted to a slightly higher field. The largest chemical shift and line-broadening has been observed for the resonances of Me-9, whereas the Me-10 group remains practically unchanged. At the molar ratio **5:2** = 0.5:1, the broadening of sharp singlets for all three methyl groups indicates a rapid intermolecular exchange of the nitrogen ligand between rhodium atoms. On further addition of ligand, the signals observed in the ^{1}H-NMR spectrum became sharp again.

*D. (Rh_2(comphanate)$_4$ × (1-benzyl-7-bromo-1,3,4,5-tetrahydro-5-(pyrid-2'-yl)-2H-1,4-benzodiazepin-2-one)) (**9**)*

When solutions of **2** and **5** are allowed to stand for an extended period of time, the signals of symmetric complex **8** disappear. In the ^{1}H-NMR spectrum, the pattern for methyl groups appears, which is characteristic for non-symmetric complexes **6** and **7**, while an increase in the numbers of other signals indicates the transformation of symmetric complex **8** into the non-symmetric diastereomers. In order to monitor this process, spectra of the sample containing **5:2** in the molar ratio 1:1 were repeatedly recorded during very long time intervals (Figure 5, Table I).

The first spectrum was recorded immediately after dissolving **2** and **5** in a molar ratio of 1:1. It shows only the signals belonging to the symmetric complex **8** (Figure 5b). After 3 hours, new, low intensity signals appear. Their intensity increases with time (Figures 5c and 5d). The intensity of the signals characteristic for the symmetric complex **8** continuously diminishes and in Figure 5d they can no longer be observed. Two pairs of signals at δ = 9.50 and 9.15, and δ = 8.00 and 7.85, respectively, appear in the spectrum recorded after 3 hours and their intensity increases with time. On the basis of the COSY spectra, they are atributted to pyridinic H-6' and H-5' atoms in two non-symmetric isomers (**A** and **B**). There is a large downfield shift for the resonances of H-5', as compared to the free ligand and to the symmetric complex **8**, Δδ = –1.85 and –0.55 ppm, respectively. H-5 on the chiral centre in **5** gives rise to two well resolved doublets at δ = 5.88 and 5.73. Their ratio changes slowly with time, and the integration makes it possible to determine the ratio of isomers **A** and **B**. The diastereotopic H-3 atoms give rise to two multiplets at δ = 5.07 and 4.54, the intensity of which decreases with the simultaneous appearance and intensity of two new signals at δ = 5.30 and 4.66. This process indicates a slow transformation of structural isomers **A** and **B**, as already deduced from the slow change of the ratio of the resonances of H-5 atoms. All the above data reveal a very slow tendency toward **A** ⇌ **B** equilibrium, which is not reached even after 14 days (Figures 5b–e).

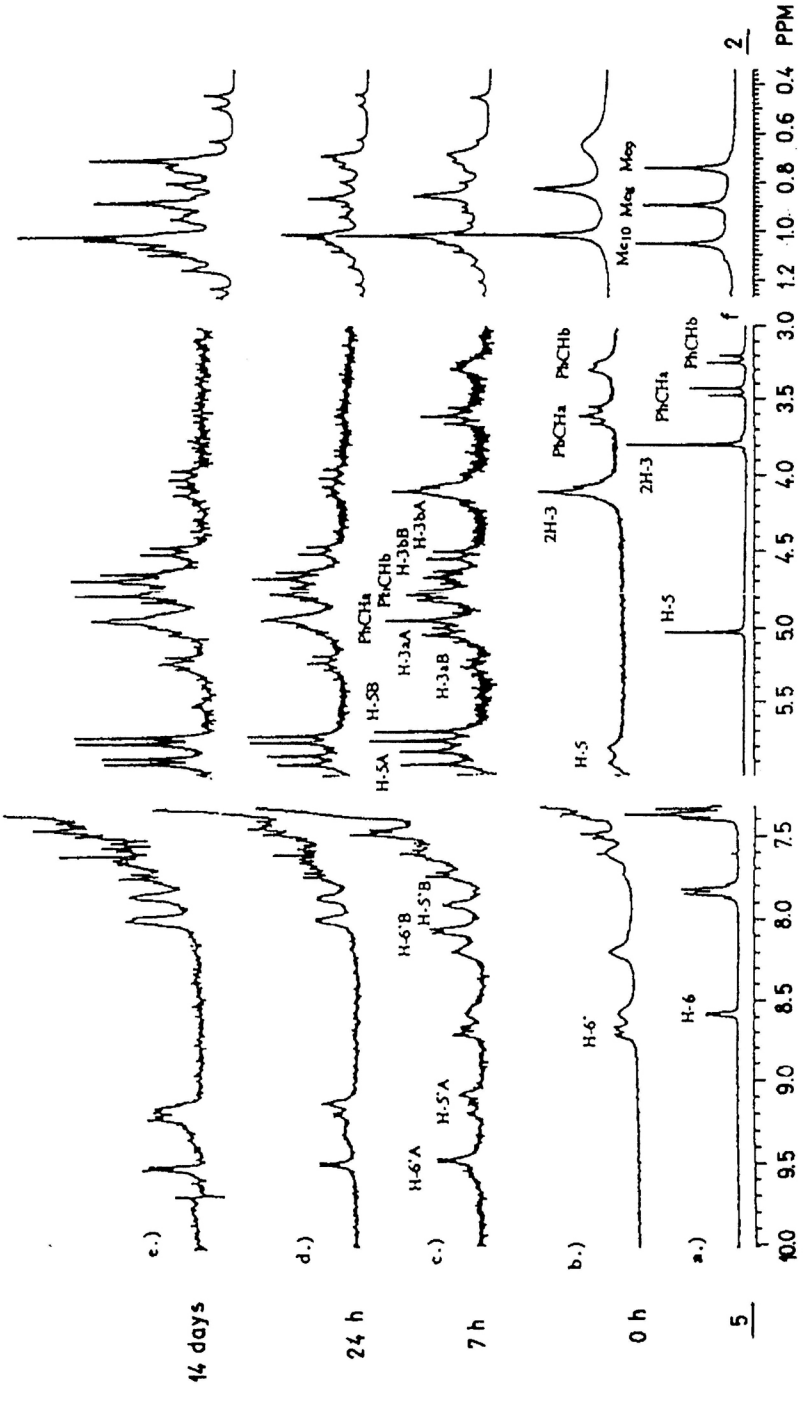
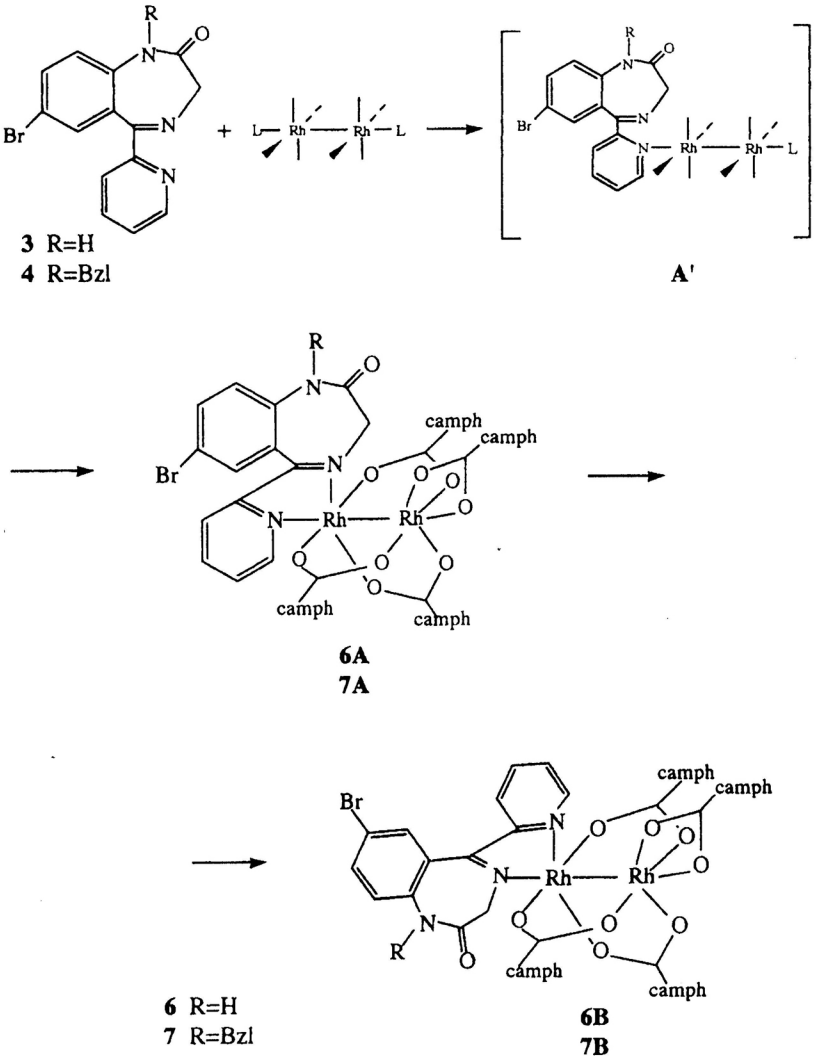


Figure 5. 300 ^{1}H-NMR spectra of **5** : **2** = 1.0 : 1.0 in deuterochloroform recorede at time intervals: a) ligand **5**; b) 0 h; c) 7 hrs; d) 24 hrs; e) 14 days; f) Rh_2(camph)$_4$ **2**.

DISCUSSION

The ^{1}H-NMR data for the *in situ* formed adducts **6** and **7** clearly show that non-symmetric bidentate 1:1 complexes are formed presumably *via* unstable monodentate symmetric 2:1 complexes, which cannot be identified (A', Scheme 1). In the 1:1 complexes, ligands **3** and **4**, which possess a conju-



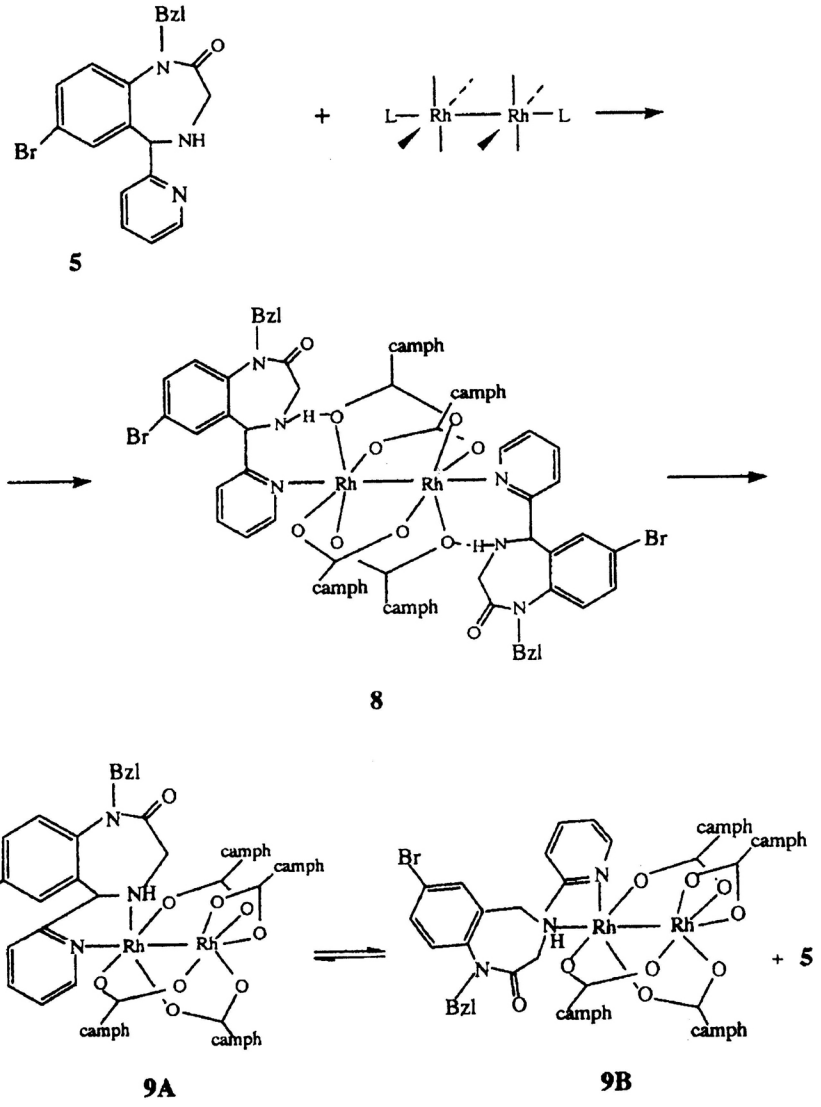
Scheme 1.

gated 1,4-diazadien system analogous to that in 2,2'-bipyridine, form stable non-symmetric adducts due to the fact that both coordinating nitrogens exhibit similar basicity ($pK_a \sim 5$) and π-accepting properties. Chemical shifts in the ^{1}H-NMR spectra for all characteristic protons suggest that N-4 and N-pyr are coordinated to the same rhodium atom by displacement of one equatorial carboxylate oxygen atom which chelates to the second rhodium atom, as outlined in Scheme 1.

Due to the non-symmetry of the 5-pyrido-1,4-benzodiazepine ligand, each complex is formed as a mixture of diastereomers **A** and **B**. It explains the appearance of two doublets for H-6' atoms, two multiplets for each of the two diastereotopic H-3 atoms, and multiplication of the signals from diastereotopic benzylic protons. We assume that the less stable diastereomers **A** are formed *via* monodentate-bound ligand in **A'**. The initial binding of N(pyr) to the axial position of the Rh atom is kinetically favoured because of the higher π-acceptor ability of this nitrogen. It is followed by the binding of the less reactive N-4 to the equatorial position of Rh(II). This is accompanied by displacement of one equatorial carboxylate oxygen atom to the second rhodium atom, leading to formation of the *ax*(py)-*eq*(bdz) complexes **A** (py = pyridine, bdz = benzodiazepine). Complexes **A** are, therefore, a result of kinetic control. They possess more bulky groups in the equatorial position, where strong repulsive interactions with the camphanate take place. Consequently, these diastereomers rearrange to the thermodynamically preferred isomers **B**, with the *ax*(bdz)-*eq*(py) mode of binding. Such a rearrangement, if occurring on the pentacoordinated Rh atom, can follow one of the well known mechanisms, such as Berry's pseudorotation or the »turnstile« rotation mechanism.[19]

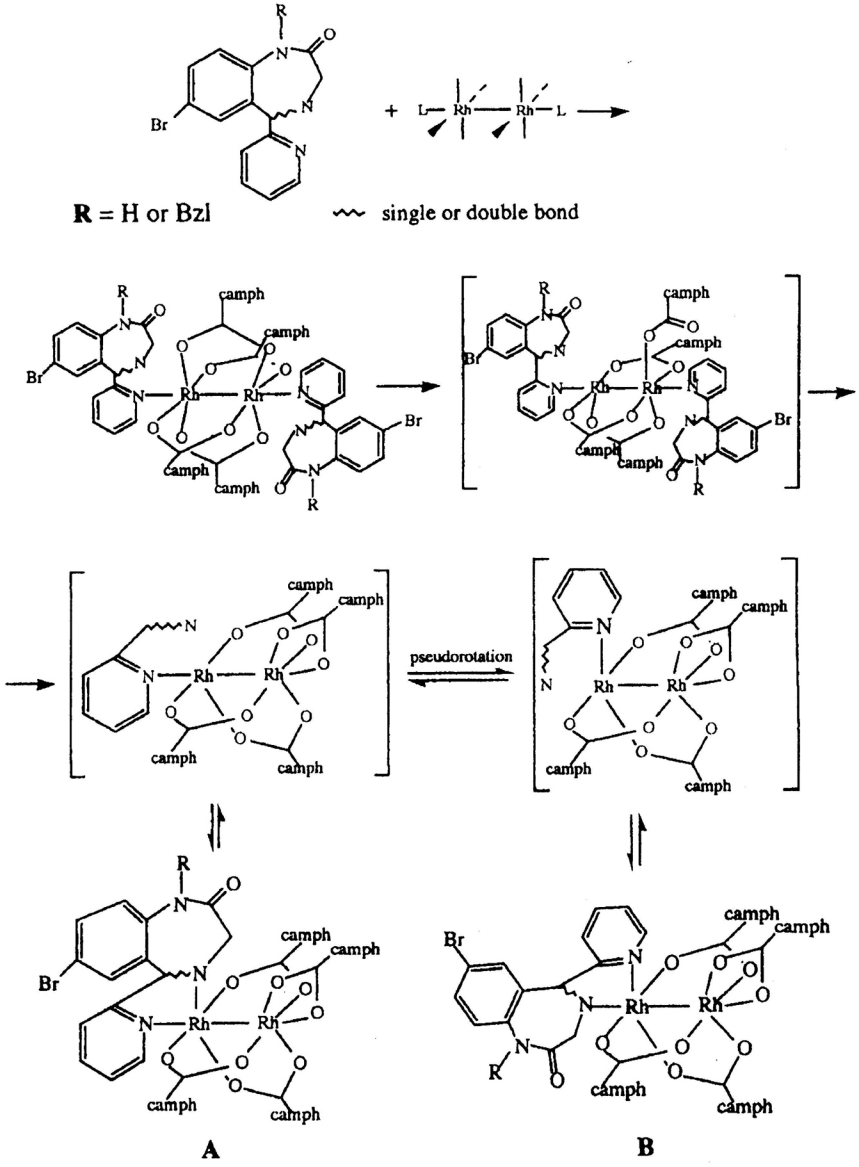
This sequence of events is supported by the fact that, at the molar ratio **4:2** = 0.5:1, a small amount of the second isomer is observed (Figures 1b and 3b). After gradual addition of **4** (Figures 1c and 1d) or prolonged time (Figures 3c and 3d), its formation is preferred. Two multiplets of low intensity at δ = 5.56 and 4.58 in **7** are attributed to two diastereotopic H-3 atoms of diastereomer **B**. Their intensity increases either by increasing the molar ratio of **4:2** or with time, thus revealing the rearrangement of **7A** to **7B** (Figures 1 and 3). Additional multiplicity of the benzylic methylene AB system in the spectrum of **7** supports this finding. H-6' is shifted upfield on complexation of **4** appearing at a molar ratio **4:2** = 0.5:1 as two multiplets at δ = 10.41 and 10.36; at the molar ratio 1:1, it gives rise to two doublets at δ = 8.38 and 8.30. On further addition of **4**, the H-6'-doublet of free ligands appears apart from the two latter doublets (Figure 1d).

In contrast to ligands **3** and **4**, the corresponding 4,5-dihydro-congener **5** forms a rather stable symmetrically ligated 2:1 adduct **8**, which slowly transforms into the non-symmetrically ligated 1:1 adduct **9**, wherein a benzodiazepine derivative is bound in the bidentate mode (Scheme 2).



Scheme 2.

Two molecules of 4,5-dihydro-ligand **5** are coordinated *via* pyridine nitrogen to both rhodium atoms of **2**. Since pyridine nitrogen is more basic (pK_a-5), and exhibits better π-accepting properties than N-4, it is preferred for the coordination, to the axial position of the Rh atom. The secondary amine nitrogen of the non-aromatic 1,4-benzodiazepinone ring enters into



Scheme 3.

equatorial position displacing one equatorial carboxylate oxygen atom to the second Rh atom, forming the *ax*(py)-*eq*(bdz) complex **9A**. This is a result of kinetic control, as explained for **6A/7A** and **6B7B**. In contrast to complex **7A**, which rearranges quickly to **7B**, the diastereomer **9A** rearranges slowly to

the thermodynamically preferred isomer **9B**, with a *ax*(bdz)-*eq*(py) binding mode, presumably by the same mechanism as described for **7A** (Scheme 3). A slow change in the ratio of the H-3 and H-5 resonances indicates slow equilibration, which has not been reached even after 14 days (Figures 5b–e).

We assume that monodentate binding of **5** is favoured by formation of a hydrogen bond between NH-4 and the equatorial carboxylate oxygen in dimer **8** (Scheme 2). The temperature coefficient of NH-4 proton (-2×10^{-3} ppm/°C), in the range from –40 to 40 °C, strongly suggests[20] that NH-4 is included in the hydrogen bond with one of the camphanate oxygens. The absence of π-accepting properties of N-4 atoms in **5**, at variance to the same position in **3** and **4**, makes the N-H bonding a favourable interaction. Similar behaviour has been observed for adenosine ligands containing exocyclic amino substituent in the 1,4-position to the coordinating N-7 atom.[21–23] This type of interaction with adenine groups is of importance for the biological, carcinostatic activity of rhodium dinuclear complexes with achiral carboxylic acids.[3]

CONCLUSIONS

This ^{1}H-NMR study has afforded some valuable information about the structure and stability of the adducts between the non-symmetric 1,4-bisnitrogen ligands **3–5** and Rh_2(camphanate)$_4$ **2**. Ligands **3** and **4**, which possess a conjugated 1,4-diazadien system analogous to that in 2,2'-bipyridine, form stable non-symmetric 1:1 complexes **6** and **7**, presumably *via* unstable symmetric 2:1 complexes, which cannot be identified in solution by ^{1}H-NMR. Ligand **5**, possessing an unconjugated 1,4-diaza system, behaves as pyridine derivatives and forms the relatively stable symmetric 2:1 complex **8**, which slowly transforms into the 1:1 bidentate non-symmetric complex **9**. The bidentate character of the latter ligand is diminished by the absence of the π-accepting ability of the unconjugated 1,4-bisnitrogen subunit.[16,24,25] Finally, all ligands form two diastereomeric non-symmetric complexes, as confirmed by the appearance of diastereotopy for all protons on complexation. Depending on the structure of the chelating pyrido-benzodiazepines, *i.e.* on different coordinating ability of benzodiazepine nitrogen, two different rates of rearrangement of monodentate to bidentate complexes **6A, 7A** and **9A** to **6B, 7B** and **9B** have been noticed, as well. Isomerization of complex **7A** into **7B** is completed in less than 3 hours, whereas both xomplexes **9A** and **9B** are present in the reaction mixture even after 14 days.

Finally, we assume that different coordination modes of nitrogen bidentate ligands to the rhodium atoms in $Rh_2(OCOR)_4$ species may give rise to different reactivities and, consequently, different catalytic activities. The results concerning the catalytic activity of dirhodium tetracarboxylates with chelated benzodiazepines will be reported elsewhere.

EXPERIMENTAL

Materials

Compounds **2–5** were prepared as already described[12,14–17]

Attempts at preparation and ^{1}H-NMR monitoring of the formation of adducts **6–9**. Following a recently described procedure,[3a] attempts were made to isolate adducts **7** and **8**. Acetonitrile was substituted for ethanol, since we have found the former to be unsuitable for the preparation of the adducts of $Rh_2(OAc)_4$ with benzodiazepines **3–5**. Ligands **4** and **5** were stirred for 24 hours at room temperature under argon with $Rh_2(camph)_4$ in molar ratios 1:1 and 2:1, respectively. Thereafter, the slurry containing a lot of uncomplexed material was refluxed for another 24 hours. During this period, the colour of the reaction mixture containing **7** changed slowly from green to red, while the solution of the adduct **8** remained green. The solvent was removed *in vacuo* and the crude complex precipitated by dichloromethane-ether. The TLC and ^{1}H-NMR-spectra revealed that both isolated substances consisted of uncomplexed ligands, a complex and some impurities. Thus, complexes **6–8** are not stable enough, and therefore their structure and properties were studied in solution.

NMR experiments

The ^{1}H-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 ^{1}H-NMR spectrum was collected using a single 30° (5 μs) pulse, 1s of relaxation delay time, the aquisition time of 2.0 s, and with a total sweep width of 3000 Hz sampled with 12K points. Two-dimensional experiments: homonuclear ^{1}H^{1}1H chemical shift correlation (COSY) spectra were performed at 25 ± 1 °C using a standard sequence of the Varian software package.

Typically, Rh_2(camphanate)$_4$ (10 mg, 0.01 mmol) was dissolved in an NMR-tube by gentle heating in $CDCl_3$ (0.5 ml). Four equal portions, each containing 0.005 mmol of benzodiazepines **3–5**, were added. After each addition, the ^{1}H-NMR spectrum was recorded. The experiments concerning measurements at time intervals were performed as follows: Rh_2(camphanate)$_4$ (5 mg, 0.005 mmol) was dissolved in an NMR-tube in $CDCl_3$ (0.5 ml) and 1 mg (0.0025 mmol) of benzodiazepine **4**, and 2 mg (0.005 mmol) of benzodiazepine **5**, were added, respectively. The NMR spectra were recorded immediately after mixing of the components, and afterwards at determined time intervals within a 14 day interval.

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REFERENCES

1. R. Marčec, *React. Kinet. Catal. Lett.* **31** (1986) 337.
2. R. Marčec, Z. Raza and V. Šunjić, *J. Mol. Catal.* **69** (1991) 25.
3. (a) S. P. Perlepes, J. C. Huffman, J. H. Matonic, K. R. Dunbar and G. Christou, *J. Am. Chem. Soc.* **113** (1991) 2770, and the references cited therein. (b) C. A.

Crawford, J. H. Matonic, W. E. Streib, J. C. Huffman, K. R. Dunbar and G. Christou, *Inorg. Chem.* **32** (1993) 3125.
4. (a) D. M. L. Goodgame, C. J. Page and D. J. Williams, *Inorg. Chim. Acta* **153** (1988) 219; (b) D. M. L. Goodgame, C. A. O'Mahonoy, C. J. Page and D. J. Williams, *Inorg. Chim. Acta* **175** (1990) 141; (c) T. M. Dyson, E. C. Morrison, D. A. Tocher, L. D. Dale and D. I. Edwards, *Inorg. Chim. Acta* **169** (1990) 127; (d) M. S. Nothenberg, G. K. P. Takeda and R. Najjar, *J. Inorg. Biochem.* **42** (1991) 217.
5. (a) N. Farrell, M. D. Vargas, Y. A. Mascarenhas and M. T. P. Gambardella, *Inorg. Chem.* **26** (1987) 1426; (b) N. N. Farrell, *J. Inorg. Biochem.* **14** (1981) 261; (c) N. Farrell, *J. Chem. Soc., Chem. Commun.* (1980) 1014.
6. (a) G. Pneumatikakis and N. Hadjiliadis, *J. Chem. Soc. Dalton Trans.* (1979) 596; (b) K. Aoki H. Yamazaki, *J. Am. Chem. Soc.* **106** (1984) 3691.
7. F. A. Cotton and T. R. Felthouse, *Inorg. Chem.* **20** (1981) 600.
8. (a) F. A. Cotton and T. R. Felthouse, *Inorg. Chem.* **21** (1982) 2667; (b) P. A. Agaskar, F. A. Cotton, L. R. Falvello and S. Hahn, *J. Am. Chem. Soc.* **108** (1986) 1214.
9. (a) H. Brunner, H. Kluschanzoff and K. Wutz, *Bull. Soc. Chim. Belg.* **98** (1989) 63; (b) H. Brunner, K. Wutz and M. P. Doyle, *Monatsh. Chem.* **121** (1990) 755.
10. S. Hashimoto, N. Watanabe and S. Ikegami, *Tetrahedron Lett.* **31** (1990) 5173.
11. (a) M. P. Doyle, P. D. Brandes, A. P. Kazala, R. J. Pieters, M. B. Jarstfer, L. M. Watkins and C. T. Eagle, *Tetrahedron Lett.* **31** (1990) 6613; (b) M. N. Protopopova, M. P. Doyle, P. Muller and D. Ene, *J. Am. Chem. Soc.* **114** (1992) 2755; (c) M. P. Doyle, G. A. Devora, A. O. Nefedov and K. G. High, *Organometallics* **11** (1992) 549.
12. B. Kojić-Prodić, R. Marčec, B. Nigović, Z. Raza and V. Šunjić, *Tetrahedron: Assymmetry* **3** (1992) 1.
13. B. Klaić, Z. Raza, R. Marčec, V. Vinković and V. Šunjić, *Spectrosc. Lett.* **28** (1995) 683.
14. *U. S. Pat.* **3**, 886141 (1975); *Chem. Abstr.* **83** (1975) 193407h.
15. T. Kovač, B. Belin, T. Fajdiga and V. Šunjić, *J. Heterocycl. Chem.* **17** (1980) 59.
16. P. Čudić, B. Klaić, Z. Raza, D. Šepac and V. Šunjić, *Tetrahedron* **47** (1991) 5295.
17. V. Vinković, Z. Raza and V. Šunjić, *Spectrosc. Lett.* **27** (1994) 269.
18. J. Halpern in J. D. Morrison (Ed.) *Asymmetric Synthesis*, Vol. 5, Academic Press, Orlando, 1985, p. 41.
19. A. Yamamoto, *Organotransition Metal Chemistry*, New York, J. Wiley&Sons, 1986, pp. 189–191.
20. E. S. Stevens, N. Sugawara, G. M. Bonora and C. Toniolo, *J. Am. Chem. Soc.* **102** (1980) 7048.
21. L. G. Marzilli, *Prog. Inorg. Chem.* **23** (1977) 255.
22. T. Sorrel, L. A. Epps, T. I. Kirstenmacher and L. G. Marzilli, *J. Am. Chem. Soc.* **99** (1977) 2173.
23. J. R. Rubin, P. P. Naromy and M. Sundaralingay, *Acta Crystallogr.* **C 47** (1991) 1712.
24. Ref. (19), pp. 54–75.
25. H. T. Dieck, L. Stamp, R. Diercks and C. Mueller, *Nouv. J. Chimie* **9** (1985) 289.

SAŽETAK

Struktura i relativna stabilnost adukata dirodijeva tetrakamfanata s 5-pirido-1,4-benzodiazepinima i njihovim 4,5-dihidro-analogom; prvi predstavnici nesimetričnih bidentatnih 1,4-didušikovih liganada

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^{1}H-NMR spektri adukata dirodijeva tetrakamfanata i 5-pirido-1,4-benzodiazepin-2-ona **3–5** pokazuju dva različita načina kompleksiranja. Ovisno o strukturi kelatirajućeg piridobenzodiazepina, zapažaju se dva tipa kinetičkog i dinamičkog profila. Ligandi **3** i **4**, koji posjeduju 1,4-didušikovu podjedinicu s 4π elektronima, ponašaju se kao bidentatni ligandi, tvoreći kinetički stabilne 1:1 adukte, nesimetrične diastereomere **6B, 7B**. Ligand **5** (4,5-dihidro derivat spoja **4**) ponaša se kao piridinski derivat, tvoreći kinetički stabilan, simetrični 2:1 adukt **8**, koji se vrlo polagano izomerizira u nesimetrični 1:1 adukt **9**. Relativna stabilnost adukta **8** pripisuje se vodikovoj vezi N(4)-H-O(kamfanil), kao i slaboj koordinacijskoj sposobnosti nekonjugiranog, piramidnog N(4) atoma.