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Dirhodium tetraacylate complexes and monovalent ligands. Adduct formation in solution as monitored by NMR spectroscopy

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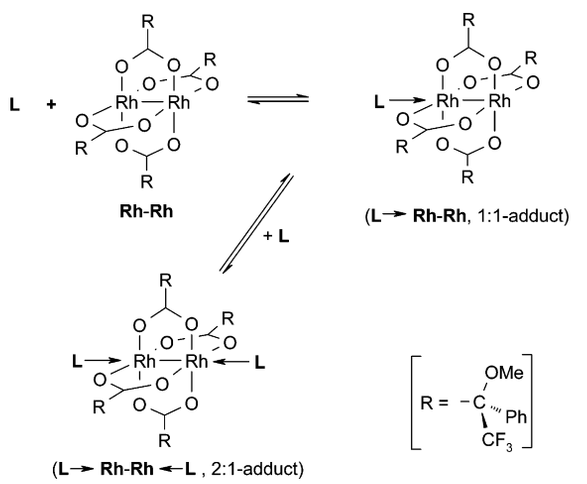
Evidences of adduct formation between the dirhodium complex Rh_2[(*R*)-MTPA$_4$] (**Rh–Rh**; MTPA-H = Mosher acid) and various monovalent ligands **L** were obtained in solution by using NMR spectroscopy. Strongly binding ligands, *e.g.* selenoethers or nitriles, prefer **L** ⟶ **Rh–Rh** ⟵ **L** adducts whereas weaker ligands, *e.g.* olefins with low steric hindrance, tend to form oligomers with bridging **L** molecules: ⋯ **Rh–Rh** ⋯ **L** ⋯ **Rh–Rh** ⋯ . Larger steric congestion forces olefins to avoid bridge situations or even prohibits adduct formation at all.

Introduction

Dirhodium and other dinuclear complexes have been studied intensively during the last few decades.[1] Important applications are the use of dinuclear complexes as homogeneous catalysts[2] and as auxiliaries in the chirality determination of compounds with various functional groups by circular dichroism.[3] In the last few years we have proven that the dirhodium complex Rh_2[(*R*)-MTPA$_4$] (**Rh–Rh**; MTPA-H = methoxytrifluoromethylphenylacetic acid ≡ Mosher acid; Scheme 1) is an excellent solvating NMR auxiliary for chiral recognition of monovalent ligands where the ligating atom or group is of low Lewis basicity ("Dirhodium Method").[4] Although much work has been done on the structure of such adducts in the solid state,[1,5] knowledge about the formation and structure of adducts in solution is still scarce.[1] In a first approach, we have recently applied ^{1}H and ^{13}C NMR as well as IR spectroscopy to study how chiral xanthine derivatives are ligated to the axial position of **Rh–Rh** and how this differs in solution and in the solid state.[6] During the course of our previous studies on various monovalent functionalities[4] we had sometimes encountered evidences which partly appeared to be contradictory in terms of diverging adduct formation modes. Therefore, we regarded it necessary to perform a surveying study and gain a better understanding of the various kinds of kinetically instable adducts which may exist in solution depending on the experimental conditions. The results of this study are described here.



Scheme 1 Adduct formation between monovalent ligand molecules **L** and the dirhodium complex Rh_2[(*R*)-MTPA$_4$] (**Rh–Rh**; MTPA-H ≡ methoxytrifluoromethylphenylacetic acid = Mosher acid).

Results and discussion

We have shown that ligands **L**, *e.g.* olefins, nitriles, selenides, iodides, epoxides, sulfoxides and various phosphorus chalcogenides, form kinetically unstable adducts with **Rh–Rh** so that the chemical shifts of ligand nuclei are averages of free and ligated **L** molecules (Scheme 1).[4] ^{1}H chemical shifts of the ligand molecules are hardly affected by adduct formation; and even for ^{13}C such "adduct formation shifts ($\Delta\delta$)" are moderate or nearly absent. However, if the ligand is chiral and not enantiopure, there are numerous signals which are split into two because of the existence of diastereomeric adducts. This is called dispersion, $\Delta\nu$ (in Hz). Very recently, we found selenium atoms being the first ligands in our project where the adducts are stable enough to see them separately in a low-temperature NMR experiment.[4g,7] These measurements allowed to identify two existing types of adducts: **L** ⟶ **Rh–Rh** and **L** ⟶ **Rh–Rh** ⟵ **L**, the 1 : 1- and 2 : 1-adducts, respectively (see Scheme 1). This prompted us to start a study to see what the experimental conditions for a maximum concentration of the respective adducts are. Thereby, we wanted to find out the best molar ratio of the constituents (the ligand **L** and **Rh–Rh**) for detecting diastereomeric dispersions.

For this study we chose three different types of ligands **L**, namely the phenylselenenylalkanes **1** and **2** representing monoatomic binding sites with free electron pairs and large binding constants,[4g,i] 2-phenylpropionitrile (**3**) for a diatomic functional group with an *n*-orbital at nitrogen plus π-bonds[4c] as well as 1-menthene (**4**) and limonene (**5**)[1a] representing olefins with their π-systems as exclusive binding sites (Scheme 2). Ligands **1**–**3** were racemates, **4** and **5** were pure (+)-4*R*-enantiomers. All chemical shifts of **1**–**5** as well as $\Delta\delta$- and $\Delta\nu$-values are collected in the Tables 1 (^{1}H) and 2 (^{13}C).

Selenides

As stated above,[4g] it is possible to observe separately the adducts of selenides and **Rh–Rh** with varying stoichiometries by NMR spectroscopy at low temperatures. The experiments proved that the equilibra are shifted strongly towards the adducts (large binding constants); *i.e.*, practically no free selenide will be observed as long as free rhodium sites are available.

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Table 1 ^{1}H NMR chemical shifts (δ, in ppm) for compounds **1**–**5** as well as signal shifts ($\Delta\delta$, in ppm) and signal dispersion ($\Delta\nu$, in Hz) in their **Rh–Rh** adducts[a,b]

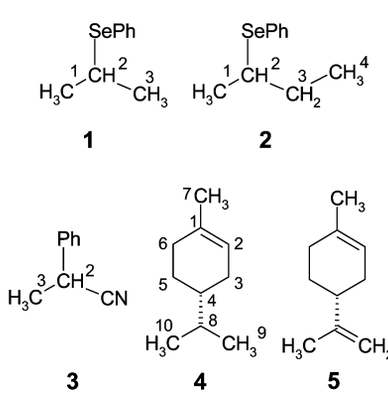
	1		**2**			**3**				**4**		**5**	
	δ	$\Delta\delta$	δ	$\Delta\delta$	$\Delta\nu$	δ	$\Delta\delta$	$\Delta\nu$		δ	$\Delta\delta$	δ	$\Delta\delta$
H-1	1.43	+0.10/ +0.09[c]	1.40	+0.10/ +0.10	1.6				H-2	5.37	+0.42	5.40	+0.81
H-2	3.45	+0.57	3.24	+0.63/ +0.62	6–7	3.90	+0.35/+0.35	~1	H-3	1.94 (qa)[e]	−0.14	2.12[f]	−[d]
										1.74 (qe)[e]	+0.26	2.04[f]	−[d]
H-3	1.43	+0.09/ +0.10[c]	1.70	+0.33/ +0.33	2.0	1.64	+0.14/+0.14	<1	H-4	1.21	+0.08	2.08	+0.02
			1.61	+0.12[d]	<1								
H-4			1.00	−0.02/ −0.03	3.4				H-5	1.75 (qe)[e]	+0.01	2.05[f]	~ +0.05
										1.23 (qa)[e]	+0.06	1.96[f]	~ +0.01
H-*o*	7.55	+0.25	7.55	+0.26	<1	−[d]	−[d]	−[d]	H-6	2.00[f]	~+0.1	1.81[f]	−[d]
										1.92[f]	~+0.1	1.77[f]	−[d]
H-*m*	7.28–7.25	−[d]	~7.26	~−0.1	−[d]	−[d]	−[d]	−[d]	H-7	1.64	+0.05	1.65	+0.18
H-*p*	7.28–7.25	−[d]	~7.26	~+0.04	−[d]	−[d]	−[d]	−[d]	H-8	1.46	−0.05		
									H-9	0.89[g]	−0.02	4.70	+1.12[h]
												4.70	+1.11[h]
									H-10	0.87[g]	−0.03	1.73	−0.20

[a] At 400.1 MHz; at room temperature in $CDCl_3$. [b] The magnitudes of $\Delta\delta$- and $\Delta\nu$-values refer to 1 : 1-molar ratios of **Rh–Rh** and the ligands. [c] Since CH_3-1 and CH_3-3 are prochiral in the free ligand, two different signals can appear in the adduct. Stereodifferentiation cannot be provided. [d] Signal could not be evaluated due to overlap and/or signal complexity. [e] Notation: qe = *quasi*-equatorial, qa = *quasi*-axial. [f] No stereodifferentiation possible. [g] Assignment may be reversed. [h] An assignment of the diastereotopic protons in the adducts was not made.

Table 2 ^{13}C NMR chemical shifts (δ, in ppm) for compounds **1**–**5** as well as signal shifts ($\Delta\delta$, in ppm) and signal dispersion ($\Delta\nu$, in Hz) in their **Rh–Rh** adducts[a,b]

	1		**2**			**3**				**4**		**5**	
	δ	$\Delta\delta$	δ	$\Delta\delta$	$\Delta\nu$	δ	$\Delta\delta$	$\Delta\nu$		δ	$\Delta\delta$	δ	$\Delta\delta$
C-1	24.2	−1.7[c]	21.6	−2.8/−2.9	8	121.6	−1.1/−1.1	~1	C-1	133.9	+2.4	150.3	+8.3
C-2	33.8	+4.8	41.5	+4.5/+4.5	0	21.5	+0.1/+0.1	~1	C-2	121.1	+0.3	120.7	−2.0
C-3	24.2	−1.7[c]	30.5	−1.9/−1.9	2	31.3	+0.7/+0.7	<1	C-3	29.0	+0.2	30.7	−0.2
C-4			12.3	−0.5/−0.6	3				C-4	40.1	−0.2	41.1	−0.3
C-*i*	129.6	−1.0	129.5	−0.9/−0.9	0	137.1	−0.5/−0.5	0	C-5	26.5	−0.3	30.9	+0.6
C-*o*	134.8	+0.1	134.9	0.0	<1	126.7	+0.1/0.0	2	C-6	30.9	+0.3	28.0	−2.0
C-*m*	128.8	0.0	128.8	+0.2	0	129.2	+0.1/+0.1	1	C-7	23.5	+0.3	23.5	+0.6
C-*p*	127.3	−0.3	127.3	+0.4	−[d]	128.1	+0.1/+0.1	1	C-8	32.3	−0.1	133.8	+6.0
									C-9	20.0[e]	0.0	108.4	−5.4
									C-10	19.7[e]	0.0	20.8	+1.4

[a] At 100.6 MHz; at room temperature in $CDCl_3$. [b] The magnitudes of $\Delta\delta$- and $\Delta\nu$-values refer to 1 : 1-molar ratios of **Rh–Rh** and the ligands. [c] Separate signals for C-1 and C-3: δ = 22.53 and 22.46. [d] No signal dispersion observed due to overlap. [e] May be reversed.



1 **2** **3** **4** **5**

Scheme 2 Structures of the ligand molecules **1**–**5**.

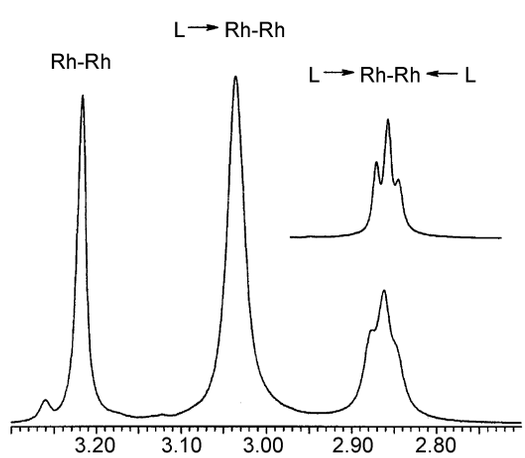


Fig. 1 ^{1}H NMR signals of the methoxy groups in the Mosher acid residues of the various adducts of **2**, in $CDCl_3$ at 215 K; molar ratio **2** : **Rh–Rh** = 1 : 1.3. The inserted signal corresponding to the **2** ⟶ **Rh–Rh** ⟵ **2** adduct, is resolution-enhanced.

Moreover, the 2 : 1-adduct **L** ⟶ **Rh–Rh** ⟵ **L** is energetically favoured.[4g] Signal dispersions $\Delta\nu$ (in Hz) can be identified for most of the protons of the chiral selenide **2** so that chiral recognition is no problem in this class of compounds.[4d,i]

There is, however, another parameter to observe the existence of the adducts: the ^{1}H signals of the Mosher acid methoxy groups display clearly different chemical shifts for the various adduct species (Fig. 1). This allows one to follow the changes of the relative concentration of the dirhodium species involved by increasing the amount of selenide (NMR titration). Fig. 2

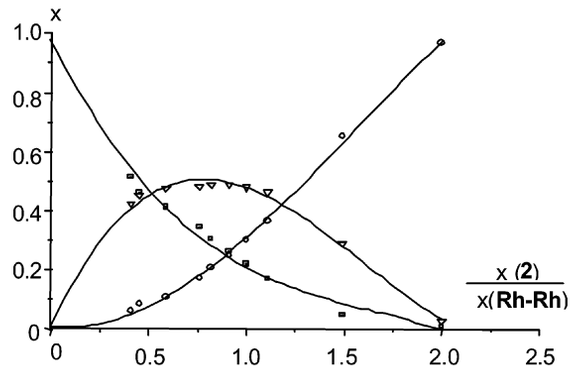


Fig. 2 Molar fractions x of free **Rh–Rh** (■), its **2** ⟶ **Rh–Rh** (▽) and **2** ⟶ **Rh–Rh** ⟵ **2** (O) adducts depending on the molar ratios of **2** : **Rh–Rh**, observed from ^{1}H signals of the Mosher acid methoxy groups.

exemplifies the result for the racemic 2-phenylselenenylbutane (**2**). It can be seen that at low proportions of **2** (0.5 to 1 molar) the major component is the 1 : 1-adduct **2** ⟶ **Rh–Rh** which goes up quickly to *ca.* 50%. As the content of **2** increases, the concentration of the 2 : 1-adduct **2** ⟶ **Rh–Rh** ⟵ **2** increases as well, paralleled by a corresponding decrease for the free **Rh–Rh** complex which nearly disappears at *ca.* 1.5 moles. Finally, at two molar ratio all rhodium sites are occupied by ligand molecules of **2** (**2** ⟶ **Rh–Rh** ⟵ **2**).

As a conclusion, it is advisable to restrict the **2** : **Rh–Rh** ratio to *ca.* 0.5 : 1 for avoiding unwanted high proportions of **2** ⟶ **Rh–Rh** ⟵ **2** adducts. However, dispersion effects are not very sensitive as to which type of adduct exists so that a higher amount of **2** may even be advantageous; it affords a higher overall-concentration of **2** and hence a shorter experimental recording time.

It is interesting to note that the methoxy ^{1}H signal of the Mosher acid residues in the **2** ⟶ **Rh–Rh** ⟵ **2** adduct (Fig. 1; $\delta \approx 2.86$) consists of three signals because there are four different diastereoisomeric adducts **I**–**IV**:

I: (*R*)-**2** ⟶ **Rh–Rh**$^{(R)}$ ⟵ (*R*)-**2**,
II: (*S*)-**2** ⟶ **Rh–Rh**$^{(R)}$ ⟶ (*S*)-**2**,
III: (*R*)-**2** ⟶ **Rh–Rh**$^{(R)}$ ⟵ (*S*)-**2**,
IV: (*S*)-**2** ⟶ **Rh–Rh**$^{(R)}$ ⟶ (*R*)-**2**.

Note that **III** and **IV** are not identical because the two rhodium atoms in **Rh–Rh** are diastereotopic. The same is valid for **2** ⟶ **Rh–Rh** as compared to **Rh–Rh** ⟵ **2**; they are diastereomers. However, the chemical shift difference associated to this kind of diastereomerism seems to be so low that it could not be observed before in any experiment using **Rh–Rh** as a chiral auxiliary. In Fig. 1 the methoxy ^{1}H line width of the 1 : 1-adduct (δ = 3.04) is about 10 Hz whereas that of the free **Rh–Rh** (δ = 3.22) is only 5 Hz. Although coalescence effects cannot be excluded, this may be an indication that the former signal consists of two close overlapping singlets. Thus, the methoxy signal of the Mosher acid residues in the **Rh–Rh** complex is able to reflect the chirality of both ligand molecules in the **2** ⟶ **Rh–Rh** ⟵ **2** adduct since they are flanked by these ligand molecules. In contrast, the atoms of a given ligand molecule cannot identify the chirality of the second ligand molecule on the opposite side of the **Rh–Rh** moiety (in terms of chemical shift sensitivity). We assign the most intensive central peak to the adducts **III** and **IV** with ligands of both enantiomeric forms of **2** inside the adduct because it cannot be expected that their chemical shift difference is large enough to be detected (see above). The assignment of the two flanking signals to the diastereomeric 2 : 1-adducts **I** and **II** can be performed only by using a non-racemic mixture of **2** which was not available.

Job's method of continuous variation is suitable to determine the stoichiometry of complexes and adducts in the range of rapid exchange and even for not too high binding constants.[8] Here, the product of the molar fractions x of the ligand and the corresponding complexation shifts ($\Delta\delta$), observed for given x-values, are plotted as a function x. The favoured stoichiometry of an adduct can then be determined by identifying the molar fraction of the adduct components at the curve maximum. Sharp breaks in the curve indicate high formation constants whereas flat maxima point to loose binding. Fig. 3 shows

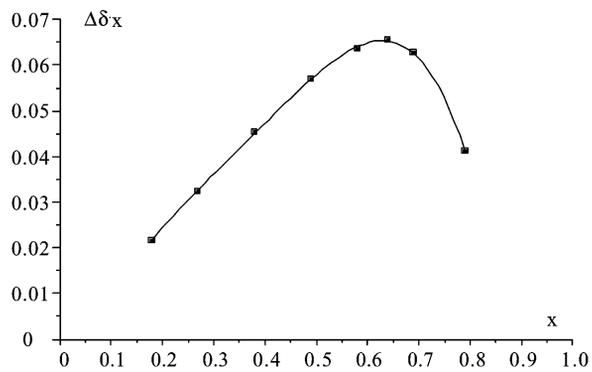


Fig. 3 Job plot for H-3 in the adducts of **2**; for explanation see text.

a representative Job-plot for one of the two diastereotopic H-3 atoms in the racemic mixture of **2** (δ = 1.73); analogous curves are observed for the two methyl proton signals. As expected, it turns out that the curve is quite sharp and the maximum exists at a molar fraction of *ca.* 0.65 for **2**, a value which is close to that expected for a molar ratio of **2** : **Rh–Rh** = 2 : 1. This is in complete agreement with the statements above concerning the binding constants and the existence of **2** ⟶ **Rh–Rh** and **2** ⟶ **Rh–Rh** ⟵ **2** adducts (Fig. 2) and confirms the reliability of the Job plot method in the present molecular systems.

Nitriles and olefins

Nitriles[4c] and olefins[4a] are typical ligands forming rapidly exchanging adducts with **Rh–Rh** which cannot be seen separately by NMR even at low temperatures. Thus, it was impossible before[4a,c] to find out the magnitude of the binding constants. Therefore, we recorded Job plots for the nitrile **3** and the two olefins **4** and **5** as representative molecules. The results are exemplified in the Figs. 4 and 5, respectively.

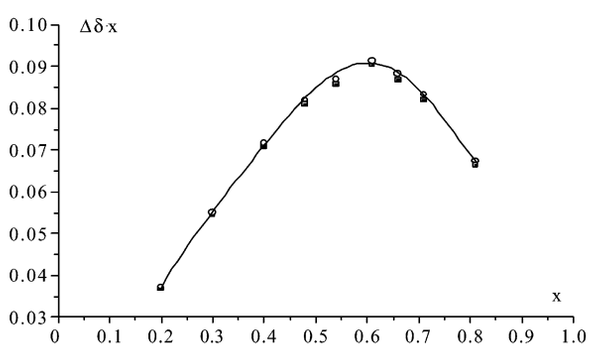


Fig. 4 Job plot for protons of the two diastereotopic methyl groups in the adducts of **3**; for explanation see text.

The Job plot of the methyl protons in the nitrile **3** (Fig. 4) is similar in shape to those for the selenides. However, the maximum is at a significantly lower molar fraction, namely *ca.* 0.60. The results for H-2 (not depicted here) are analogous. This indicates a molar ratio of 3 : 2 for the components **3** and **Rh–Rh** suggesting solution-state oligomers such as a conglomerate of one **3** ⟶ **Rh–Rh** and **3** ⟶ **Rh–Rh** ⟵ **3** adduct, *i.e.*, two **Rh–Rh** fragments are interconnected by a bridging **3** with two more

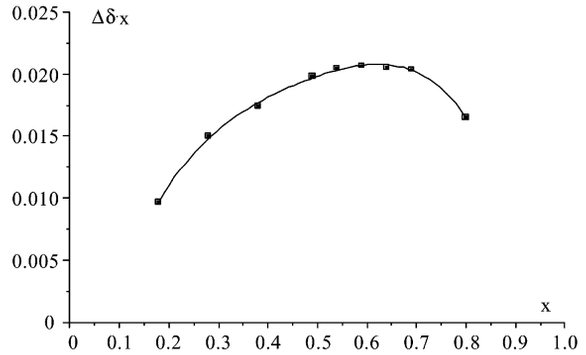
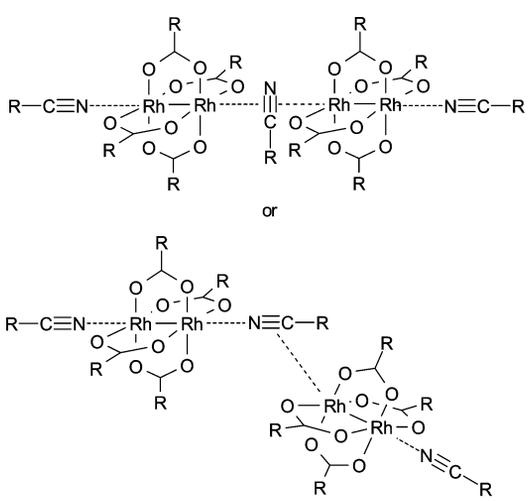


Fig. 5 Job plot for H-2 in the adduct of (*R*)-menthene (**4**); for explanation see text.

molecules of **3** at the terminal rhodium atoms. Thereby, we can consider this species as an intermediate in the "switch" process of ligand exchange[9] if the molar ratios of **3** and **Rh–Rh** are between 1 : 1 and 2 : 1. This situation is reminiscent of the adducts of $Rh_2[CF_3COO_4]$ and THF[5a] or $Rh_2[CF_3COO_4]$ and DMSO[5b] where – in the solid state – the ligand oxygen of THF and DMSO, respectively, bridges two dirhodium complexes in a zig-zagged polymeric chain.

In a study of chiral nitriles with a great structural diversity we identified some closer contact of the alkyl/aryl residues of the nitriles to the Mosher acid residues in **Rh–Rh**.[4c] This is not consistent with a end-on complexation *via* the free electron pair of the nitrogen atom which necessarily implies a linear arrangement of the atoms Rh–Rh ⟵ N≡C–C and, hence, a large distance between **Rh–Rh** and the alkyl/aryl residues of the nitrile molecules. Therefore, we assumed that some side-on complexation of the cyano group *via* the π-electron (η^2) might be effective. However, considering the Job plots mentioned above it is evident now that – irregardless of the binding mode – such close contact would necessarily exist if the nitrile group serves as a bridge between two **Rh–Rh** moieties (Scheme 3).



Scheme 3 Tentative binding modes at a bridging nitrile molecule.

The Job curve for the olefinic H-2 in (*R*)-menthene (**4**) is quite flat (Fig. 5); that for H-7 (methyl group attached to the double bond; not shown here) is similar. This shows that the adduct formation constant for the olefins is clearly lower; the equilibria (Scheme 1) are not as biassed as for selenides or nitriles. Nevertheless, we find that maxima close to 0.60, again suggesting oligomers.

The situation for limonene (**5**) with two different olefinic binding sites, however, is more complicated. Fig. 6 shows that the maximum for H-9 in the exocyclic double bond (upper curve) is again 0.60; the same is observed for H-10 (not

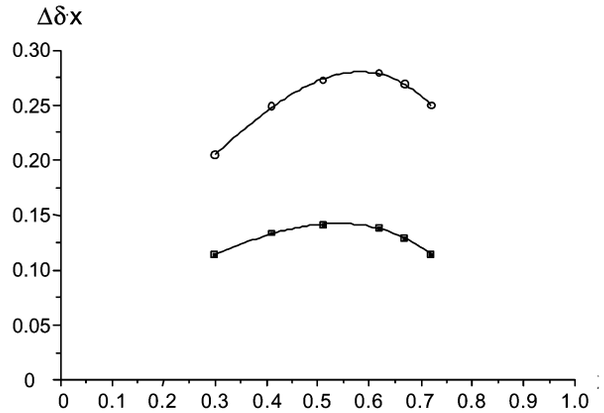


Fig. 6 Job plot for H-2 (lower curve) and H-9 (top curve) in the adduct of (*R*)-limonene (**5**); for explanation see text.

depicted). On the other hand, the corresponding signal of H-2 in the endocyclic double bond (lower curve in Fig. 6) and for H-7 which is not depicted, show maxima at *ca.* 0.50 only. Thus, the exocyclic double bond seems to be able to bridge two dirhodium complexes in a way similar to the nitrile and menthene whereas the endocyclic double bond seems to prefer 1 : 1 stoichiometries. A tentative explanation for this surprising difference is to assume the existence of oligomers with limonene molecules bridging dirhodium complexes by their exocyclic double bond whereas the endocyclic double bond can occupy only terminal positions; *i.e.* such a double bond cannot be situated between two dirhodium complex molecules. This explanation is consistent with a significant difference in the adduct formation shifts $\Delta\delta$ which were determined by us earlier.[4a] These values are nearly double as large for the exocyclic compared to the endocyclic double bond (see also Table 1) indicating an analogous difference in binding constants. It should be noted that this sequence is reversed when the methyl group 7 in limonene is lacking as *e.g.* in 4-vinylcyclohexene (compound **4** in reference 4*a*). Clearly this methyl is the major obstacle for an efficient binding of this endocyclic olefinic bond. Olefins with even more severe steric congestion, *e.g.* camphene (compound **6** in reference 4*a*), do not bind at all.

Experimental

Compounds

The selenides **1** and **2** have been described before.[10] The nitrile **3** and the olefins **4** and **5** are commercially available. The synthesis of **Rh–Rh** has been reported earlier.[4a]

NMR measurements

Room-temperature ^{1}H (400.1 MHz) and ^{13}C (100.6 MHz) measurements of the free ligands **1**–**5** (Scheme 2) were performed on a Bruker DPX-400 spectrometer equipped with a QNP probe head. The ligands were dissolved in 0.7 ml $CDCl_3$; concentrations were 0.094 mol l^{-1}, in analogy to those in the chiral recognition experiments (see below). Chemical shift standard was internal tetramethylsilane (δ = 0) for ^{1}H and ^{13}C. Signal assignments are based on ^{1}H{^{1}H} NOE-difference, DEPT, HMQC and HMBC experiments (standard Bruker software). Digital resolutions were 0.24 Hz point^{-1} in the ^{1}H and 1.53 Hz point^{-1} in the ^{13}C NMR spectra.

In a typical experiment, 45.2 mg **Rh–Rh** (0.04 mmol) and a molar equivalent of the respective ligand compound **1**–**5** in 0.7 ml $CDCl_3$, and 7 μl (1 drop) of acetone-d_6 were added to increase the solubility of **Rh–Rh**.[4e] Thus, the magnitudes of $\Delta\delta$- and $\Delta\nu$-values (Tables 1 and 2) refer to mixtures of 1 : 1 molar ratios.

Temperature-variable ^{1}H (500.1 MHz) spectra were recorded in the presence of **Rh–Rh** on a Bruker DRX-500. Digital resolutions were 0.37 Hz point^{-1} in the ^{1}H NMR spectra. Temperatures varied from 213 to 333 K and were read from the instrument panel; no further measures for more precise temperature determinations were taken.

Job plots

Equimolar solutions (0.026–0.048 M) of ligand and **Rh–Rh** in $CDCl_3$ (containing a trace of acetone-d_6) were prepared in volumetric flasks and mixed in various amounts. These mixed solutions were subjected to ^{1}H NMR measurements at 400.1 MHz and room temperature.

Conclusion

The following conclusions can be drawn from experiments described in this work:

(a) NMR titration experiments can be monitored only with strongly ligating functional groups, *i.e.* if the life-time of an adduct molecule is large on the NMR time-scale. This is the case for selenoethers (**Se**) at 215 K in chloroform.[9,11] **Se** ⟶ **Rh–Rh** (1 : 1-adducts) are formed first but **Se** ⟶ **Rh–Rh** ⟵ **Se** (2 : 1-adducts) appear already at low molar concentrations of **Se**. If two moles of **Se** are added, only **Se** ⟶ **Rh–Rh** ⟵ **Se** exists. Job plots confirm this result; the curve maximum appears at a **Se** molar fraction of *ca.* 0.65; *i.e.* 2 : 1. Thus, Job plots give reliable results in this adduct system.

(b) The Mosher acid residues in **Rh–Rh** are able to differentiate the chirality of both ligands in **Se** ⟶ **Rh–Rh** ⟵ **Se** *via* their methoxy ^{1}H signals but, in contrast, a ligand cannot recognize the configuration of the second ligand molecule because they are isolated on opposite sides of the dirhodium complex.

(c) Therefore, for chiral recognition experiments it is not necessary to restrict the molar ratio of **Se** : **Rh–Rh** to low values (*ca.* 0.5) in order to keep the concentration of 2 : 1-adducts (**Se** ⟶ **Rh–Rh** ⟵ **Se**) low. Rather, it is advisable to choose ratios of 1–1.5 where the concentration of the ligand is higher giving greater sensitivity in the NMR experiment.

(d) Nitriles are ligands with medium binding constants, and their chirality can be monitored by the "Dirhodium Method" easily. In contrast to the selenoethers, Job plots (curve maximum at *ca.* 0.60, *i.e.* 3 : 2 stoichiometry) indicate that nitriles have a larger tendency to form oligomers by bridging two dirhodium moieties. This explains earlier NMR data that indicated a non-linear arrangement of the atom Rh–Rh ⟵ N≡C–C.[4c]

(e) Carbon–carbon double bond π systems (olefins) are weak ligands with low binding constants.[4a] They display a tendency to form oligomers (Job plot curve maximum at *ca.* 0.60, *i.e.* 3 : 2). If, however, they are sterically hindered, they can bind to only one dirhodium moiety (Job plot curve maximum at 0.50; *i.e.* 1 : 1-stoichiometry) or fail totally if the steric congestion is too large.[4a]

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