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Journal of Molecular Structure 750 (2005) 7–17
Journal of MOLECULAR STRUCTURE
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Studies on adducts of rhodium(II) tetraacetate and rhodium(II) tetratrifluoroacetate with some amines in $CDCl_3$ solution using ^1H, ^{13}C and ^{15}N NMR

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Received 21 February 2005; revised 31 March 2005; accepted 31 March 2005
Available online 31 May 2005

Abstract

^1H, ^{13}C and ^{15}N NMR spectroscopy has been applied for investigation of amine adducts with rhodium(II) tetraacetate dimer and rhodium(II) tetratrifluoroacetate dimer in $CDCl_3$ solution. Subsequent formation of two adducts, 1:1 and 2:1, was proved by NMR and VIS titration experiments, and by NMR measurements at reduced temperatures, from 233 to 273 K. The adduct formation shift, defined as $\Delta\delta = \delta_{adduct} - \delta_{ligand}$ and characterizing complexation reaction, varies from ca. 0 to +1.6 ppm for ^1H, from ca. −10 to +6 ppm for ^{13}C and from −4.4 to −39 ppm for ^{15}N NMR. Formation of N–Rh bond slows the inversiof on the nitrogen atom and generates, in the case of *N*-methyl-(1-phenylethyl)-amine, a nitrogenous chiral center in the molecule. VIS spectra of amine-dirhodium salt mixture contain two bands in the 532–597 nm spectral range, assigned to 1:1- and 2:1-adducts.

Keywords: NMR; ^1H NMR; ^{13}C NMR; ^{15}N NMR; Amines; Adduct formation shift; Dirhodium complex; Dirhodium tetraacylate; Titration

1. Introduction

Rhodium(II) tetraacylate dimers (Scheme 1) are very well known [1] and numerous papers have proved their importance. Rhodium(II) tetraacetate was applied by organic chemist as the homogenous catalyst; rhodium(II) tetratrifluoroacetate was used as a reagent in the preparation of isomerically pure α,β-unsaturated carbonyl compounds, e.g. some papers published recently [2–9] and references cited herein. Rhodium(II) tetraacylate dimers have been applied as auxiliary ligands in determination of absolute configuration of chiral compounds by electronic spectroscopy [10–13]. The Mosher's acid derivative of rhodium(II) can act as a chiral recognition reagent in NMR spectroscopy, useful in determination of optical purity of chiral compounds [14–23].

All applications of dirhodium tetraacylates are based on initial adducts formation with organic molecule, thus the knowledge of ligation mode and composition of the solution is of great importance. Generally, dirhodium dimers are able to produce various adducts with organic ligands, namely 1:1- and 2:1-adducts with ligands in axial position (Scheme 1) and more complex structures with rearranged dirhodium cores [1,24]. Although the structure of an adduct in the crystalline state is well defined and can be determined by X-ray technique, the composition of the solution is not obvious, due to ligand exchange and various equilibria between species.

NMR spectroscopy appeared as a useful tool for the investigation of dirhodium complexes with organic ligands containing selenium, sulphur or phosphorus atom [17–23]. Recent ^1H, ^{13}C and ^{15}N NMR studies include adducts with mesoionic compounds and derivatives of pyridines [15,25]. In order to extend these studies, some amines have been selected as model ligands for the further examination. There were two purposes of the work. First, is it possible to detect all species existing in solution by NMR spectroscopy? Secondly, how do the NMR parameters reflect adduct formation? Rhodium(II) tetraacetate dimer $Rh_2[ac]_4$ and rhodium(II) tetratrifluoroacetate dimer $Rh_2[tfa]_4$ have been applied as metal substrate; the set of various amines used, **1–11**, are presented on Scheme 1. Since the solvents containing the N, O or S heteroatom (i.e. DMSO, DMF,

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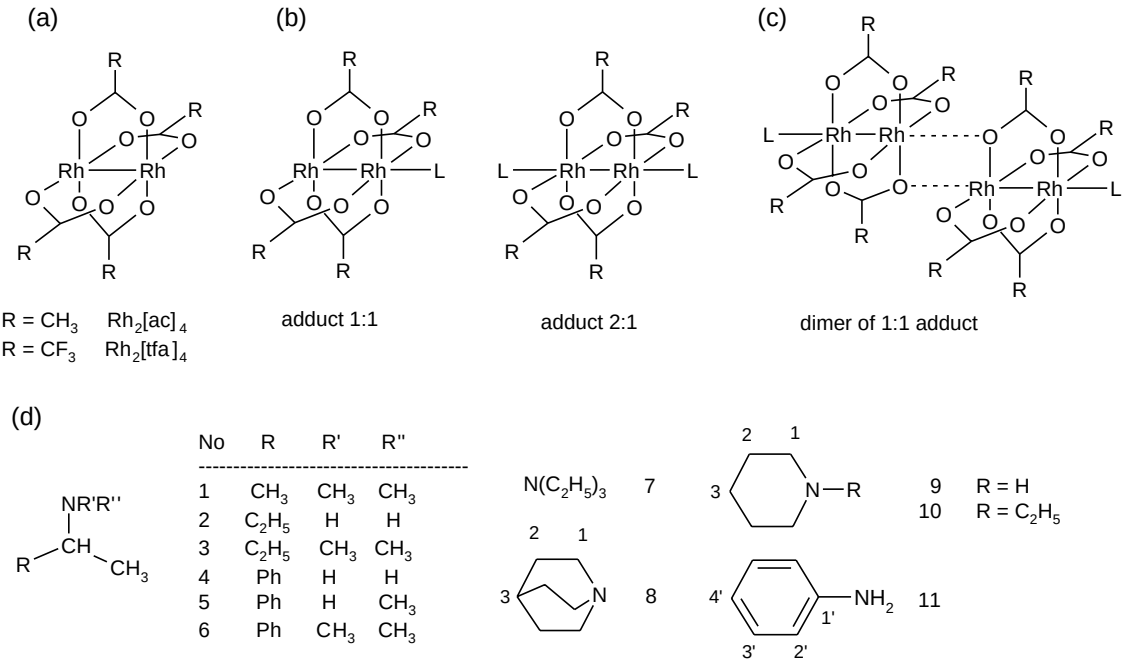
doi:10.1016/j.molstruc.2005.03.035



Scheme 1. Compounds discussed in the present paper. (a) Rhodium(II) tetraacylate dimers; (b) the axial 1:1- and 2:1-adducts of dirhodium(II) tetraacylate and organic ligands L; (c) dimeric form of 1:1 adduct [30]; (d) amines used as model ligands.

acetone, acetonitrile, methanol) are able to bind the dirhodium core and compete with amines for the complexation site, $CDCl_3$ has been used as the solvent of choice for all experiments.

2. Experimental

All ^1H. ^{13}C and ^{15}N NMR measurements were carried out on a Bruker DRX-500 spectrometer using the XWIN NMR acquisition and processing program. The 5 mm triple broadband inverse probe equipped with z-gradient coil was used for ^1H, ^{13}C and ^{15}N NMR measurements. Variable temperature experiments were recorded with the BVT 3000 temperature unit. Temperatures were read directly from the instrument panel; no additional temperature corrections were done.

Amines and dirhodium salts are commercially available. In the case of chiral amines racemic mixtures were used. Amines were dried over KOH pellets and distilled; then a weighted amount of amine was dissolved in $CDCl_3$ (99.8% D atom, stabilized by Ag), using 1 cm^3 volumetric flask, in order to obtaining ca. 0.8 M amine stock solution. All samples were prepared in situ, in the NMR tubes. A weighted quantity of dirhodium salt, from 6 to 12 mg, was placed into the NMR tube, and dissolved $Rh_2[tfa]_4$ or suspended $Rh_2[ac]_4$ in 0.7 ml of $CDCl_3$. Then a suitable volume of amine solution was added to the NMR tube by the 25 μl syringe and the sample was measured. All measurements of a given amine and rhodium salt combination were performed using one NMR sample, by subsequent addition of amine solution into the tube. Typically, the solutions containing 0.5:1, 1:1, 1.5:1, 2:1 and 2.5:1 ligand to rhodium salt molar ratios were measured.

Due to poor solubility of $Rh_2[ac]_4$ in $CDCl_3$, the sample containing $Rh_2[ac]_4$ and 0.7 ml of solvent after addition of each volume of amine stock solution, was placed for a few minutes in the ultrasonic bath and then stored for a next few minutes until insoluble material was deposited on the bottom of NMR tube. Since ligation of metal salt is a driving force transporting $Rh_2[ac]_4$ to the solution, such a procedure causes different real constitution of the solution than calculated one, based on quantity of reagents used. As a consequence, the real composition of the solution was determined by means of signal integration in a suitable ^1H NMR spectrum. In contrast, solubility of $Rh_2[tfa]_4$ in $CDCl_3$ is higher, and the real constitution of the solution is the same as the quantity of reagents applied.

The amine solution, of ca. 0.04 M, was used for running of the ligand reference spectra.

Residual solvent peaks were used as secondary chemical shift standards: $\delta(^1H) = 7.26$ ppm ($CDCl_3$ residual signal), $\delta(^{13}C) = 77.2$ ppm ($CHCl_3$ signal) or $\delta(^{13}C) = 77.0$ ($CDCl_3$ central signal). All foregoing chemical shifts are given with respect to TMS signals, (0 ppm). ^{15}N NMR spectra were referred to external CH_3NO_2 signal (0 ppm).

^1H NMR spectra were gained with parameters acquisition time 2.5 s, flip angle 30°, relaxation delay 1 ms and spectral width ca. 13 ppm; from 16 to 64 scans were acquired, depending on the sample. 32K points were used for data acquisition and Fourier transformation; thus giving the spectral digital resolution of 0.2 Hz per point.

^{13}C, ^{1}H and ^{15}N,^{1}H 2D correlation experiments were gained by means of inverse gradient technique. ^{13}C,^{1}H HSQC (phase sensitive, E/A-TPPI gradient selection with decoupling during acquisition), ^{13}C,^{1}H HMBC (gradient selection, magnitude mode, no decoupling during acquisition) and ^{15}N, ^{1}H HMQC (gradient selection, magnitude mode, no decoupling during acquisition) techniques using 'invietgs', 'inv4gplplrnd' and 'inv4gplrnd' Bruker's pulse programs were applied.

Typically, a 512×2048 matrix, zero filled to 1024×2024 was used for ^{13}C,^{1}H 2D HSQC and HMBC spectra, with parameters acquisition time of 0.27 s, relaxation delay 1.2 s, and 2–8 scans per experiment. Spectral width of 160 ppm in the F_2 (^{13}C) domain and 9 ppm in the F_2 (^{1}H) domain were used giving spectral digital resolutions of ca. 20 Hz per point (^{13}C) and ca. 2.2 Hz per point (^{1}H). A 256×2048 matrix, zero filled to 1024×2048 was used for gaining ^{15}N,^{1}H HMQC correlation spectra. The parameters acquisition time 0.27 s, relaxation delay 1.5 s, a delay from 50 to 60 ms for evolution of long range $^{n}J(^{15}N–^{1}H)$ coupling, and spectral width of 9 ppm in the F_2 (^{1}H) domain giving spectral resolution of ca. 2.2 Hz per point was used. Usually, the measurements were run twice: a preliminary experiment with spectral width of 200 ppm in F_1 (^{15}N) domain, and the second spectrum with reduced spectral width, 30 ppm, giving spectral resolution ca. 1.5 Hz per point. Typically, from 32 to 64 scans per experiment were acquired. However, in the case of some samples, no signals were observed after 64 scans per experiment; in such case ca. 800–1000 scans were taken on and only 64×2048 matrix, zero filled to 512×2024, was used (overnight experiment). Despite the poor FID resolution in F_1 (^{15}N) domain, the experiments were sufficient for satisfactory results.

^{19}F NMR spectra were conducted on a Varian Mercury 400 apparatus, using 5 mm broadband probe. The spectra were gained with parameters acquisition time 1.5 s, flip angle 30°, relaxation delay 4 s and spectral width ca. 50 ppm; typically 16 scans were acquired. 57K(64K) points were used for data acquisition and Fourier transformation, respectively, giving the resulting spectral digital resolution of 0.58 Hz per point. The spectra were referred to ^{19}F peak of external $CFCl_3$ (0 ppm).

Absorption measurements (VIS) were carried out on a Varian Cary IE spectrometer using $CDCl_3$ as solvent, in order to retain the same experimental condition as for NMR experiment.

3. Results and discussion

All ^{1}H, ^{13}C and ^{15}N NMR data are collected in Table 1.

3.1. $Rh_2[tfa]_4$ adducts with amines

The solubility of rhodium(II) tetratrifluoroacetate $Rh_2[tfa]_4$ in $CDCl_3$ is relatively high relative to rhodium(II) tetraacetate $Rh_2[ac]_4$, thus quantity of $Rh_2[tfa]_4$ added to the NMR tube dissolved completely. Consequently, the solution can contain potentially adducts, uncomplexed ligand and uncomplexed $Rh_2[tfa]_4$. Adducts of $Rh_2[tfa]_4$ with primary or secondary amines appeared unstable in the solution and decomposed during measurement, within few hours. Thus, with some exceptions, they were not measured. Generally, NMR spectra of the amine-$Rh_2[tfa]_4$ mixture gained at room temperature contain, with exceptions of **1** and **8**, only one set of averaged signals each. In the case of **1** and **8**, the signals of both adducts were observed even at room temperature; only temperature increase up to 320 K caused signal coalescence. Application of low temperature NMR technique allowed observing the signals of all species in solution. Such phenomenon was in contrast to the experiments with $Rh_2[ac]_4$, when temperature decrease usually did not cause the signals separation (see next Section).

The ^{1}H NMR spectra of **8**-$Rh_2[tfa]_4$ mixtures shown in Fig. 1 illustrate the typical titration experiment. At the beginning of titration (0.6:1), the spectrum contains only 1:1-adduct signals. Adding a next portion of the amine (1.7:1) leads to the appearance of the second set of signals belonging to the 2:1-adduct. Finally (2.3:1), only the signals of the 2:1-adduct and the signals of uncomplexed amine are observed.

The ^{1}H and ^{13}C NMR data of three 1-phenylethylamines, **4**, **5** and **6** (Table 1) illustrate the influence of ligand structure on adduct spectral properties. These amines possess NH_2, $NH(CH_3)$ and $N(CH_3)_2$ group, respectively. As it was mentioned, the solution containing $Rh_2[tfa]_4$ and primary or secondary amines was unstable. However, time-efficient running of experiments allowed obtaining diagnostic data also for **4** and **5**. The ^{1}H NMR spectra of **4**, **5** and **6**, conducted at 273 K, contained two sets of signals deriving from the 1:1- and 2:1-adduct. It is worth noting that the two $N(CH_3)_2$ methyl groups in **6** appeared non-equivalent in adduct, resulting two signals in NMR spectrum (Fig. 2). Non-equivalency of methyl groups can be caused either by influence of the neighbouring chiral centre, or by hindered rotation around carbon–nitrogen $(Ph)(H)(CH_3)C$–N bond. Absence of such non-equivalent methyl groups in the case of achiral tertiary amine **1** suggests rather the former reason. An analogous evidence (i.e. two non-equivalent methyl groups) was observed for the **3**-$Rh_2[tfa]_4$ adduct.

However, the question arises why non-equivalency of $N(CH_3)_2$ groups is not observed in the case of $Rh_2[ac]_4$ complexes, e.g. for $Rh_2[ac]_4$ adducts with **3** or **6** (Table 1). Different behaviour of amine-$Rh_2[ac]_4$ complex can be rationalized by assuming the fast ligand exchange. Generally, the NMR signals of individual $Rh_2[tfa]_4$ adducts can be observed quite easily, at relatively high temperature. In contrast, even low temperature experiments are usually ineffective for amine-$Rh_2[ac]_4$ complexes. Thus, the ligand exchange seems to be faster in the case of $Rh_2[ac]_4$ adducts.

Table 1
^{1}H, ^{13}C and ^{15}N NMR data (in ppm) of some amines and their adducts with dirhodium(II) tetracetate dimer $Rh_2[ac]_4$ and dirhodium(II) tetratrifluoroacetate dimer $Rh_2[tfa]_4$ in $CDCl_3$ solution

Amine	Atom	Free ligand[a]	L: $Rh_2[ac]_4$=1: 1	L: $Rh_2[ac]_4$=2:1	L: $Rh_2[tfa]_4$=1:1	L: $Rh_2[tfa]_4$=2:1
		δ (ppm)	$\Delta\delta=\delta_{adduct}-\delta_{free\ ligand}$ (ppm)[b]			
1			303 K[c]		273 K[d]	
	CH	2.59 [54.7]	1.04 (+4.6)	0.77	1.15 (n.o.)	1.07 (+5.1)
	$CH(CH_3)_2$	1.01 [18.5]	0.35 (+0.1)	0.26	0.39 (+0.4)	0.37 (−0.5)
	$N(CH_3)_2$	2.23 [41.1]	0.52 (+3.1)	0.41	0.58 (+4.0)	0.64(+3.8)
	N	−347.7	−17.2	n.m	−15.0	−7.9
2			303 K[c]			
	CH	2.77 [48.4]	0.84 (+2.5)	0.88		
	CH_3CH	1.02 [23.4]	0.50 (−3.0)	0.50		
	CH_2	1.31 [32.8]	0.71, 0.47 (−1.5)	0.70, 0.46	n.m.	n.m
	CH_3CH_2	0.88 [10.6]	0.27 (−1.0)	0.26		
	NH_2	1.16	[4.31] br	n.o.[e]		
	N	−339.5	−14.5	n.m		
3			303 K[c]		263 K[d]	
	CH	2.36 [60.9]	0.99 (+4.3)	0.76	1.09 br (+4.2)	1.09 br (+4.2)
	CH_3CH	0.93 [13.4]	0.41 (−1.3)	0.30	0.48 (−1.5)	0.45 (−1.5)
	CH_2	1.26, 1.53 [26.2]	[1.43, 2.13] (−0.5)	[1.39, 2.00]	[1.90, 1.54 m] (−0.6)	[1.98, 1.54 m] (−0.6)
	CH_3CH_2	0.88 [11.2]	0.12 (+0.9)	0.09	0.04 (+0.5)	0.06(+0.5)
	$N(CH_3)_2$	2.21 [40.9]	0.53 (+2.4)	0.42	0.63 (+5.4);	0.68(+4.8);
					0.53 (+0.3)	0.58(+0.3)
	N	−351.1	−13.2	n.m.	−4.4[f]	
4			303 K[c]		273 K[d,g]	
	CH	4.12 [51.3]	0.72 (+2.8)	0.78	0.68	0.79
	CH_3	1.39 [25.9]	0.48 (−2.7)	0.48	0.47	0.47
	(C1′)	[147.7]	– (−2.4)			
	H2′(C2′)	7.34 m [125.8, 127.9]	0.29 [126.2]	0.29	0.32	0.32
	H3′(C3′)	7.34 m	0.14 [128.9]	0.11	0.17	0.17
	H4′(C4′)	7.23 m [126.8]	0.15 (+0.7)	0.11	0.20	0.21
	NH	1.54	[4.74]	[4.59 br]	[5.29]	[5.06]
	N	−338.8	−15.2	n.m.	n.m	n.m.
5			263 K[h,i]		263 K[d,g,i,j]	
	CH	3.64 [60.2]	1.36 (−2.6)	0.95br	1.33* (−0.7)	1.41 (−1.5)
			0.90* br (+2.7)		0.96 (+3.6)	1.03*(+2.7)
	CH_3	1.36 [23.8]	0.43 (−9.8)	0.34	0.44* (−9.6)	0.45(−9.9)
			0.32* (−0.2)		0.30 (−1.5)	0.33*(−1.6)
	NCH_3	2.31 [34.5]	0.48 (−4.8)	0.43	0.55* (−3.8)	0.65 (−4.6)
			0.37*(+3.1)		0.36 (+3.5)	0.47*(+2.9)
	(C1′)	– [145.4]	n.m.	n.m.	n.m	n.m.
	H2′(C2′)	7.31 m 128.4, 126.5]	0.31; 0.23 [126.8]	0.23	0.30 m [126.9]	0.30 m [127.3]
	H3′(C3′)	7.31 m	0.18 [128.1]	0.15	0.22 m [128.3]	0.20 m [128.7]
	H4′(C4′)	7.24 [126.8]	0.15 (+0.3)	0.11	0.20 m (+1.1)	0.17 m (+1.1)
	NH	n.o.[e]	[4.87], [4.58]	[4.58 br]	[5.41*], [5.19]	[5.11], [4.89]
	N	−340.1	−18.2[k]	−10.5[k]	−16.6*, −17.4	n.m.
6			303 K[c]		273 K[d]	
	CH	3.25 [65.9]	1.26 (+1.4)	0.88	1.56 (+1.1)	1.62 (+0.3)
	CH_3	1.38 [20.1]	0.28 (−2.5)	0.21	0.29 (−2.2)	0.32 (−2.2)
	$N(CH_3)_2$	2.20 [43.1]	0.41 (+0.5)	0.30	0.42 (+5.4)	0.51 (+4.8)
					0.64 (−4.3)	>0.69 (−4.7)
	C1′	– [144.0]	– (−4.2)		– (−6.9)	– (−6.3)
	H2′(C2′)	7.30 m [127.4, 128.1]	0.24 [129.7]	0.17	0.31 [130.5]	
	H3′(C3′)	7.30 m	0.13 [127.7]	0.09	0.20 [128.3]	
	H4′(C4′)	7.23 [126.8]	0.15 (+0.6)	0.09	0.24 (−0.5)	
	N	−342.9	−16.1	−9.1	−19.1	−13.5
7			303 K[c]		273 K[d]	
	CH_2	2.49 [46.3]	0.63 br (+1.7)	0.38	0.81 (+2.8)	0.87 (+1.9)
	CH_3	1.00 [11.6]	0.18 (−2.1)	0.09	0.22 (−2.7)	0.20 (−2.7)
	N	−331.6	−19.9	n.m.	−21.6	−16.0
8			233 K[d]		303 K[d]	
	H1 (C1)	2.84 [47.8]	0.68 (+2.0)	0.76 (+1.4)	0.79 (+3.2)	0.83 (+2.3)
	H2 (C2)	1.52 [26.7]	0.26 (−0.6)	0.20 (−0.4)	0.61 (+0.1)	0.54 (+0.3)
	H3 (C3)	1.72 [20.7]	0.44 (−0.4)	0.38 (−0.1)	0.54 (+0.0)	0.48 (+0.4)

(*continued on next page*)

Table 1 (*continued*)

Amine	Atom	Free ligand[a]	L: $Rh_2[ac]_4$ = 1: 1	L: $Rh_2[ac]_4$ = 2:1	L: $Rh_2[tfa]_4$ = 1:1	L: $Rh_2[tfa]_4$ = 2:1
		δ (ppm)	$\Delta\delta = \delta_{adduct} - \delta_{free\ ligand}$ (ppm)[b]			
	N	−364.5	n.o.[l]	n.o.[l]	−13.7	−8.6
9		223 K	233 K[d]			
	H1(C1)	2.98_{eq}, 2.51_{ax} [46.9]	0.81_{eq}, 0.73_{ax} (+2.1)	0.94_{eq}, 0.80_{ax} (+2.3)		
	H2 (C2)	1.56_{eq}, 1.40_{ax} [26.5]	[1.98, 1.85] (+1.1)[m]			
	H3 (C3)	1.72_{eq}, 1.26_{ax} [24.1]	[2.03, 1.79] (0.0)[m]		n.m.	n.m.
	NH	n.o.	[4.40][n]	[4.13][o]		
	N	−340.5[k]	−24.0	−11.1		
10		233 K	223 K[p]		263 K[p]	
	H1 (C1)	2.94; 1.74 [53.9]	[3.61, 3.27] (−1.8)			[3.67, 3.31] (−0.5)
	H2 (C2)	1.62, 1.50 [25.7]	[2.14, 1.52[m]] (−6.3)			[2.23, 1.67] (−5.4)
	H3 (C3)	1.69, 1.12 [24.3]	[1.91[m], 1.65[m]] (0.0)			[1.98, 1.69[m]] (0.1)
	CH_2	2.32 [52.8]	1.00 (−6.7)			1.12 (−5.3)
	CH_3	1.06 [12.2]	0.11 (−1.3)			0.12 (−1.2)
	N	−326.1	−39.0		−33.6	
11		([q])	243 K[q]		243 K[q]	
	(C1′)	[146.3]	– (−2.7)			
	H2′(C2′)	6.74 [115.1]	0.69 (+4.2)	0.62		
	H3′(C3′)	7.17 [129.3]	0.22 (−0.2)	0.19		
	H4′(C4′)	6.77 [118.5]	0.39 (+3.8)	0.32		
	NH_2	3.64	[6.28]	[6.17]	[7.12]	[6.93]
	N	−326.8	−17.0	−13.3	−25.1	−17.7

Abbreviations: n.m., not measured; n.o, not observed in the spectrum; br, broad signal; m, unresolved multiplet; ax,eq, axial and equatorial hydrogen atom, respectively.

[a] Reference chemical shifts for free (uncomplexed) ligand: ^1H chemical shifts (ppm), ^{13}C chemical shifts (squared brackets, ppm) and ^{15}N chemical shifts (ppm). All reference data were collected at 303 K with exceptions of data for **9** and **10**, obtained at 233 K.

[b] ^1H, ^{13}C (in parenthesis) and ^{15}N NMR adduct formation shifts, defined as $\Delta\delta = \delta_{adduct} - \delta_{free\ ligand}$ (ppm). The suitable chemical shifts (ppm) are given in square brackets if $\Delta\delta$ was not calculated due to lack of the signal assignments.

[c] The $\Delta\delta$ data for the solutions in equilibrium containing 1:1 and 2:1 mixture of reagents; only one set of the signals at averaged positions is observed (i.e. no signals of the individual adducts have been detected).

[d] The $\Delta\delta$ values calculated using the chemical shifts of the individual 1:1- and 2:1-adducts.

[e] The signal too broad to be observed.

[f] Measurement at room temperature (303 K); the value for the 1.5: 1 equilibrium mixture.

[g] The sample is unstable.

[h] The signals of 1:1-adduct in the 0.5:1-mixture of reagents have been observed at 263 K. The signals of 2:1-mixture are broad; no signal separation is observed.

[i] Asterisk denotes the major component in the solution (if assigned).

[j] No significant differences between the spectra taken at 263 and 303 K.

[k] Measurements at room temperature (303 K).

[l] No signals after overnight acquisition.

[m] ^1H chemical shifts taken from ^{13}C–^1H 2D correlation spectra. ^1H and ^{13}C chemical shifts are similar for both adducts, the signals are not assigned precisely.

[n] Triplet, 12 Hz.

[o] Triplet, 13.5 Hz.

[p] The signals are not assigned precisely to the two adducts due to the signal overlapping.

[q] The 100% ^{15}N-enriched aniline was used. The NH signal appears as a doublet; $^1J(^{15}N–^1H)$ = 78 Hz for free aniline, 73 Hz for the $Rh_2[ac]_4$ 1:1-adduct and 72 Hz for the $Rh_2[tfa]_4$ 1:1-adduct. The signals at averaged position are observed for the $Rh_2[ac]_4$ -aniline mixture; the signals of both adducts are observed for the $Rh_2[tfa]_4$ mixture. However, the signals are broad and not assigned completely.

On the other hand, exchange of the methyl groups via nitrogen inversion is possible only in the free ligand, not in the adduct. Consequently, the rate of methyl group exchange is significantly greater in the case of the $Rh_2[ac]_4$ complex making both methyl groups equivalent.

The most interesting behaviour was noted for the **5**-$Rh_2[tfa]_4$ complexes, containing a $NH(CH_3)$ group. Formation of the N–Rh bond prevents inversion on nitrogen atom, and induces new, a nitrogenous chiral centre in the adduct. Considering that **5** contains a second chiral atom, two diastereoisomers, RR(SS) or RS(SR) are formed by binding the amine. If 'A' denotes the first diastereoisomer and 'B' the second one, one can expect five adducts, potentially existing in the solution: A-[Rh–Rh], B-[Rh–Rh], A-[Rh–Rh]-A, A-[Rh–Rh]-B and B-[Rh–Rh]-B. Consequently, three different signals of 'A' are expected on NMR spectrum: one signal of the 1:1-adduct and two signals of two diverse 2:1-adducts. The same is expected for 'B'.

The signal of the $N(CH_3)$ methyl group reflects the formation of all these adducts signal (Fig. 3). Two doublets at δ = 2.67 and 2.86 ppm appearing at the beginning of titration were assigned to A and B isomers of 1:1-adduct; the signal multiplicity could be explained by the $^3J(NH\text{-}CH_3)$ coupling of 6.4 Hz. Then, under titration, the doublets of

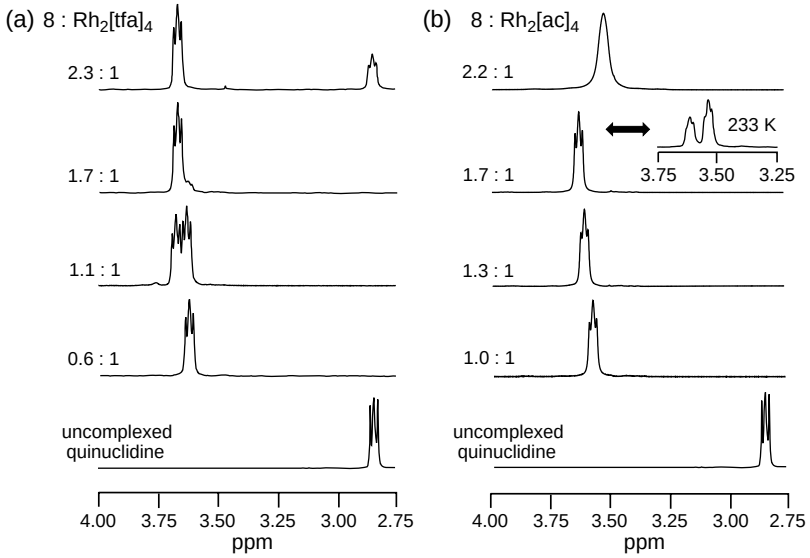


Fig. 1. The ^{1}H NMR titration experiment of quinuclidine **8** and rhodium(II) tetraacylate dimers; the α signal of **8** is shown in the spectra. The concentration of dirhodium salt was constant; the concentration of **8** increased under titration. (a) NMR titration of $Rh_2[tfa]_4$, at 303K. The signal of uncomplexed amine and the signals of two adducts are visible at room temperature; (b) NMR titration of $Rh_2[ac]_4$, at 303 K. Inset shows the spectrum taken at 233 K. The signals of both adducts are visible at low temperature.

1:1-adduct vanished; instead two triplet-like signals appeared, at $\delta = 2.78$ and 2.96 ppm. Assuming that each triplet consists of two overlapped doublets, one signal can be assigned to A molecules in 2:1-adducts, and second one to B molecules. It should be noted that analogous signals of the NH hydrogen atoms also could be observed in ^{1}H NMR spectra. (Table 1). The formation of two 1:1 diastereoisomers was also observed for **5** and $Rh_2[ac]_4$ (Table 1).

The NMR data lead to the general conclusion that $Rh_2[tfa]_4$ tends to form subsequently the 1:1- and 2:1-adducts, even with tertiary amines. In contrast, $Rh_2[ac]_4$ tends to form only the 1:1 adduct with tertiary amines, under similar experimental condition (see next section). This finding is in agreement with VIS experiment (see below; Fig. 5).

3.2. $Rh_2[ac]_4$ adducts with amines.

In contrast to $Rh_2[tfa]_4$, the solubility of rhodium(II) tetratrifluoroacetate $Rh_2[ac]_4$ in $CDCl_3$ is relatively low. A real composition of the sample solution depends on the equilibrium between solution and insoluble rhodium salt, thus differs from the ratio of components added (see Section 2). For example, a mixture of one equivalent of $Rh_2[ac]_4$ and 0.5 equivalent of amine in $CDCl_3$, yielded usually a solution containing ca. 1:1 molar ratio of components and insoluble

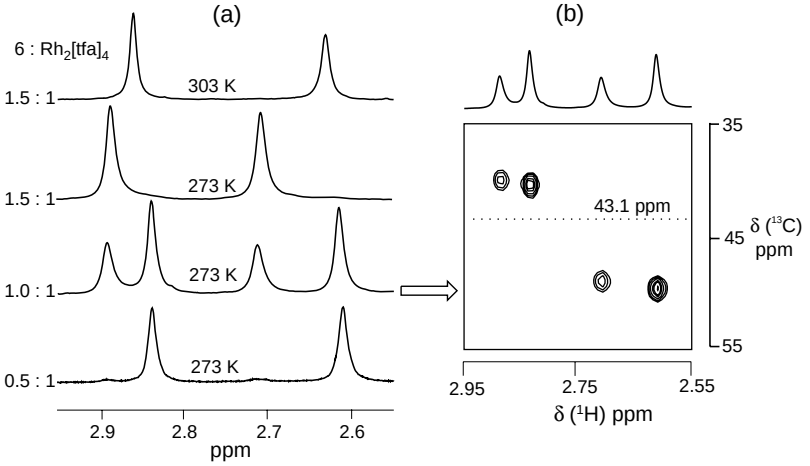


Fig. 2. The ^{1}H NMR spectra of **6**-$Rh_2[tfa]_4$ mixture. The signals of $N(CH_3)_2$ group are shown. (a) The signals of either one or two adducts are seen at 273 K, depending on the ligand to rhodium salt ratio. The absences of 1:1 adduct signals in 1.5:1 mixture of reagents is worth noting. Only averaged signals are visible at room temperature, but non-equivalency of two methyl groups are retained; (b) ^{13}C-^{1}H correlation spectrum of 1:1 mixture. Opposite $\Delta\delta(^{13}C)$ signs of the two $N(CH_3)_2$ methyl groups are observed. The $N(CH_3)_2$ groups of uncomplexed amine resonate at $\delta = 43.1$ ppm.

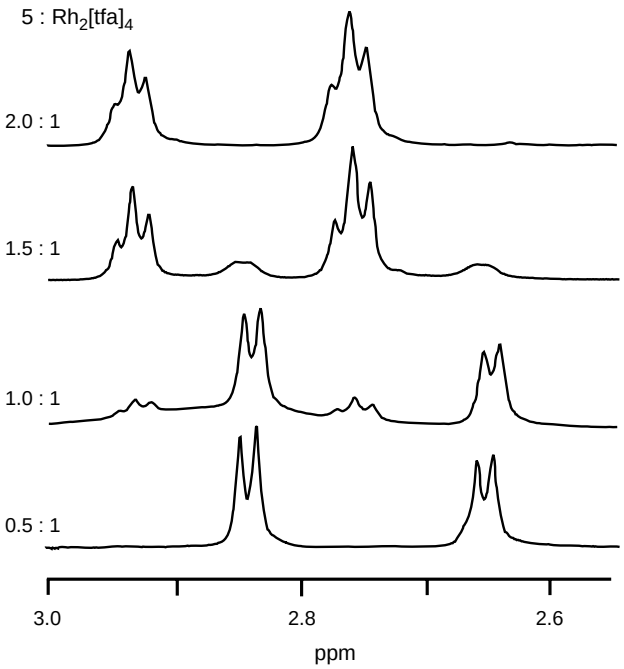


Fig. 3. The ^{1}H NMR spectra of **5**-$Rh_2[tfa]_4$ mixture at 273 K. The signals of NCH_3 methyl group are shown. Depending on the ligand to rhodium salt ratio, the signals of two 1:1-adducts (doublets) or the signals of three 2:1-adducts (triplet-like signals) are visible. For explanation see text.

$Rh_2[ac]_4$ at the bottom of NMR tube. Due to the poor solubility of $Rh_2[ac]_4$, the solution contained mainly adducts and eventually uncomplexed amine; there was no significant concentration of uncomplexed $Rh_2[ac]_4$. Then under titration insoluble dirhodium salt gradually dissolved. The colour of the solution depends on the molar ratio of components, and varies from blue (1:1 ratio) via violet (1.5:1 ratio) to red (2:1 ratio).

The solution of an amine and $Rh_2[ac]_4$ is expected to contain adducts and uncomplexed ligand to be in equilibrium, by analogy to $Rh_2[tfa]_4$. However, only one set of averaged signals was observed in NMR spectra conducted at room temperature, due to the fast ligand exchange (on NMR time scale). Application of low temperature was supposed to decrease ligand exchange rate and to allow observing the signals of individual species. Unfortunately, low temperature NMR technique appeared, generally, ineffective in the case of $Rh_2[ac]_4$. Temperature reduction resulted either in signal broadening or made the spectra interpretation difficult. Quinuclidine (**8**) appeared to be an exception. At low temperature (233 K) ^{1}H signals split proving the presence of two adducts (Fig. 1, right). Low temperature experiment were successful partly for **5** as well. ^{1}H and ^{13}C NMR chemical shifts changes remained the sole proof of complexation in the case of other amines. Generally, two kinds of ^{1}H NMR signal responses were observed under titration. As an example of the first manner one can consider the titration experiment of **8**-$Rh_2[ac]_4$ (Fig. 1, right). At the beginning of the titration, i.e. for the 1:1 mixture, a high-frequency shift of the ^{1}H signal was observed. Next, further a high-frequency shift occurred until an excess of the ligand, more than two equivalents, was reached. Finally, the a low-frequency shift (shift back) was noted. Simultaneously, the colour of the solution changed from blue to violet and finally to red. Such behaviour can be explained by stepwise formation of two adducts $L\cdot Rh_2[ac]_4$ and $L_2\cdot Rh_2[ac]_4$, and by equilibria: $L + Rh_2[ac]_4 \rightleftharpoons L\cdot Rh_2[ac]_4$ and $L\cdot Rh_2[ac]_4 + L \rightleftharpoons L_2Rh_2[ac]_4$. The equilibrium was shifted towards the adduct formation; thus there was no significant concentration of the unbonded amine in the solution until all uncomplexed dirhodium salt was consumed. After that, free ligand appeared in the solution causing 'shift back' of the ^{1}H signal. Such behaviour was observed also for the amines **2**, **4**, and **9**, i.e. for all primary and secondary amines.

The signals of **1**, **3**, **6** and **7** (tertiary amines) exhibited high-frequency shift at the beginning of titrations. Then, only 'shift back' phenomena were observed under titration, and the solution remained blue. On addition of very large ligand excess, ca. 10–20 equivalents, caused colour transformation to red. Such a result indicates that the tertiary amines tend to form mainly 1:1-adducts and the stability of their 2:1-adducts is low with respect to primary and secondary amines. Quinuclidine (**8**) forming both 1:1-and 2:1-adducts with $Rh_2[ac]_4$ is an exception.

The case of **5**-$Rf_2[ac]_4$ adduct is worth noting. ^{1}H NMR spectra of **5**-$Rf_2[ac]_4$ mixtures, recorded at room temperature, exhibited only one set of averaged signals. The spectrum of **5**-$Rf_2[ac]_4$ as an equimolar mixture, taken at 263 K, contained the signals of two different 1:1-adducts (1:0.9 ratio). These adducts could be identified as two 1:1-diastereoisomers, like in the case of $Rh_2[tfa]_4$ (see previous section). Only broad ^{1}H signals were observed for a 2:1 $Rh_2[ac]_4$-**5** mixture despite the low temperature; thus, the information on individual adducts was lost. However, the presence of the 2:1-adduct in this mixture was proofed by VIS data (see below, Fig. 5)

The NMR data lead to the conclusions that the primary and secondary amines yield two kinds of adducts with $Rh_2[ac]_4$ in $CDCl_3$, 1:1 and 2:1, similarly to $Rh_2[tfa]_4$. Adducts are formed gradually, depending on the ligand to $Rh_2[ac]_4$ ratio. In contrast to $Rh_2[tfa]_4$, tertiary amines tend to form the 1:1-adducts only with $Rh_2[ac]_4$; no significant concentration of 2:1-adducts was observed, at least in ca. 0.4 mM solutions. The amines **2** and **3** or the amines **4**, **5** and **6** can illustrate such feature. The amines possessing exposed lone pair, like quinuclidine (**8**), seem to be an exception.

3.3. ^{1}H and ^{13}C NMR adduct formation shifts

The change of a ligand chemical shifts caused by complexation can be expressed by the adduct formation shift $\Delta\delta$, defined as $\Delta\delta = \delta_{\text{adduct}} - \delta_{\text{uncomplexed ligand}}$ (Table 1). Generally, in the case of $Rh_2[tfa]_4$, the signals

of both adducts could be observed in NMR spectra at reduced temperature. The $\Delta\delta$ values of $Rh_2[tfa]_4$ adducts given in the Table are related to the individual species. In contrast, low temperature NMR appeared usually ineffective in the case of $Rh_2[ac]_4$ adducts, due to fast ligand exchange (with exception of the amine **5** and **8**). In consequence, only the $\Delta\delta$ values of equilibrium mixtures (1:1 and 2:1 ligand to $Rh_2[ac_4]$ ratio) are given in the Table.

Adduct formation resulted in high-frequency shift of all ^1H signals. Positive $\Delta\delta(^1H)$ values of hydrogen atom attached to carbon did not exceed 1.6 ppm. However, $\Delta\delta(^1H)$ of NH group reached values of ca. 3 ppm. The $\Delta\delta$ magnitude decreased with the hydrogen–nitrogen distance reduction, i.e. the distance from the ligation site. The ^1H NMR data of $Rh_2[tfa]_4$ adducts with **7** and **8** can serve as a typical example (Table 1). Some irregularities have been also observed, e.g. $Rh_2[tfa]_4$ adducts with **1**, **3**, **5** and **6**. For these adducts, maximal $\Delta\delta$ values from 0.96 to 1.62 ppm have been noted for the N–C*H* signal (tertiary hydrogen atom) whereas smaller values from 0.36 to 0.69 ppm have been found for NCH_3 methyl group, in spite of similar distance from the nitrogen atom. Very similar $\Delta\delta$ values, from 0.29 to 0.48 ppm, have been observed for farther N–CH–CH_3 methyl group. The **8**-$Rh_2[ac_4]$ adduct is another example; $\Delta\delta$ value for H(3) is greater than for (H2).

Dependence of ^{13}C chemical shifts on the adduct structure is not so obvious. $\Delta\delta(^{13}C)$ values observed appear in the range from +5.4 to −9.9 ppm. Typically, a few ppm values, either positive for the α-carbon atoms or negative for β-carbon atoms have been observed, e.g. in the $Rh_2[tfa]_4$ adduct with **7** or the $Rh_2[ac]_4$ adducts with **2**, **3**, **4**, **6**, **7** or **8**. On the other hand, more complex relationships were also noted, e.g. 1:1-adducts of $Rh_2[ac]_4$ and **5**. $\Delta\delta(^{13}C)$ values of −2.6 ppm for the N–*C*H atom, of −9.8 ppm for the N–CH–*C*H_3 atom and −4.8 ppm for the NCH_3 atom were found for the one 1:1-adduct, whereas the values of +2.7, −0.2 and +3.1 ppm were noted for the second one. Large $\Delta\delta$ differences for both diastereoisomers, in particularly of the CH-*C*H_3 atoms, are of interest. One should point also to the $Rh_2[tfa]_4$ adducts with the amines possessing $N(CH_3)_2$ groups, e.g. **6**. Two non-equivalent CH_3 groups exhibit positive and negative $\Delta\delta(^{13}C)$, respectively, of ca. +5 and −5 ppm. Thus, sign and magnitude of $\Delta\delta(^{13}C)$ depend rather on the ligand arrangement in the adduct than on the carbon-nitrogen distance.

3.4. ^{19}F NMR experiments

^{19}F NMR measurements of **8**-$Rh_2[tfa]_4$ mixtures, at 303 K, were acquired for the comparison purposes. A spectrum of $Rh_2[tfa]_4$ in $CDCl_3$ contained one signal, at $\delta = -75.0$ ppm. The spectrum of amine-$Rh_2[tfa]_4$ mixtures contained two signals, at $\delta = -75.0$ ppm ($Rh_2[tfa]_4$) and −75.2 ppm (the 1:1-adduct). The 1:1 mixture of components resulted in two signals in the spectrum, at $\delta = -75.2$ ppm (the 1:1-adduct) and −75.4 ppm (the 2:1-adduct). Finally, only one signal at $\delta = -75.4$ ppm was observed for 2:1-mixtures. Considering the fact that chemical shift of fluorine nucleus varies within the range of hundreds ppm, ^{19}F NMR technique is relatively insensitive in the case of our model reaction.

3.5. ^{15}N NMR experiments

With a view to the fact that nitrogen atom is directly involved in adduct formation, ^{15}N chemical shift is expected to be the most diagnostic NMR parameter describing the complexation process. The 2D inverse technique allows obtaining the ^{15}N–^1H correlation spectra using diluted samples containing a few milligrams of amine. The most accurate and reliable results stem from experiments showing signals of all species in the solution, i.e. measurements of $Rh_2[tfa]_4$ adducts at low temperatures.

Ligation caused significant changes of ^{15}N chemical shifts. The $\Delta\delta(^{15}N) = \delta(^{15}N)_{adduct} - \delta(^{15}N)_{free\ ligand}$ value varied from −4 ppm (**3**-$Rh_2[ac]_4$ adduct), to −39.0 ppm (**10**-$Rh_2[tfa]_4$ adduct). Typically, $\Delta\delta$ values of −10 to −20 ppm have been observed. There was not straightforward relationship between amines structure and $\Delta\delta$ magnitudes. If the signals of individual adducts were detectable, the $\Delta\delta(^{15}N)$ magnitudes of 1:1-adduct were greater than those of the respective 2:1-adducts for a given amine and dirhodium salt combination (Fig. 4). The typical difference was equal to ca. 6 ppm. This rule was not fulfilled for mixtures in equilibria, e.g. mixtures of $Rh_2[ac]_4$ with **5** or **6**. In the latter case, $\Delta\delta(^{15}N)$ was disturbed by the presence of uncomplexed amine. Such findings exhibit that two ligand molecules, attached to the two-dirhodium sites, are not independent. It is worth noting that ^{15}N NMR technique is able to recognize diastereoismers, e.g. ^{15}N data for two 1:1 **5**-$Rh_2[tfa]_4$ adducts (Table 1).

Previously, $\Delta\delta(^{15}N)$ values covering the range from −53 to −75 ppm have been found for pyridines; a value of ca. −40 ppm has been noted for mesoionic oxatriazole [25]. Thus, the $\Delta\delta(^{15}N)$ values observed for rhodium carboxylate adducts with the amines discussed here are relatively low.

3.6. VIS experiments

Effective colour change of the $Rh_2[ac]_4$ or $Rh_2[tfa]_4$ solution under titration by amine from blue to violet and finally to red suggests the use of electronic absorption spectroscopy in the visible light (VIS) as a supplemental tool of examination. The measurements were done using three amines with similar structure, 1-phenylethylamine **4** (primary amine), *N*-methyl-1-phenylethylamine **5** (secondary amine) and *N*,*N*-dimethyl-1-phenylethylamine **6** (tertiary amine). Some results of titration VIS experiments are collected on the Fig. 5.

Typically, the red shifted band, within the range 575–597 nm appeared at the beginning of titration. Then, under titration, this band vanished, instead of that blue

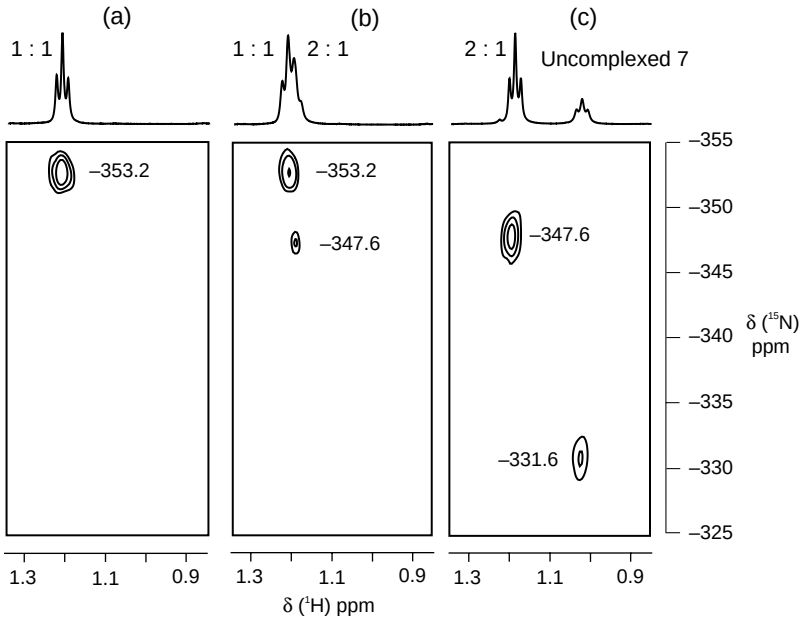


Fig. 4. Example of the ^{15}N–^{1}H correlation experiments of **7**-$Rh_2[tfa]_4$ mixtures, at 263 K. Depending on ligand to rhodium salt ratio, the signals of 1:1 adduct (a), 1:1- and 2:1-adducts (b) 2:1-adduct and uncomplexed ligand (c) are visible.

shifted band was formed, in 532–547 nm. These signals were assigned to the 1:1 and 2:1 adduct, respectively. Isobestic point clearly indicated the subsequent formation of both 1:1 and 2: 1 adducts. The spectra set of **6**-$Rh_2[ac]_4$ mixture was an exception; in this case practically one band was noted, at 597 nm. In fact, slight blue band shift under titration can be observed, but the equilibrium is clearly shifted towards the 1:1-adduct. Thus, VIS titration

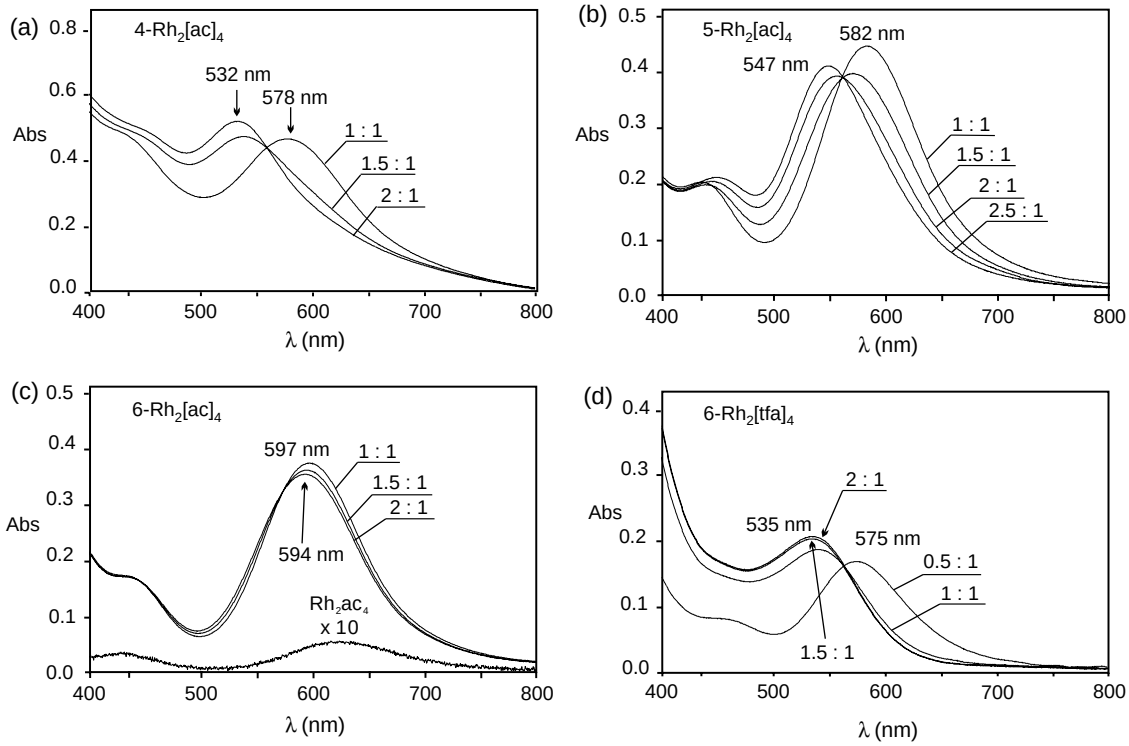


Fig. 5. VIS absorption electronic spectra (titration experiment) of $Rh_2[ac]_4$, $Rh_2[tfa]_4$ and **4**–**6**. The concentration of the dirhodium salt was constant; the amine concentration was increased; ca. 7 mM solutions of dirhodium salt in $CDCl_3$ were used. The formation of two adducts is clearly visible (a, b and d). The formation of mainly 1:1-adduct is observed for **6**-$Rh_2[ac]_4$ (c). Tenfold enlarged spectrum of $Rh_2[ac]_4$ in $CDCl_3$ (saturated solution) is shown for comparison purposes (c).

experiments are in agreement with NMR findings and provide information on adduct stoichiometry.

3.7. The adduct structure

The structure of the 2:1-adduct in the solution is rather clear. The most possible structure consists of the dirhodium core and two axially bonded ligands. ^{1}H NMR spectra of $Rh_2[ac]_4$-adducts contained only one CH_3 signal of $Rh_2[ac]_4$ core revealing equivalency of all methyl groups and confirming axial ligation mode. The same was observed in ^{19}F NMR spectroscopy for $Rh_2[tfa]_4$ adducts. Such ligand arrangement was found, by X-ray, for the following adducts: $Rh_2(tBuCOO)_4$ with NEt_3 [26], $Rh_2[tfa]_4$ with PPh_3 [27], and $Rh_2[ac]_4$ with $NH(C_2H_5)_2$ [28] or pyridine [29]. One can expect that the adduct structures in solution and in solid state are similar.

Axial ligation mode is expected also for 1:1-adducts. However, the structure of the whole adduct is not obvious. It is known that the dirhodium salt tends to form 2:1-adducts. The unoccupied site of a 1:1-dirhodium complex usually bonds either a solvent or a water molecule or just an oxygen atom of the second dirhodium unit [1]. In the crystalline state, the dimeric 2:2 structure has been found in the case of $Rh_2[ac]_4$ and PhNC (Scheme 1). As similar dimeric structure was observed for the adduct of $Rh_2[ac]_4$ with triphenylphosphine [30].

Our NMR and VIS data does not allow to state what is the real structure of the 1:1-adduct in the solution, monomeric or dimeric. Precisely speaking, in the present paper the 1:1-adduct means dirhodium core with one site occupied by one molecule of amine, while the 2:1-adduct means one dirhodium core containing two molecules of amine.

The ^{1}H NMR data of the $Rh_2[tfa]_4$ with piperidine **9** adduct provide some information on this ligand's arrangement. The NH signal of the amine shows triplet-like structure, with 'large' coupling constant of ca. 13 Hz. Such multiplicity can be explained by vicinal coupling of axial NH hydrogen with the two axial α-hydrogens in the ring. Consequently, the dirhodium unit is attached to the ring via equatorial N–Rh bond.

3.8. Conclusions

The results of NMR and VIS measurements can be summarized as follows:

(i) In titration experiments, amines and dirhodium salts, $Rh_2[ac]_4$ and $Rh_2[tfa]_4$, form 1:1- and-2:1 adducts subsequently. Tertiary amines with $Rh_2[ac]_4$ tend to form only 1:1-adducts under similar experimental conditions, i.e. in $0.2 \div 0.4$ mM solutions. Quinuclidine (**8**) containing exposed lone electron pair and giving 2:1-adduct with $Rh_2[ac]_4$, is an exception.

(ii) NMR measurements conducted at low temperatures allow observing the signals of both $Rh_2[tfa]_4$-amine adducts in solution. In contrast, low temperature technique is less effective in the case of $Rh_2[ac]_4$ adducts. Temperature decrease causes often broadening of NMR signals only. However, there are exceptions from this rule.

(iii) It is known [31] that dynamic effects visible in NMR spectrum caused by ligand exchange depend on ligand exchange rate, $\Delta\delta$ values and temperature. Since $\Delta\delta$ values (adduct formation shifts) are comparable for both $Rh_2[ac]_4$ and $Rh_2[tfa]_4$ adducts (for the same amine), different behaviour of $Rh_2[ac]_4$ and $Rh_2[tfa]_4$ adducts with respect to temperature change suggests slower ligand exchange in the case of $Rh_2[tfa]_4$.

(iv) Formation of Rh–N bond slows down structure inversion of nitrogen atom. Hindered inversion causes, in certain cases, either non-equivalency of two $N(CH_3)_2$ methyl groups or formation of nitrogenous chiral centre in the case of secondary amines ($R'R''NH$).

(v) The adduct formation shift $\Delta\delta = \delta_{adduct} - \delta_{ligand}$ (ppm) is a useful NMR parameter characterizing the binding process. $\Delta\delta(^1H)$ is positive and does not exceed the value of 2 ppm. The magnitude of $\Delta\delta(^{13}C)$ does not exceed a few ppm; the sign of $\Delta\delta(^{13}C)$ is either positive or negative. The $\Delta\delta(^{15}N)$ values of the nitrogen atom, involved in binding, occur within the range from -4 to -39 ppm. Generally, the magnitude of $\Delta\delta(^{15}N)$ of 1:1-adducts is a few ppm lower than that of 2:1-adducts.

(vi) Typically, VIS spectra of the rodium tetracarboxylate-amine mixture taken on in $CDCl_3$ contain two bands in the 532–597 nm spectral range. Red bands can be assigned to 1:1-adducts, whereas blue shifted bands refer to 2:1 adducts. VIS titration experiments exhibiting isobestic point confirm consecutive formation of two adducts.

Acknowledgements

This work was supported by the State Committee for Scientific Research under Grant No. 4 T09A 060 25.

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