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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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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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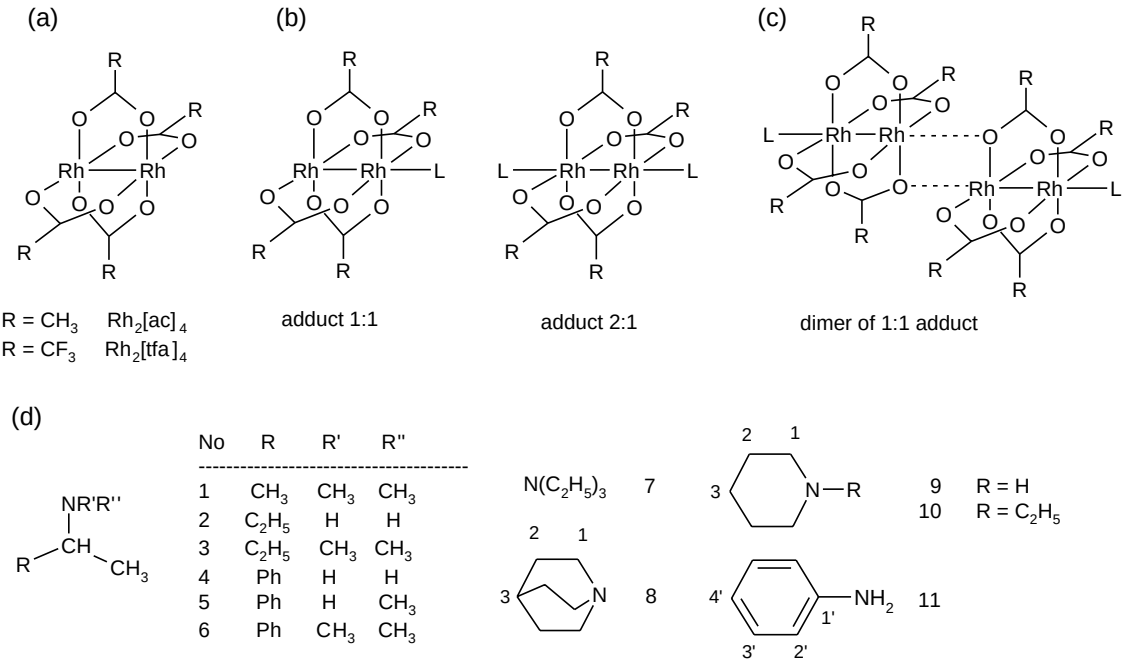

Scheme 1. Compounds discussed in the present paper. (a) Rhodium(II) tetraacylate dimers; (b) the axial 1:1- and 2:1-adducts of dirhodium(II) tetraacylate and organic ligands L; (c) dimeric form of 1:1 adduct [30]; (d) amines used as model ligands.

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.