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Abstract. The two vinylidene complexes *Cp(CO)$_2$RePt(μ-C=CHPh)(PPh$_3$)(CO)* and *Cp(CO)$_2$RePt(μ-C=CHPh)(PPh$_3$)$_2$* and their precursors *PPh$_3$* and *P(PPh$_3$)$_4$* were studied by solid-state nuclear magnetic resonance. We analysed ^{31}P cross-polarization spectra acquired in static conditions and with magic angle spinning. The chemical shift tensors of each sample were determined by fitting their spectra using SIMPSON simulations.

1. Introduction

Transition metal heteronuclear vinylidene complexes are interesting in the fields of chemistry and catalysis due to the possibility of their participation in stoichiometric and catalytic syntheses of some organic substances used in industry and medicine [1-7]. They can be used in the synthesis of organometallic compounds, can participate in catalytic processes, and they also perspective in synthesizing functional polymetallic materials [1]. Binuclear rhenium-platinum catalysts are more effective than catalysts based on a single metal, since they have increased mechanical stability and high selectivity, and can be used in oil reforming processes [2].

NMR spectroscopy in the liquid and solid states is traditionally used to study molecular structure, nature of chemical bonds and intermolecular interactions of substances. In this paper, the heterobinuclear vinylidene complexes *Cp(CO)$_2$RePt(μ-C=CHPh)(PPh$_3$)CO* (*RePt(PPh$_3$)CO*) and *Cp(CO)$_2$RePt(μ-C=CHPh)(PPh$_3$)$_2$* (*RePt(PPh$_3$)$_2$*) [3] and their precursors *triphenylphosphine* (*PPh$_3$*) and *tetrakis-(triphenylphosphine)platinum(0)* (*Pt(PPh$_3$)$_4$*) were studied using solid-state ^{31}P nuclear magnetic resonance (NMR) spectroscopy.

These vinylidene complexes were already studied by NMR in liquids, and isotropic chemical shifts and J-coupling constants were obtained [3]. But due to the fast rotational and translational motion of molecules in the solution, anisotropic effects such as dipole-dipole interactions and anisotropy of the chemical shift tensor are averaged to zero. Since the chemical shift tensor is directly related to the electron density near the nucleus, to know this information is important in the analysis of chemical bonds of a substance. Using solid-state NMR spectroscopy, we can obtain this information and draw conclusions about the electronic structure of matter [10-11].

A comparative analysis of the data will allow us to clearly show what changes occur in the chemical bonds between the atoms of platinum and phosphorus. A slight change in the composition of a molecule

of the vinylidene complex strongly affects the shape of the NMR spectral line and the chemical shift tensor, which can be used to control the production of substances.

The chemical shift is described by the second-rank tensor $\boldsymbol{\sigma}^i$, which is a part of the chemical shift Hamiltonian [8]:

$$\hbar H_{CS} = \hbar \sum_i \gamma_n^i \mathbf{I}^i \cdot \boldsymbol{\sigma}^i \cdot \mathbf{B} \qquad (1)$$

where $\mathbf{I}^i$ is the nuclear spin, $\boldsymbol{\sigma}^i$ is the second-rank tensor; $\mathbf{B}$ is the external constant magnetic field, $-\boldsymbol{\sigma}^i \cdot \mathbf{B}$ is the magnetic field induced by electrons at the point of the *i*-th nucleus.

In the general case, the screening constant can be represented as the sum of two terms:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_p + \boldsymbol{\sigma}_d \qquad (2)$$

where the first term is usually called *diamagnetic*, and the second one - *paramagnetic*. The diamagnetic term depends only on the electron density in the ground state and makes a negative contribution (shielding) to the field at the nucleus. The paramagnetic term depends on the excited states and makes a positive contribution (de-shielding) to the field at the nucleus. In the case of a core *s*-electrons, only the first term is nonzero. In other cases, competition between paramagnetic and diamagnetic shieldings is possible.

The J-coupling constant $\mathbf{J}$ is an isotropic part of the second-rank tensor $\mathbf{J}^{ik}$, which is a part of the spin-spin interaction Hamiltonian:

$$\hbar H_J = \hbar \sum_{i<k} \mathbf{I}^i \cdot \mathbf{J}^{ik} \cdot \mathbf{I}^k, \qquad (3)$$

2. Experimental

2.1. Samples
Powdered samples of heterobinuclear vinylidene complexes *RePt(PPh₃)CO* and *RePt(PPh₃)₂* and their precursors *PPh₃* and *Pt(PPh₃)₄* were prepared in the Institute of Chemistry and Chemical Technology SB RAS [3-5].

2.2. Spectrometer
Solid-state ^{31}P NMR cross-polarization (CP) spectra of the powdered samples in static and magic-angle spinning (MAS) conditions were acquired using a spectrometer Bruker AV300 operating at a frequency of 121.5 MHz.

2.3. Software
All the spectra were acquired on a spectrometer operated by xWin-NMR. Analysis of the spectra was performed in the program TOPSPIN 2.1. The spectra were fitted using the program for simulating NMR experiments SIMPSON [9].

2.4. Fitting of spectra
All spectra had a list of parameters such as *J-coupling* constant, isotropic chemical shift δ_{iso}, anisotropy $\Delta\delta$ and the asymmetry parameter η of the chemical shift tensor δ_{ij}. We could simulate a spectrum based on these parameters using SIMPSON by varying the parameters of nuclear Hamiltonian. As a result, the model spectrum will be obtained, that can be compared with experimental spectra. Thus, each spectrum could be fitted using the model spectrum by varying the parameters.

Firstly, the CP-MAS spectrum should be fitted because of the high resolution of the spectral line. At this step the isotropic chemical shift and *J-coupling* constant can be determined.

The second step is to fit the CP spectrum acquired in static conditions. During this step the anisotropy of the chemical shift tensor can be determined.

3. Results and Discussion

The solid-state ^{31}P NMR spectra of all samples are shown on figure 1.
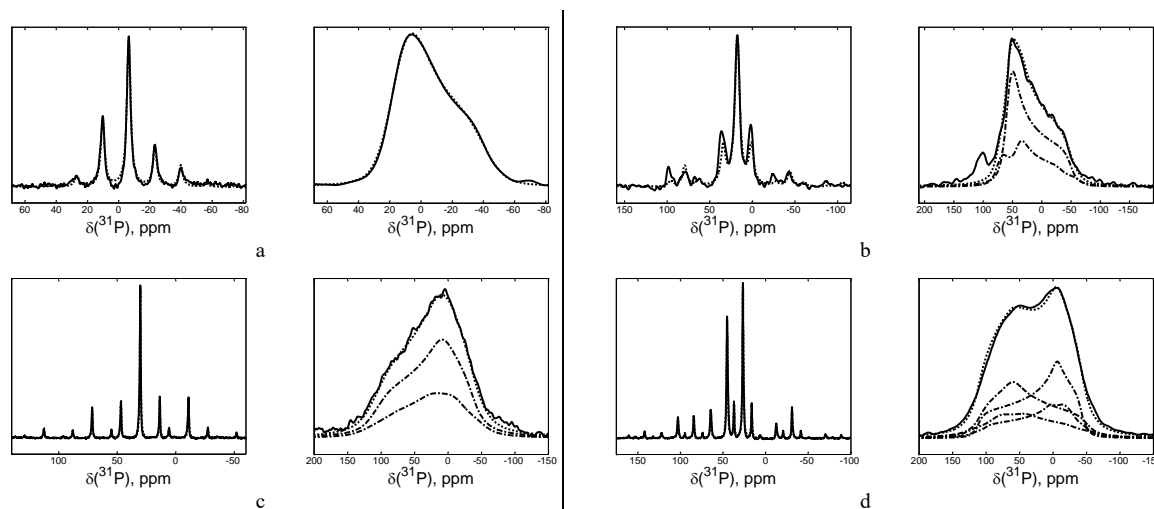
Figure 1. ^{31}P CP-MAS and CP NMR spectra
a - *PPh₃*, b - *Pt(PPh₃)₄*, c - *RePt(PPh₃)CO*, d - *RePt(PPh₃)₂*.
Solid line – experimental, dotted line – approximation, dash-dotted line – parts of approximation

All the ^{31}P CP NMR spectra acquired in static conditions represent lines broadened by the dipole-dipole interactions and anisotropy of the chemical shift tensor.

On the ^{31}P CP-MAS spectra the dipole-dipole interactions are completely averaged by the rotation of the sample and the use of proton noise decoupling. From these spectra, the isotropic chemical shift of the ^{31}P NMR line of the spectrum for each solid-state sample, as well as the J-coupling constant for samples containing a platinum atom, can be determined.

Without presenting the results of the spectra approximation, we can draw some conclusions from the shape of the NMR spectra line. The parameters of the chemical shift tensor vary widely for each sample. In addition to the isotropic shift of the NMR spectral line to the weak field, there is a change in the anisotropy of the chemical shift tensor due to the redistribution of the electron density around the phosphorus nucleus. Thus, comparing the NMR spectra of the *Pt(PPh₃)₄* precursor and vinylidene complexes, the sign of the anisotropy sharply reverses in *RePt(PPh₃)CO*, and in *RePt(PPh₃)₂* the lines of magnetically nonequivalent phosphorus nuclei are observed. The analysis of the CP-MAS NMR spectrum of the *RePt(PPh₃)₂* sample shows that the values of the *J-coupling* constants of magnetically nonequivalent phosphorus nuclei vary greatly. By approximating each spectrum according to the method described in Section 2.4, we can clearly see the differences between the spectra.

Based on the analysis and simulation of the NMR spectra of the samples, the parameters of the chemical shift tensors and *J-coupling* constants between the platinum and phosphorus nuclei were obtained, as is summarized in the following table:

Table 1. The parameters of chemical shift tensors and *J-coupling* constants of the ^{31}P NMR spectra of all the samples

Sample	δ_{iso}, ppm	$\Delta\delta$, ppm	η	$J(Pt-P)$, Hz
PPh₃	-6.6	-36	0	–
Pt(PPh₃)₄	9.25	-70	0	4000
RePt(PPh₃)CO	31.15	82	0.55	4035
RePt(PPh₃)₂	P₁: 46.2	-90	0.55	4675

P$_2$: 27.7	90	0.4	2525

When the structure of the sample is complicated, changes in the parameters of the chemical shift tensor of the phosphorus nucleus are observed. Since the chemical shift is directly related to the electron density around the nucleus, analyzing the changes in the chemical shift tensor, the effect of the chemical bond on electron shells can be explained. According to formula (2), the chemical shift is the sum of two contributions - diamagnetic and paramagnetic. Diamagnetic shielding makes a negative contribution to the magnetic field of the nucleus. That is, the larger the diamagnetic shielding, the greater is the magnetic field to be applied to observe the resonance. In this case, $\boldsymbol{\delta_{iso}}$ decreases. In our case, an increase of $\boldsymbol{\delta_{iso}}$ is observed if the chemical bond of the phosphorus nucleus is complicated. Consequently, a significant paramagnetic contribution to magnetic shielding (de-shielding) is observed, which depends on the excited states of the electron shells.

During the formation of tetrakis-(triphenylphosphine)platinum, the isotropic chemical shift of the phosphorus nucleus moves toward the weak field by 15.85 ppm relative to pure triphenylphosphine. At the same time, there is an almost twofold increase in the anisotropy of the chemical shift tensor, which for the axially symmetric tensor indicates an increase in the magnetic shielding $\delta_{XX} = \delta_{YY} = \delta_\perp$ along the X and Y axes of the coordinate system associated with the chemical shift tensor of triphenylphosphine relative to the component $\delta_{ZZ} = \delta_{||}$, since in this case $\Delta\delta = \delta_{||} - \delta_\perp$. It is assumed that the Z axis of the chemical shift tensor is directed along the chemical bond between phosphorus and platinum, based on the symmetry of the triphenylphosphine molecule.

Upon transition to vinylidene complexes, in addition to the isotropic shift and anisotropy, the asymmetry parameter of the chemical shift tensor also changes. The symmetry both of the tensor and molecular electron shells changes as well. Therefore, the reasoning used in the previous paragraph to analyze the parameters of the chemical shift tensor does not make sense. Nevertheless, it is important to note that the value of the isotropic shift $\boldsymbol{\delta_{iso}}$, as well as the value of $\boldsymbol{J(\mathbf{Pt} - \mathbf{P})}$, carry structural information about this complex. Knowing the value of $\boldsymbol{J(\mathbf{Pt} - \mathbf{P})}$, we can draw some conclusions about the *cis*- and *trans*-isomers of phosphorus nuclei in the complexes. According to publications [10–11], phosphorus nuclei with $\boldsymbol{J(\mathbf{Pt} - \mathbf{P})} > 4000$ Гц are in the *trans*-position with the rhenium nucleus and have a short chemical bond with the platinum nucleus: the phosphorus nucleus denoted in this paper as a P$_1$ for *RePt(PPh$_3$)$_2$*, and the only phosphorus nucleus for *RePt(PPh$_3$)CO*. Consequently, the *cis*-isomer with respect to the rhenium nucleus with a long P-Pt chemical bond for the *RePt(PPh$_3$)$_2$* complex will be the phosphorus nucleus, denoted as P$_2$, and the group *(-CO)* for the *RePt(PPh$_3$)CO*.

An increase of $\boldsymbol{\delta_{iso}}$ of the phosphorus nuclei in the complexes indicates the transfer of electron density from the ligand to the platinum nucleus. So, the de-shielding occurs [10] and the chemical bonds is strengthened. The nucleus P$_1$ in *RePt(PPh$_3$)$_2$* has a larger $\boldsymbol{\delta_{iso}}$, than P$_2$, and has a stronger bond with the platinum nucleus. The nucleus P$_2$ is less de-shielded and tends to be replaced by other more stable ligands, as happened in the sample *RePt(PPh$_3$)CO*.

4. Conclusions

Four samples of compounds containing phosphorus were studied by solid-state NMR spectroscopy: vinylidene complexes *Cp(CO)RePt(μ-C=CHPh)(PPh$_3$)CO* and *Cp(CO)$_2$RePt(μ-C=CHPh)(PPh$_3$)$_2$* and their precursors *triphenylphosphine* and *tetrakis-(triphenylphosphine)platinum(0)*. ^{31}P NMR spectra of these samples were acquired by cross-polarization in static conditions, and also using spinning of the sample at a magic angle.

From the ^{31}P CP and CP-MAS NMR spectra, the *J-coupling* constants and parameters of chemical shift tensors for each sample were obtained by the analysis and simulation in the program SIMPSON.

A comparison of the parameters of the phosphorus chemical shift tensors upon transition to a substance with a more complex structure confirms that the formation of vinylidene complexes is associated with the transfer of electron density from phosphorus to platinum and strong de-shielding of phosphorus nuclei, as evidenced by an isotropic shift to the weak field. In the parameters of the

phosphorus chemical shift tensors, changes due to the formation of the phosphorus-platinum bond are observed.

A comparison of the *J-coupling* constants of magnetically nonequivalent phosphorus nuclei in $Cp(CO)_2RePt(\mu\text{-}C=CHPh)(PPh_3)_2$ clearly indicates that the phosphorus nucleus, denoted as P_1, is more de-shielded and has a stronger bond with the platinum nucleus relative to P_2. This difference cannot be explained by the difference in the donor ability of the same phosphine ligands of the compound, and the most probable reason appears to be the difference in the ability of the platinum atom to reverse electron density transfer to phosphorus atoms. In this case, of significance is which ligand is located in the *trans*-position from the phosphorus atom.

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