

Investigation of Re-Pt vinylidene complex Cp(CO)₂RePt(μ-C=CHPh)(PPh₃)₂ by solid-state NMR

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Introduction

In this paper, the heterobinuclear vinylidene complex Cp(CO)₂RePt(μ-C=CHPh)(PPh₃)₂ [1] was studied using solid-state ³¹P and ¹⁹⁵Pt nuclear magnetic resonance (NMR) spectroscopy. Heterometallic vinylidene complexes of rhenium and platinum can be used in the synthesis of organometallic compounds and organic substances and also have a prospect in the synthesis of functional polymetallic materials [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. The molecular structure of the complex was established by X-ray diffraction analysis [3]. This complex was not studied by solid-state NMR spectroscopy methods earlier.

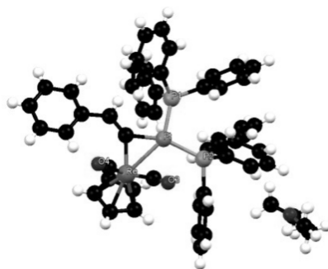


Figure 1. Molecular structure of complex according to X-ray data

Analysis of NMR spectra

³¹P NMR spectra

The ³¹P and ¹⁹⁵Pt NMR cross-polarization (CP) spectra of powdered complex in static and magic-angle spinning (MAS) conditions were acquired using the Bruker AV300 spectrometer operating at 121.5 MHz (³¹P) and 64.2 MHz (¹⁹⁵Pt) frequencies.

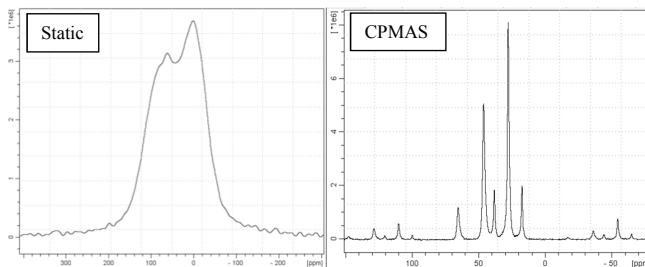


Figure 2. ³¹P static and CP/MAS NMR spectra

Each of the two nonequivalent phosphorus nuclei in complex are bonded to the platinum nucleus. The static spectrum represents a line broadened by dipole-dipole interaction and high chemical shift anisotropy. The peaks assigned to both phosphorus nuclei are clearly distinguishable. The same is observed on the well resolved ^{31}P CP/MAS NMR spectrum. The CP/MAS spectrum consisted of two pseudo-triplets due to indirect spin-spin interaction with the ^{195}Pt nucleus. The magnitudes of J-coupling for nonequivalent phosphorus nuclei ($J_1 = 4600$ Hz and $J_2 = 2600$ Hz) are clearly exhibit ligand *trans*-effect. Prior to determination of ^{31}P chemical shift tensor parameters, the isotropic chemical shift was determined based on the CP/MAS spectrum. In the next step the model spectrum was fitted to the static spectrum (fig.3). Fitted parameters of the chemical shift tensor of ^{31}P are summarized in the table 1, where nucleus P₁ (46.5 ppm) is in a trans-position relative to rhenium, and nucleus P₂ (28 ppm) is in a trans-position relative to the vinylidene fragment.

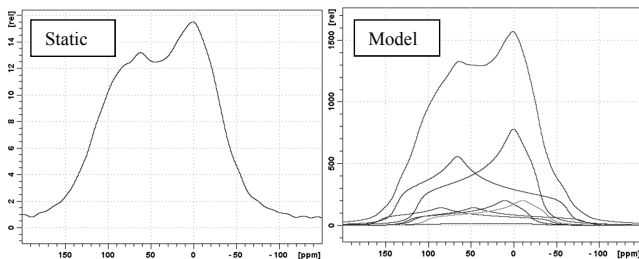


Figure 3. Approximation of the ^{31}P static NMR spectrum

^{195}Pt NMR spectra

Due to 33.8% natural abundance of NMR-active platinum isotope the NMR spectra has a low signal-to-noise ratio. The spectrum is broadened by chemical shift anisotropy. Because of this difficulties arise in the study of samples for this nucleus.

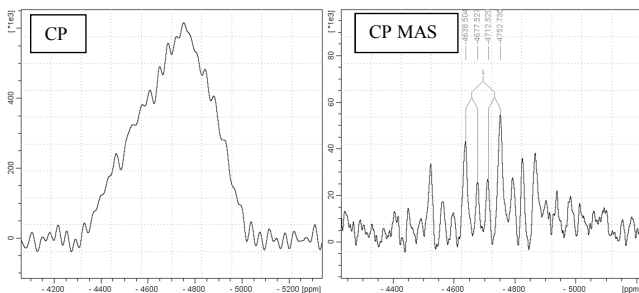


Figure 4. ^{195}Pt CP-static and CP/MAS NMR spectra

The width of static spectrum on the half height is about 25 kHz and largely determined by chemical shift anisotropy. Application of MAS at low frequencies a large number of rotational satellites appear on the spectrum complicating the analysis of the spectrum. However, while spinning the sample at high frequencies was not applicable since information about the chemical shift anisotropy is lost. Therefore, information evident from ^{31}P spectra was used to set the MAS frequency to 7200 Hz ($J_1 + J_2$) so that the rotation satellites from first and fourth split resonance lines overlap. This allowed to gain greater signal-to-noise ratio and to acquire spectrum which was sufficient for determination of the chemical shift tensor.

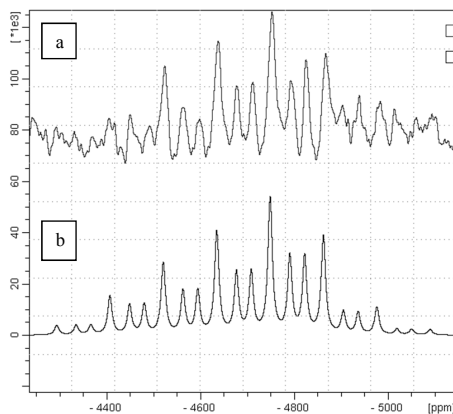


Figure 5. Comparison of model and experimental spectra, a) ^{195}Pt NMR CP/MAS spectrum, b) model spectrum

Characteristic features of rotational satellites overlapping in the model spectrum are in good agreement with the experimental spectrum. The parameters of the ^{195}Pt chemical shift tensor are summarized in the following table:

Table 1 – The parameters of the chemical shift tensor of ^{31}P and ^{195}Pt

Nucleus	δ_{iso} , ppm	Δ , ppm	η	δ_{11} , ppm	δ_{22} , ppm	δ_{33} , ppm
$^{31}\text{P}_1$	46.5	-110	0.65	136.35	64.85	-64.4
$^{31}\text{P}_2$	28	85	0.35	112.6	0	-31.78
^{195}Pt	-4670	350	0.6	-4314	-4734	-4944

Denotation: Δ – anisotropy, η – asymmetry, δ_{ii} – principal axis of tensor

High chemical shift anisotropy of nuclei is due to the electron configuration of molecular orbitals, when unpaired electrons on the unfilled shells induce paramagnetic currents at the location of sensitive nuclei and shift the resonant line to a strong or weak field depending on the direction of the constant magnetic field. For further analysis of the electron density along interatomic bonds, quantum-mechanical calculations are planned in order to estimate the paramagnetic contribution of electrons to the chemical shift of nuclei.

References

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