catalyst activity. The conversion of cyclohexane on a  $Pd/\gamma-Al_2O_3(H_2S)$  sulfidized sample at 460°C and 470°C ( $w = 0.5 h^{-1}$ ) amounts to 90.5 % and 97.2 %, respectively. The yield of benzene in this case is as high as 95–100 %. Nevertheless, the dehydrogenation of cyclohexane on this contact is accompanied by cracking, which results in gaseous products and coke. The aluminum-palladium catalyst has higher cracking activity than the sulfidized sample: its specifically dehydrogenative activity manifests itself only at 480°C, when the yield of benzene increases to 98 % at 98.7 % conversion.

The addition of 0.5 mass. % Re to the sulfidized catalyst enables the dehydrogenation of cyclohexane at  $400^{\circ}$ C. As the temperature rises to  $450^{\circ}$ C, the conversion

of cyclohexane reaches 91.5 % and the benzene content in the catalysate amounts to 91 %. A twofold decrease in the content of Pd and Re in the catalyst reduces the benzene content in the catalysate from 91 % to 52 %, other conditions being the same.

The 0.5 % Pd/Sibunite catalyst possesses a dehydrogenative activity similar to that of the sulfidized aluminum—palladium contact. At 430—440°C and w =1.2 h<sup>-1</sup> the yield of benzene was 82—89 % whereas the conversion of cyclohexane was 86.4—91.2 %.

Thus, it has been shown that alumina for gas dehumidification and Sibunite can be successfully used as catalyst supports for palladium catalysts in the dehydrogenation of cyclohexane at 440–450°C, atmospheric pressure, and  $w = 1.2 \div 1.5 \text{ h}^{-1}$ .

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## Hindered rotation of ligands in *cis*-[PtR<sub>2</sub>Cl<sub>2</sub>] complexes

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The temperature dependence of the <sup>1</sup>H NMR spectra of cis-[Pt(II)R<sub>2</sub>Cl<sub>2</sub>] complexes was studied in DMSO at 18–100°C (R is 2-methyl and 2,5-dimethylpyridine). The broadening of the signals from the methyl groups or hydrogen atoms in the *ortho*-positions of heteroaromatic ligands is due to the coexistence of two forms of the *cis*-complexes in solution. These forms arise from the hindered rotation of asymmetrical ligands around the Pt–N bond.

**Key words:** platinum(II), *cis*-complexes; <sup>1</sup>H NMR spectra, temperature dependence; asymmetrical ligands, hindered rotation.

The <sup>1</sup>H NMR spectra of *cis*-complexes of Pt with 2picoline, cis-[Pt(2-Pic)<sub>2</sub>Cl<sub>2</sub>] (1), and with 2,5-lutidine, cis-[Pt(2,5-Lut)<sub>2</sub>Cl<sub>2</sub>] (2), in DMSO at ~20°C differ markedly from those of similar complexes containing aromatic ligands with other substitution patterns (e.g., 3-, 4-Pic, Py), as well as from those of the *trans*-configurated complexes of the same composition. This distinction is manifested in noticeable broadening of the signals from the protons and methyl groups in positions 2 and 6 of the pyridine nucleus. The broadening diminishes when the protons or Me groups move away from the coordinated N-atom. At the same time the <sup>1</sup>H NMR spectra of complexes with the trans-configuration are unexceptional, their shape being determined by the type of substitution in the ring and the coordination with metal atom.

The nature of the changes in question can be inferred from the <sup>1</sup>H NMR spectra of cis-[Pt(2,5-Lut)<sub>2</sub>Cl<sub>2</sub>] given

in Fig. 1. At 18°C two broadened signals of the *o*-H atoms at  $\delta$  9.2 and 8.78 with approximately equal integral intensity, a broadened signal at  $\delta$  3.2 (2-Me group), and a narrow signal at  $\delta$  2.32 (5-Me group) are observed. Heating of the sample is accompanied by a collapse of the *o*-H signals at 50°C, followed by the appearance of a doublet at  $\delta$  9.0 (90°C) with splitting  $J_{\text{Pt-H}} = 38$  Hz. The signals of the 2-Me group are compressed into a singlet with the <sup>195</sup> Pt satellites,  $J_{\text{Pt-Me}} = 12$  Hz.

In the case of complex 1, the reshaping of the o-H signals with temperature  $(18 \rightarrow 100^{\circ}\text{C})$  follows the pattern of classical exchange narrowing. Eventually this leads to the appearance of the o-H signals at  $\delta$  9.05. Their extra splitting  $({}^{1}\text{H}-{}^{195}\text{Pt}, J_{\text{Pt}-\text{H}} = 38 \text{ Hz})$  is typical of Pt(II) pyridine complexes with a *cis*-configuration.<sup>1</sup>

The temperature-dependent changes in the shape of the spectra are reversible. The Pt satellites are retained throughout the temperature interval, which suggests an



**Fig. 1.** <sup>1</sup>H NMR spectra of complex **2**: 18°C (*I*); 50°C (*2*); 70°C (*3*); 90°C (*4*).

intramolecular character for the process. Thus it can be stated that the reason for the above changes in the <sup>1</sup>H NMR spectra is an exchange process involving the two forms of the *cis* Pt-complexes where the protons are magnetically non-equivalent. This non-equivalence is particularly evident for the *o*-H atoms, decreases for the 2-Me groups, and becomes practically invisible for the H atoms and Me groups in positions 3 and 4. This nonequivalence is probably associated with the mutual orientation of the *cis*-positioned ligands, that is, with the existence of the two possible conformations for the complex in solution. Their energy-controlled occupancies are approximately equal, which implies that the interconversion barrier is low.

The structure of cis-[PtPy<sub>2</sub>Cl<sub>2</sub>] is known.<sup>2</sup> In the crystal lattice the planes of the pyridine rings are located at an angle to the plane of the coordination square. The coupling constants  $J_{Pt-H}$  are equal for cis-[PtPy<sub>2</sub>Cl<sub>2</sub>] and for all of the studied cis-complexes with Me-substituted pyridine ligands, including cis-[Pt(2-Pic)<sub>2</sub>Cl<sub>2</sub>].<sup>1</sup> Therefore it may be assumed that the peculiarities of the <sup>1</sup>H NMR spectrum of the latter are associated not with a change in the nature of the Pt—N bond, but rather with the geometry of the ligands and their mutual disposition. Since for other cis complexes with Py, 3-Pic, and 4-Pic as ligands such spectral anomalies are not observed, the confomations of cis-complexes incorporating o-substituted pyridine ligands are defined, in solution, by the two types of mutual orientation of the ligands in the

complex.

Taking into account that the cis-configuration of the



ligands shifts the signals of the *o*-H atoms upfield, the signals of complex 2 at  $\delta$  8.78 can be assigned to the **B**-form, and those at  $\delta$  9.2 to the **A**-form. The transition between the two forms occurs according to the usual mechanism of hindered rotation about the Pt-N bonds.

The relatively rapid replacement of the 2-Pic and 2,5-Lut ligands with solvent molecules at elevated temperatures detected by the emergence of signals in the <sup>1</sup>H NMR spectra attributable to a free ligand, may be of interest. On heating the *cis*-complexes of Py and 3-, 4-Pic under the same conditions, no displacement of ligands from the coordination sphere could be noticed. This demonstrates the destabilizing effect of the bulky *o*-Me group and, hence, the relative instability of *cis* complexes with *o*-Me-substituted pyridines as ligands.

Prolonged heating of 1 in DMSO with an excess of the ligand gives rise to a new form (in a mixture with the starting one) with spectral parameters as follows: IR spectrum, v (cm<sup>-1</sup>): 818 v.w, 725 w, 470 w; <sup>1</sup>H NMR spectrum,  $\delta$ : 8.85 (d,  $J_{Pt-H} = 32$  Hz); 7.80 (t); 3.20 (s,  $J_{Pt-H} = 11$  Hz).

Judging from the value of  $J_{Pt-H}$ , the new complex must have *trans* geometry. This follows from the fact that the  $J_{Pt-H}$  constant for *trans*-[PtR<sub>2</sub>Cl<sub>2</sub>] (where R = Py, 3-Pic, 4-Pic) is usually 32-33 Hz, whereas for the respective *cis*-[PtR<sub>2</sub>Cl<sub>2</sub>] it is 38-40 Hz (cf.<sup>1</sup>).

## Experimental

Synthesis of the complexes was carried out using a procedure similar to that described in ref.<sup>3</sup> In the case of cis-[Pt(2-Pic)<sub>2</sub>Cl<sub>2</sub>], the addition of a small amount of 2-picoline N-oxide brings about a more than tenfold decrease in the crystallization time. The compounds were identified by elemental analysis (Pt, N, C, Cl) and by <sup>1</sup>H NMR spectra recorded on a Tesla-BS-597 (100 MHz) spectrometer in DMSO-d<sub>6</sub> in the temperature range 18 $\rightarrow$ 100°C. IR spectra (in KBr pellets) were taken on a Specord-75-IR spectrophotometer, in the 400–900 cm<sup>-1</sup> region.

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