Letters to the Editor

Photoinduced interconversion of *cis*- and *trans*-isomers of bis(1,1,1-trifluoro-5,5-dimethyl-2,4-hexadionato)platinum(II) studied by dynamic NMR spectroscopy

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Photochemical reactions involving noble metal β-diketonates in solutions have been studied only for several compounds.[1] In this work, the process of the reversible *cis—trans*-photoisomerization of bis(1,1,1-trifluoro-5,5-dimethyl-2,4-hexadionato)platinum(II) (**1**) was studied by ^{1}H and ^{13}C NMR spectroscopy[2,3] using an experimental setup similar to that for studying photochemically induced dynamic nuclear polarization.[4] The ratio of the *cis*- and *trans*-isomers of complex **1** in $CDCl_3$ is equal to 1 : 1.

^{1}H NMR spectrum of isomer *cis*-**1**, δ: 6.11 (s, 1 H, CH); 1.20 (s, 9 H, $\mathrm{Bu^t}$). ^{1}H NMR spectrum of isomer *trans*-**1**, δ: 6.11 (s, 1 H, CH); 1.19 (s, 9 H, $\mathrm{Bu^t}$). In the ^{13}C NMR spectrum of isomers *cis*-**1** and *trans*-**1**, the signals of the $\mathrm{Bu^t}$ groups are observed at δ 27.37 and 27.29, respectively. UV spectrum of compound **1** ($CHCl_3$), λ_{max}/nm (ε): 312 (5600), 412 (1700), 463 (90), 488 (20), 514.5 (5).

The absorption band (AB) at λ_{max} = 463 nm is assigned to the $\pi \rightarrow \pi^*$ transitions that are localized on the ligand,[1] and upon the irradiation in the region of this AB, a more efficient photoisomerization of compound **1** compared to photodecomposition processes can be expected. The study of the ^{1}H NMR spectra under "dark" conditions in the temperature range from 213 to 333 K shows that isomers *cis*-**1** and *trans*-**1** are kinetically stable in the NMR time scale, *i.e.*, no *cis—trans*-isomerization is observed. Based on the ratio of the integral intensities of the signals of protons of the $\mathrm{Bu^t}$ groups of isomers *cis*-**1** and *trans*-**1**, the thermodynamic equilibrium constant of the system studied (K) is equal to 1.0(1) and is temperature-independent. Under the irradiation of compound **1** by an argon laser, the ^{1}H NMR spectra exhibit the coalescence of the signals of protons of the $\mathrm{Bu^t}$ groups of isomers *cis*-**1** and *trans*-**1** caused by the degenerate photoinduced chemical exchange. The broadening of the signals in the ^{1}H NMR spectra related to the nonhomogeneity of the static magnetic field was specially monitored by the signals from the protons of cyclohexane and did not exceed 0.15 Hz. For the determination of the effective rate (k_{eff}) and the quantum yield (φ) of the photoisomerization of compound **1**, the shape of the "exchange-broadened" signal was studied in terms of the known procedures of dynamic NMR regarding the two-position degenerate exchange.[5] The φ value was calculated by the equation

$$\varphi = hcN_A k_{eff}[1]/[\Sigma\lambda_i W(\lambda_i)].$$

Under the experimental conditions, the power of the radiation absorbed by molecules of **1** per unit volume $W(\lambda_i)$ was calculated by the Lambert—Beer formula for λ_i = 514.5 and 488 nm and turned out to be equal to 1.76 and 2.66 W mL^{-1}, respectively; [1] = 0.016 mol L^{-1}; the volume was equal to 0.28 mL; T = 293 K. It is established that k_{eff} = 0.5(1) s^{-1} and φ = 0.43(11). The results of studying the mechanism of the photo-

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isomerization reaction of compound 1 will be presented elsewhere.

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Surface tension of adsorbtive in the Hill equation for polymolecular adsorption

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A simple and fairly exact expression for the b constant in the Hill equation of polymolecular adsorption is proposed:

$$\ln(p_s/p) = b\theta^{-3}, \qquad (1)$$

where p is the equilibrium vapor pressure of an adsorbate; p_s is the saturation vapor pressure of a liquid at the temperature of the adsorbate; and θ is the adsorption in units of a dense monolayer. The expression for b is as follows:

$$b = 2.5\sigma_0 V_0/(RTd), \qquad (2)$$

where σ_0 and V_0 are the surface tension and molar volume of the adsorbate in the state of a normal liquid, respectively; d is the diameter of the molecules of the adsorbate; T is the temperature; and R is the universal gas constant.

In order to derive Eq. (2), let us compare two systems: I, the adsorption system consisting of an adsorption layer in the form of a liquid film on a planar surface of a solid adsorbent; and II, the "liquid" system that represents a bulk volume of a liquid with the planar liquid—vapor interface. In both systems, at the gas phase interface, a tangential pressure p_T exists that decreases when the distance (τ) from the boundary surface of zero thickness increases. Let us assume that the known equation[1] holds for both systems:

$$p_T = p + C\tau^{-3}, \qquad (3)$$

where C is the constant related to the parameters of interaction of the molecules of a liquid with each other and with the molecules of neighboring phases; p is an external pressure. Let us denote $C = C^I$ for the first system and $C = C^{II}$ for the second system. Previously,[2] the following expression was found for system I:

$$b = -3C^I V_0/(RTd^3). \qquad (4)$$

In order to estimate the C^{II} value for the second system, we assume that whole volume of a liquid, beginning from the boundary layer, is separated into layers one molecule thick that are parallel to the boundary layer. Let us denote the constant tangential pressure acting in the i layer and changing jumpwise from one layer to another as p_T. The tension of the i layer (σ_i), taking into account Eq. (3), is determined by the expression

$$\sigma_i = (p - p_{T,i})d = -C^{II}/(i^3 d^2),$$

where $\tau = id$. Apart from the critical temperature, it can be accepted with enough accuracy that the surface ten-

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