

## Generation of $\sigma$ -Aryl Platinum(IV) Complexes in Mechanically Activated Reaction of $K_2PtCl_6$ with Arenes

A. A. Shubin<sup>1</sup>, S. A. Mitchenko<sup>2</sup>, E. V. Khomutov<sup>2</sup>, V. V. Kovalenko<sup>2</sup>, and I. P. Beletskaya<sup>3</sup>

<sup>1</sup> Tugan-Baranovskii Donetsk State University of Economics and Trade, Donetsk, Ukraine

<sup>2</sup> Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine,  
ul. R. Lyuksemburg 70, Donetsk, 83114 Ukraine  
e-mail: samit@skif.net

<sup>3</sup> Faculty of Chemistry, Lomonosov Moscow State University, Moscow, Russia

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**Abstract**—Mechanical activation of  $K_2PtCl_6$  in the presence of gaseous arenes RH (where R = Ph, MeC<sub>6</sub>H<sub>4</sub>) gives rise to the corresponding  $\sigma$ -aryl platinum(IV) complexes, whose formation is confirmed by the <sup>1</sup>H NMR and IR spectra and chemical testing. The reaction with toluene gives a statistical mixture of the corresponding *meta*- (66%) and *para*-isomeric complexes (33%) with an overall energy yield of 0.08  $\mu$ mol/J. According to the results of *ab initio* calculations, the energies of the isomers are fairly similar; therefore, their formation is equally probable from the viewpoint of thermodynamics.

Metal-complex activation of C–H bonds in hydrocarbons is one of the most actual problems in modern organic chemistry. Advances in this field largely determine progress in the development of radically new ways of transformation of hydrocarbon raw materials into valuable products; they are also important for solving a series of fundamental problems, specifically for understanding factors responsible for selectivity and reactivity of metal complexes toward hydrocarbons. Although a large number of organometallic systems capable of selectively activating C–H bonds in hydrocarbons have been reported, up to now the most promising system [1–5] is that discovered about 30 years ago by Shilov and co-workers [6]. This system consists of chloride Pt(II) and Pt(IV) complexes in aqueous solutions. A related system includes chloride Pt(IV) complexes in aqueous acetic or trifluoroacetic acid; it activates arenes [8–10], alkanes, and their derivatives [11, 12] under UV irradiation or on heating to 70–100°C. Here, primary arene activation products are  $\sigma$ -aryl platinum(IV) complexes [6–12], and the reactive species which directly cleave the C–H bond are assumed [8] to be coordinately unsaturated  $PtCl_5^-$  ions which are generated by photolysis of  $PtCl_6^{2-}$  or by thermal reaction.

We previously showed [13] that mechanical activation of crystalline  $K_2PtCl_6$  salts also promotes

heterolytic dissociation of Pt–Cl bond to give coordinately unsaturated  $PtCl_5^-$  surface complexes. Taking this into account, we expected formation of  $\sigma$ -aryl platinum(IV) complexes under heterogeneous conditions, i.e., upon mechanical activation of  $K_2PtCl_6$  in the presence of arenes. The goal of the present work was to verify the above assumption.

A 0.3-g sample of  $K_2PtCl_6$  was preliminarily subjected to mechanical treatment over a period of 60 min in an MMVE-0.005 17.37-ml glass vibrating micromill with glass balls on exposure to air.\* The vibrating mill operated at a frequency  $f$  of 50 Hz and an amplitude  $h_0$  of 5.5 mm; these parameters corresponded to a specific energy strain of about 15 W/kg. The vibrating mill was tightly capped with a rubber septum.

Potassium hexachloroplatinate(IV) was prepared by standard procedure [14]. Freshly recrystallized salt was preliminarily dried for 3 days at 120–140°C in a drying box. No appreciable effect on the reaction course was observed on prolonging the time of drying. All operations were carried out in a dry box. Benzene and toluene of chemically pure grade were preliminarily dried by distillation over metallic sodium into

\* By special experiments we showed that the reactions under study occur under argon as well.

a receiver containing 4-Å molecular sieves. The substrate (10  $\mu$ l) was added to the reactor (after preliminary mechanical treatment over a period of 1 h) through a septum using a microsyringe.

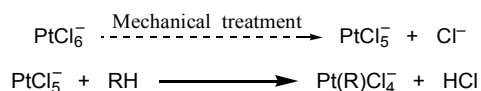
The  $^1\text{H}$  NMR spectra were recorded on a Varian Gemini instrument at 200 MHz using acetone- $d_6$  as solvent; The IR spectra were measured in KBr on a FTIR Perkin-Elmer Spectrum BX spectrometer. Chemical tests for the presence of  $\sigma$ -aryl platinum(IV) complexes were based on the known [15] decomposition of such complexes with quantitative formation of the corresponding arenes in acid aqueous  $\text{SnCl}_2$  solution. For this purpose, the reactor was preliminarily purged with dry air or argon, and the complex was extracted with water from the surface of mechanically activated  $\text{K}_2\text{PtCl}_6$ . The extract was evaporated in a stream of air without heating, and the dry residue was dissolved in 1 ml of distilled water. A 0.2-ml portion of the solution was added to a closed shaker charged with 2 ml of concentrated hydrochloric acid and excess  $\text{SnCl}_2$ . Under these conditions,  $\text{K}_2\text{PtArCl}_5$  is first reduced and then hydrolyzed [15] with liberation of gaseous arene. The concentration of the complex in the extract was determined by chromatography using an appropriate calibration curve (with respect to peak areas). GLC analysis was performed on an LKhM-8 MD chromatograph equipped with a flame ionization detector, an Ampersand data acquisition system, and a column packed with SE-30 on Inerton N-AW.

Nonempirical calculations in terms of the restricted Hartree-Fock method with the SBK basis set were performed using GAMESS software package [16]. Electronic correlation was taken into account in terms of the Moeller-Plesset second-order perturbation theory (MP2). Full geometry optimization was performed using the same basis set with account taken of electronic correlation.

We have found that mechanical activation of  $\text{K}_2\text{PtCl}_6$  in the presence of arenes (benzene and toluene) does promote formation of the corresponding  $\sigma$ -aryl platinum(IV) complexes, as shown in Scheme 1. This follows from the experimental data given below:

(1) Potassium hexachloroplatinate(IV), 0.3 g, was mechanically treated over a period of 1 h in a closed glass reactor in the presence of toluene vapor. The reaction was stopped, and the reactor was evacuated and/or purged with dry air. The resulting organo-platinum derivative was extracted into methanol, and

Scheme 1.



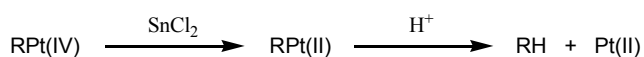
the extract was evaporated to dryness in a stream of air without heating. The  $^1\text{H}$  NMR spectrum of the residue in acetone- $d_6$  corresponded [8] to a mixture of *meta*- and *para*-isomeric  $\sigma$ -tolyl complexes: it contained an unresolved multiplet in the region  $\delta$  6.6–7.5 ppm due to aromatic protons and two singlets from the methyl protons at  $\delta$  2.26 and 2.17 ppm with an intensity ratio of 2 : 1;

(2) The IR spectrum of the dry residue (KBr) contained absorption bands at 1620 ( $\nu\text{C}=\text{C}_{\text{arom}}$ ), 806 ( $\gamma\text{C}-\text{H}_{\text{arom}}$ ), and 548  $\text{cm}^{-1}$  (assumably,  $\nu\text{Pt}-\text{C}$ );

(3) Likewise, in the IR spectrum (KBr) of the dry residue obtained in a similar way by the reaction of  $\text{K}_2\text{PtCl}_6$  (0.3 g) with benzene we observed bands at 1616, 1565 ( $\nu\text{C}=\text{C}_{\text{arom}}$ ); 749, 694 ( $\gamma\text{C}-\text{H}_{\text{arom}}$ ); and 548  $\text{cm}^{-1}$  (assumably,  $\nu\text{Pt}-\text{C}$ ).

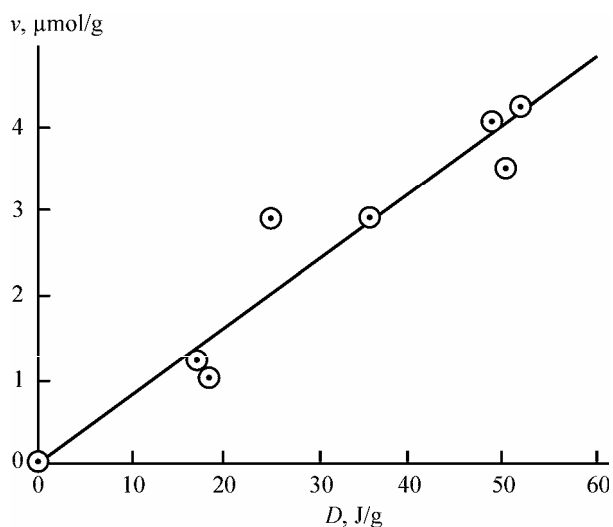
(4). Addition of aqueous solutions of the dry residues containing  $\text{RPt(IV)}$  ( $\text{R} = \text{MeC}_6\text{H}_4$ ,  $\text{Ph}$ ) to a solution of  $\text{SnCl}_2$  in hydrochloric acid leads, as expected for  $\sigma$ -organic platinum(IV) derivatives (cf. [15]), to gradual liberation of the corresponding arenes as a result of successive reduction of the  $\sigma$ -aryl platinum(IV) complexes to the corresponding platinum(II) complexes and hydrolysis of the latter (Scheme 2).

Scheme 2.



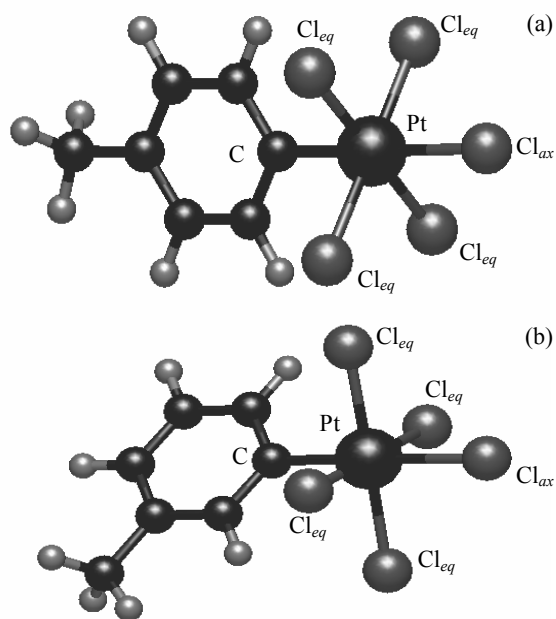
The amount of  $\sigma$ -tolyl platinum(IV) complexes linearly increases with increase in the mechanical energy absorbed by the  $\text{K}_2\text{PtCl}_6$  powder (Fig. 1). The energy yield of  $\sigma$ -tolyl platinum(IV) complexes, determined from the data given in Fig. 1, is equal to  $0.082 \pm 0.001$   $\mu\text{mol/J}$ .

Let us compare the regioselectivities observed in the platination of toluene with  $\text{PtCl}_5^-$  in the photochemical [6], thermal [8], and mechanically activated reactions. Photoinduced platination of toluene at room temperature gives exclusively the corresponding *p*-tolyl complex. In the thermal reaction at 70–100°C, platination initially occurs preferentially at the *para* position (kinetic control). However, the subsequent relatively slow isomerization of the *p*-tolyl complex



**Fig. 1.** Plot of the yield of  $\sigma$ -tolyl platinum(IV) complexes versus specific dose of the absorbed mechanical energy.

with platinum migration into the *meta* position (thermodynamic control) leads to formation of an equilibrium mixture consisting of about 33% of the *para* isomer; no *ortho*-platinated derivatives is formed for steric reasons [8]. In the mechanically activated reaction, the product was a mixture of *meta* and *para* isomers of the  $\sigma$ -tolyl complexes. No appreciable isomerization was observed during the extraction (at room temperature); the energy of activation for the *para*–*meta* isomerization is fairly high,  $\sim 25$  kcal/mol [10]. Therefore, the above mixture is formed directly



**Fig. 2.** Calculated structures of (a) *p*- and (b) *m*-tolyl platinum(IV) complexes.

during mechanically activated reaction. An obvious reason for the low regioselectivity is higher reactivity of  $\text{PtCl}_5^-$  species generated by mechanical treatment. In addition, the formation of a statistical isomer mixture in the mechanically activated reaction may be due to similar heats of formation of the isomers.

In order to check the latter assumption we performed quantum-chemical calculations of the isomeric complexes by nonempirical methods. The calculated geometric parameters, in particular the bond lengths, were in a good agreement with the experimental data obtained for structurally related complex derived from *o*-nitrotoluene and naphthalene [17]. The anionic fragment has an octahedral configuration with the platinum atom located at the octahedron center (Fig. 2). Four chlorine atoms occupy equatorial positions, and the  $\sigma$ -aryl ligand and the remaining chlorine atom (in our case) or ammonia molecule (in the complexes studied experimentally) are oriented axially. The calculated Pt–C distance is 2.07 Å (2.08 Å for the  $\sigma$ -naphthyl complex). The Pt–Cl<sub>eq</sub> bond lengths, 2.43 Å (about 2.3 Å in the  $\sigma$ -naphthyl complex), are slightly shorter than the Pt–Cl<sub>ax</sub> distance (2.53 Å). Presumably, this is explained by a strong *trans* effect of the  $\sigma$ -aryl ligand. The observed agreement between the calculated geometric parameters and those found experimentally for related complexes indicates the validity of the approximation used.

As might be expected, we obtained fairly similar total electronic energies and zero-point vibration energies for the *meta*- and *para*-isomeric  $\sigma$ -tolyl platinum(IV) complexes, which suggest equal thermodynamic probabilities for formation of the isomers.

	<i>meta</i> Isomer	<i>para</i> Isomer
Total electronic energy, a.u.	–235.6786575368	–235.6778011538
Zero-point vibration energy, a.u.	0.118655	0.118045

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