

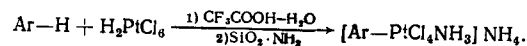
FORMATION OF σ -ARYL COMPLEXES OF
Pt(II) IN THE REACTION OF AROMATIC
COMPOUNDS WITH SALTS OF Pt(II) AND THEIR
OXIDATION UNDER THE ACTION OF H_2PtCl_6

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The heating of an aromatic compound (for example, benzene or toluene) with Na_2PtCl_4 in a mixture of $CF_3COOH-H_2O$ leads to the formation of σ -aryl complex of Pt(II), which under the action of H_2PtCl_6 can be converted to a known anionic σ -aryl complex of Pt(IV). The detected σ -derivatives of Pt(II) are intermediate compounds in the H-D exchange of aromatic hydrocarbons and the oxidation of hydrocarbons under the action of H_2PtCl_6 , catalyzed by Pt(II) salts.

It was earlier assumed that the reactions of H-D exchange in hydrocarbon under the action of Pt(II) salts in $CH_3COOD-D_2O$ or $CF_3COOD-D_2O$ medium and the oxidation of hydrocarbons under the action of H_2PtCl_6 , catalyzed by Pt(II) salts, proceed with intermediate formation of a σ -derivative of Pt(II) [1, 2]. In the latter case, the formation of the σ -complex of Pt(II) is followed by its conversion to a σ -derivative of Pt(IV) under the action of H_2PtCl_6 . Actually, recently we isolated σ -complexes of Pt(IV) from the reaction of aromatic compounds with H_2PtCl_6 in $CF_3COOH-H_2O$ medium [3-5]:



The purpose of the present work was to demonstrate the intermediate formation of a σ -complex of Pt(II) and the possibilities of its further conversion to a σ -derivative of Pt(IV) under the action of H_2PtCl_6 . A solution of Na_2PtCl_4 and an aromatic compound (benzene and toluene was used as examples) in a mixture of $CF_3COOH-H_2O$ (4:1 by volume) was heated at 80°C for 30-60 min. Then the solution was either extracted

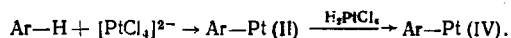
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with hexane to remove the initial aromatic compound or evaporated to dryness at reduced pressure (after which the residue was dissolved in a new portion of a mixture of $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$). Excess H_2PtCl_6 was added to the solution, it was heated for 15 at 80°C , the solvent was evaporated to dryness, and the residue was chromatographed on silica gel containing ammonia. The complexes $[\text{C}_6\text{H}_5\text{PtCl}_4\text{NH}_3]\text{NH}_4$ [yield 25% calculated on the basis of Pt(II)] and $[\text{CH}_3\text{C}_6\text{H}_4\text{PtCl}_4\text{NH}_3]\text{NH}_4$ (mixture of *m*- and *p*-isomers with ratio approximately 2:1, yield 27%), identified by the PMR method and by comparison of R_f (0.21 on Silufol, eluent acetone-hexane 1:1) with a known sample [4], were obtained. It should be noted that when a σ -complex of Pt(II) is formed, replacement of the chlorine atom by a neutral hydrogen molecule is possible. After treatment of the solution of the Pt(II) derivative formed with gaseous chlorine, a σ -aryl derivative of Pt(IV) could not be isolated.

Just as we should have expected, σ -derivatives of Pt(II) proved substantially more stable than the corresponding σ -complexes of Pt(IV). Thus, in contrast to the compounds obtained earlier $[\text{Ar}-\text{PtCl}_4\text{L}]^{n-}$, where $\text{L} = \text{H}_2\text{O}$ and $n = 1$ or $\text{L} = \text{Cl}$ and $n = 2$ [3, 4], complexes of Pt(II) decompose within several minutes in aqueous solution with liberation of metallic platinum.

Aryl derivatives of Pt(II) can be isolated in an individual state. After heating of benzene or toluene with Na_2PtCl_4 in $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ for 15 min, the solvent was evaporated under vacuum and the residue applied in acetone on a silica gel column (containing 1-2 mg ammonia per gram of silica gel), treated with hexane. An acetone-hexane mixture (2:1) elutes an orange-yellow band. The solvent was evaporated under vacuum and the residue purified by the method of thin-layer chromatography on silica gel (eluent acetone-hexane 3:2). The complexes were obtained in the form of yellow crystals, which decompose with time. A complex multiplet with $\delta = 6.60-7.29$ ppm was detected in the PMR spectrum of the phenyl complex obtained, which agrees with the presence of a Pt- C_6H_5 σ -bond in this compound. This same complex can be obtained by the interaction of Ph_2Hg with Na_2PtCl_4 in aqueous acetone at 20°C for 15 min. The solution was filtered off from the dark-colored precipitate and evaporated under vacuum. Further treatment was performed as described above. The samples were compared by the method of thin-layer chromatography on Silufol (R_f 0.66, eluent acetone-hexane 1:1) and PMR.

Thus, the data obtained agree with the reaction scheme including initial formation of a σ -aryl complex of Pt(II), followed by its oxidation to a σ -derivative of Pt(IV):



Conversion of the σ -complex of Pt(II) to a derivative of Pt(IV) can occur according to two essentially different mechanisms: replacement of a Pt(II) atom by Pt(IV) or oxidation of Pt(II) to Pt(IV) by the transfer of two atoms of chlorine.

Let us note that the formation of intermediate σ -aryl complexes of palladium(II) has been suggested for a whole series of conversions of aromatic compounds under the action of salts of Pd(II) in acid medium (the reaction of dimerization of arenes [6], the Fujiwara reaction [7], and others), and the Pt(II) complexes that we detected can be models for such conversions.

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LITERATURE CITED

1. A. E. Shilov and A. A. Shteinman, "Activation of saturated hydrocarbons by metal complexes in solutions," *Kinet. Katal.*, **18**, No. 5, 1129 (1977).
2. A. E. Shilov and A. A. Shteinman, "Activation of saturated hydrocarbons by metal complexes in solution," *Coord. Chem. Rev.*, **24**, 97 (1977).
3. G. B. Shul'pin, L. P. Rozenberg, R. P. Shibaeva, and A. E. Shilov, "Synthesis and structure of a σ -naphthalene with H_2PtCl_6 ," *Kinet. Katal.*, **20**, No. 6, 1570 (1979).
4. G. B. Shul'pin, A. E. Shilov, A. N. Kitaigorodskii, and J. V. Z. Krevor, "The reaction of hexachloroplatinic acid with aromatic compounds affording the σ -aryl complexes of platinum(IV). II. The synthesis of platinum(IV) complexes of benzene, alkylbenzenes, and chlorinated benzenes," *J. Organomet. Chem.*, **201**, No. 1, 319 (1980).
5. G. B. Shul'pin, "Investigation of the formation of σ -aryl complexes of platinum(IV) in the reaction of chloroplatinic acid with aromatic compounds," *Kinet. Katal.*, **22**, No. 2, 520 (1981).
6. I. V. Kozhevnikov and K. I. Matveev, "Oxidative coupling of aromatic systems under the action of transi-

tion-metal compounds," Usp. Khim., 47, No. 7, 1231 (1978).

7. I. Moritani and Y. Fujiwara, "Aromatic substitution of olefins by palladium salts," Synthesis, No. 9, 524 (1973).