

REACTION OF AROMATIC COMPOUNDS WITH H_2PtCl_6 IN $CF_3COOH-H_2O$ SYSTEM
LEADING TO THE PREPARATION OF ANIONIC σ -ARYL COMPLEXES OF Pt(IV)

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The metallation reactions of aromatic hydrocarbons and their derivatives by nontransition metal compounds, leading to the preparation of organometallic aryl derivatives, are well known. These reactions include mercuration, thallation, and cleavage of the aryl-hydrogen bond by alkali metal compounds. General methods for the preparation of σ -aryl derivatives of transition metals directly from the aromatic compound and the metal complex are still known for a limited number of cases only. These include the auration of aromatic compounds according to Kharash [1, 2], auration by Au(I) compounds [3], the method of photoinduced addition of tungsten to aromatic C-H bond developed by Green [4], and the oxidative addition of ruthenium [5] and iron [6] to arenes. The formation of an unstable intermediate σ -aryl complex of palladium was proposed for a series of transformations of aromatic hydrocarbons under the action of salts of this metal (oxidative combination according to van Helden [7-9], the Fujiwara reaction [10], carboxylation of arenes by carbon monoxide [11], etc.); however, such a complex has not yet been isolated. In the above we do not include the cyclometallation reactions of aromatic compounds [12-15], because although the rate of formation of σ -aryl derivatives and their stability sharply increase due to the chelate effect, nevertheless this method cannot be considered general for different arenes since a chelating group in the molecule is necessary. Lastly, the formation of intermediate σ -aryl and σ -alkyl complexes was assumed in the oxidation reaction of alkanes by hexachlorophatonic acid [16-20]. It should be noted that in contrast to metallation reactions of arenes by nontransition metals, the corresponding transformations in the series of transition elements leading to the preparation of σ -aryl complexes [21] have been studied in much less detail.

In 1979 we found [22] that the reaction between hexachloroplatinic acid and aromatic compounds in an acid medium leads to the formation of σ -aryl derivatives of Pt(IV), as demonstrated in the case of naphthalene. In the present work, the study of this reaction has been continued, and certain generalizations have been made.

σ -Aryl complexes of Pt(IV) were synthesized in an aqueous trifluoroacetic acid medium. The use of water as a solvent also leads to the formation of complexes, but in this case the yield is extremely low. Hexachloroplatinic acid is insoluble in anhydrous CF_3COOH . Usually an excess of the aromatic compounds is needed, and the reaction takes a few minutes or hours, with heating of the homogeneous solution to 70-100°C. After removal of trifluoroacetic acid, the residue is chromatographed on a silicon gel which contains ammonia (1-2 mg of NH_3 per g of silica gel). An acetone-hexane mixture (2:1) elutes the yellow or orange band of the complex. The H_2PtCl_6 remaining on the column (partly in the form of an ammonia derivative) can be washed out with water. The complex is purified by TLC on silica gel and is further recrystallized from acetone or an acetone-hexane mixture.

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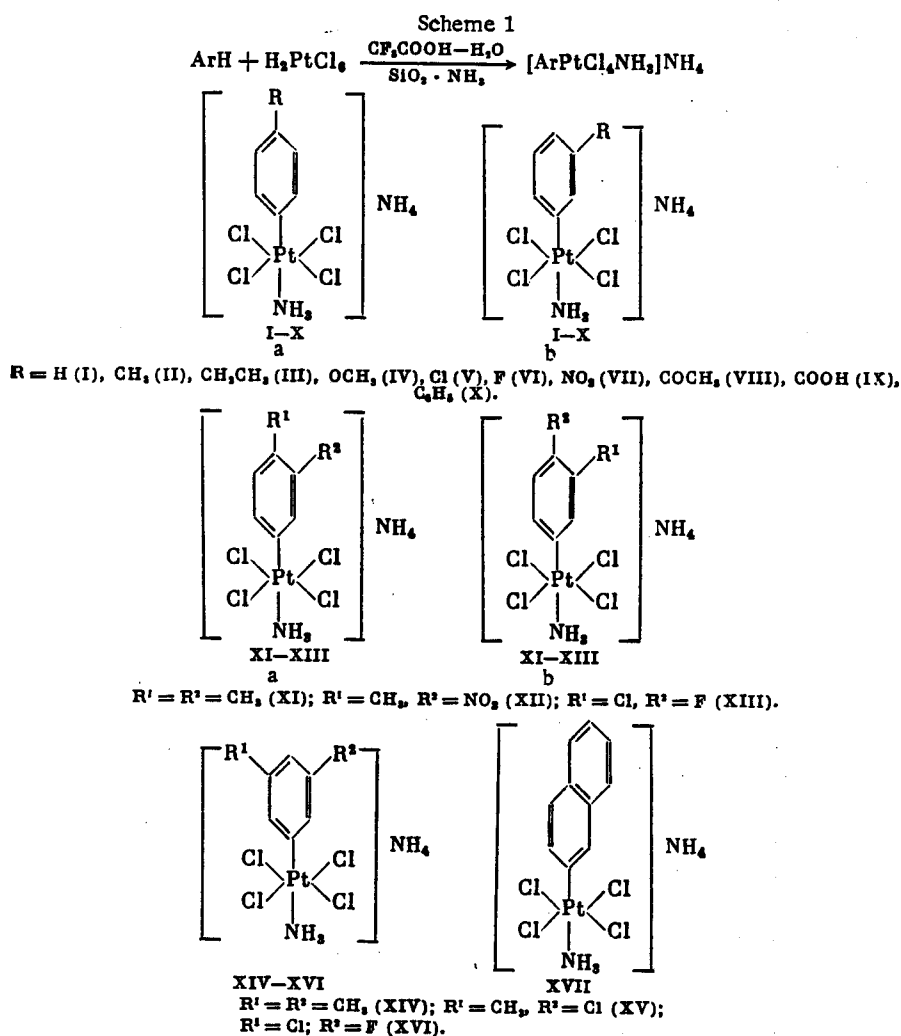
TABLE 1. Properties of σ -Aryl Complexes $[\text{ArPtCl}_4\text{NH}_3]_n\text{NH}_4 \cdot n\text{Ac}^a$

Com- pound No.	ArH	Name of complex	n	Yield, %	Found, %			Formula	Calculated, %		
					C	H	N		C	H	N
I	C_6H_6	Ammonium phenylamminetetra- chloroplateate	1	41	21.71	3.14	5.90	$\text{C}_9\text{H}_{10}\text{Cl}_4\text{N}_2\text{O}_3\text{Pt}^b$	21.30	3.55	5.52
II	$\text{C}_6\text{H}_5\text{CH}_3$	Ammonium tolyamminetetra- chloroplateate	0	14	17.74	2.89		$\text{C}_7\text{H}_9\text{Cl}_4\text{N}_2\text{Pt}$	18.16	3.02	
III	$\text{C}_6\text{H}_5\text{C}_6\text{H}_5$	Ammonium ethylphenylamminetetra- chloroplateate	0.5	28	23.37	3.88	5.48	$\text{C}_{19}\text{H}_{38}\text{Cl}_8\text{N}_4\text{O}_3\text{Pt}_2$	22.53	3.75	5.53
IV	$\text{C}_6\text{H}_5\text{OCH}_3$	Ammonium anisylamminetetra- chloroplateate	0	49	18.13	2.81	6.24	$\text{C}_7\text{H}_9\text{Cl}_4\text{N}_2\text{O}_3\text{Pt}$	17.54	2.92	5.84
V	$\text{C}_6\text{H}_5\text{Cl}$	Ammonium chlorophenylammine- chloroplateate	0.5	20	18.41	3.05		$\text{C}_{13}\text{H}_{28}\text{Cl}_{10}\text{N}_4\text{O}_3\text{Pt}_2$	17.95	2.80	
VI	$\text{C}_6\text{H}_5\text{F}$	Ammonium fluorophenylammine- tetrachloroplateate	0	35	15.37	2.40	5.95	$\text{C}_9\text{H}_{11}\text{Cl}_4\text{FN}_2\text{Pt}$	15.35	2.40	5.97
VII	$\text{C}_6\text{H}_5\text{NO}_2$	Ammonium nitrophenylammine- tetrachloroplateate	0	84	14.88	2.57	8.37	$\text{C}_9\text{H}_{11}\text{Cl}_4\text{N}_2\text{O}_3\text{Pt}$	14.57	2.23	8.50
VIII	$\text{C}_6\text{H}_5\text{COCH}_3$	Ammonium acetylphenylammine- tetrachloroplateate	0.5	30	22.01	3.25	4.80	$\text{C}_{19}\text{H}_{34}\text{Cl}_8\text{N}_4\text{O}_3\text{Pt}_2$	21.62	3.28	5.40
IX	$\text{C}_6\text{H}_5\text{COOH}$	Ammonium carboxyphenylammine- tetrachloroplateate	0.5	30	19.54	3.02		$\text{C}_{17}\text{H}_{30}\text{Cl}_8\text{N}_4\text{O}_3\text{Pt}_2$	20.78	2.87	
X	$\text{C}_6\text{H}_5\text{C}_6\text{H}_5$	Ammonium diphenylamminetetra- chloroplateate	1.5	42	32.26	3.89		$\text{C}_{33}\text{H}_{60}\text{Cl}_{12}\text{N}_4\text{O}_3\text{Pt}_3$	32.35	4.08	
XI	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	Ammonium o-xylamminetetra- chloroplateate	0.5	27	22.63	4.16		$\text{C}_{19}\text{H}_{38}\text{Cl}_8\text{N}_4\text{O}_3\text{Pt}_2^c$	22.50	3.75	
XII	$\text{C}_6\text{H}_4\text{CH}_2\text{NO}_2$	Ammonium o-nitrotolylammine- tetrachloroplateate	1	41	21.34	3.33	8.25	$\text{C}_{10}\text{H}_{10}\text{Cl}_4\text{N}_2\text{O}_3\text{Pt}^c$	21.20	3.35	7.42
XIII	$\text{C}_6\text{H}_4\text{FCl}$	Ammonium o-fluorochlorophenyl- amminetetra- chloroplateate	1.5	35	21.13	3.64	4.54	$\text{C}_{31}\text{H}_{58}\text{Cl}_{10}\text{F}_3\text{N}_4\text{O}_3\text{Pt}_3$	21.41	3.23	4.76
XIV	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	Ammonium m-xylamminetetra- chloroplateate	0	32	20.29	3.51	5.92	$\text{C}_9\text{H}_{10}\text{Cl}_4\text{N}_2\text{Pt}^d$	20.13	3.35	5.87
XV	$\text{C}_6\text{H}_4\text{ClCH}_3$	Ammonium m-chlorotolylammine- tetrachloroplateate	1	62	21.97	3.90		$\text{C}_{10}\text{H}_{10}\text{Cl}_6\text{N}_2\text{O}_3\text{Pt}^e$	22.02	3.49	
XVI	$\text{C}_6\text{H}_4\text{FCl}$	Ammonium m-fluorochlorophenyl- amminetetra- chloroplateate	1	28	19.38	2.89		$\text{C}_9\text{H}_9\text{Cl}_4\text{FN}_2\text{O}_3\text{Pt}$	19.30	2.86	
XVII	C_{10}H_8	Ammonium naphthylamminetetra- chloroplateate	2	14	31.02	4.34	4.32	$\text{C}_{10}\text{H}_{10}\text{Cl}_4\text{N}_2\text{O}_3\text{Pt}^e$	31.22	4.26	4.55

Notes. a) Ac - acetone. b) Found %: Cl 28.30; Pt 39.18. Calculated %: Cl 28.01; Pt 38.46. mp 186-187°C. c) mp 158-161°C. d) Found %: Cl 29.15. Calculated %: Cl 29.77. mp 250°C. e) mp 178°C.

The aromatic platinum derivatives thus obtained are yellow or orange crystalline substances. The data of elemental analysis and IR and NMR spectra show that two ammonia molecules are included in the composition of the complexes. X-ray diffraction analysis (with naphthalene and o-nitrotoluene complexes as examples) shows that one of the ammonia molecules plays the role of a ligand, and the other forms an ammonium cation. The anionic particle is built octahedrally, with the platinum atom in the center. The four chloride atoms are located in equatorial positions, and the axial positions are occupied by the σ -aryl ligand and an ammonia molecule. In the molecule of the σ -naphthyl complex, the Pt-C distance is 2.08 Å, the Pt-Cl distances are about 2.3 Å, and the Pt-N distance is 2.24 Å. It should be noted [22] that the water molecule in the structure of the σ -naphthyl complex should be substituted by an ammonia molecule, and the NH_4^+ ion, and not H_3O^+ , should be considered as the cation.

As aromatic compounds we used benzene, its monosubstituted derivatives (toluene, ethylbenzene, anisole, chlorobenzene, fluorobenzene, nitrobenzene, benzoic acid, acetophenone, diphenyl), disubstituted benzenes (o- and m-xylenes, m-chlorotoluene, o-nitrotoluene, o- and m-chlorofluorobenzenes), and naphthalene (see scheme 1). Some of the characteristics of the complexes obtained from these compounds are given in Table 1. We also obtained platinum derivatives of isopropylbenzene, phenol, diphenyl oxide, and aniline, which were characterized by PMR spectral data only.



The reaction between monosubstituted benzenes and hexachloroplatinic acid leads to the formation of a mixture of m- and p-isomers of σ -aryl complexes (isomers a and b in Scheme 1), as reflected in the PMR spectra (Table 2). In the spectra of the tolyl and acetophenone complexes, the methyl groups are characterized by two signals in the region around 2 ppm. In the spectrum of the complex with ethylbenzene, a duplex set of quadruplet signals of the methylene groups have been observed, while the methyl groups, which are relatively far from the plati-

TABLE 2. Data of PMR (δ , ppm, with reference to TMS), IR (ν , cm^{-1}), and Electronic Spectra (ν , cm^{-1} , ethanol)^a

Complex No.	Solvent	Aromatic protons	Other protons	Some of bands in IR spec.	UV spectrum
I	CD ₃ OD	6.93—7.11 m, 7.42—7.80 m	—	1685 Ac	36250
II	D ₂ O	6.95—7.55 m	2.33, 2.41 (CH ₃)		36400
III	D ₂ O	6.85—7.55 m	1.11 (CH ₃) 2.40—2.80	1685 Ac	36400
IV	CD ₃ OD	6.50—7.72 m	3.82 (CH ₃)		36600
V	CD ₃ OD	6.85—7.20 m, 7.35—7.80 m	—	1693 Ac	36300
VII	CD ₃ COCD ₃	7.27 t, 8.63 t, 7.80—8.30 m	—	1345, 1515 (NO ₂)	35400
VIII	D ₂ O	6.26 q, 7.53—8.20 m	2.61, 2.62 (CH ₃)	1675, 1710	
IX	D ₂ O	7.22 q, 8.20 t, 7.40—8.07 m	—	1710, 1725	
X	D ₂ O	7.10—7.90 m	—	1704, 1712	38300
XI	D ₂ O	6.64—7.40 m	2.17, 2.26 (CH ₃)		
XII	CD ₃ COCD ₃	7.08 d, 8.32 d, 7.55—8.10 m	2.54, 2.56 (CH ₃)	1358, 1530 (NO ₂)	
XIV	D ₂ O	6.84 s, 7.13 s	2.25 CH ₃		
XV	D ₂ O	7.08, 7.33	2.28 CH ₃		
XVII	CD ₃ OD	7.29—8.18 m	—	743, 813, 828, 852, 858 (C ₁₀ H ₇), 1692, 1718 Ac	

Notes. a) Ac — acetone. Numeration corresponds to that in Table 1.

num atom, have one common triplet. Similarly, the methyl groups in the spectrum of the complex with anisole give one singlet. The formation of two isomers of the complex with fluorobenzene is confirmed by the ¹⁹F NMR spectrum of the complex (Table 3), in which two multiplets are observed, which correspond to meta- and para-platinated isomers. Similarly, ortho-disubstituted benzenes in the reaction with H₂PtCl₆ give mixtures of two isomers. This is confirmed by PMR spectra of the complexes with xylene and o-nitrotoluene, each containing two signals with a singlet form, corresponding to two types of methyl groups, and by ¹⁹F NMR spectrum of the o-chlorofluorobenzene complex, in which two multiplets were found, corresponding to two isomers (the fluorine atom in the para and meta positions with respect to the platinum-containing fragment). Lastly, the meta-disubstituted benzenes give only one isomer, in which the platinum atom is present at the meta positions with respect to the two substituents. Therefore, in the PMR spectra of the m-xylene and m-chlorotoluene complexes, only single singlets of the methyl groups have been observed, and in the ¹⁹F NMR spectrum of the m-chlorofluorobenzene derivative, only one multiplet appears. We can assume that in other cases, not mentioned here, also (for example, the complex with chlorobenzene, in whose spectrum there is only one multiplet of aromatic protons — difficult to interpret) complexes are formed in the form of mixtures of meta- and para-platinated isomers. It is interesting to note that according to the data of NMR spectra, samples of complexes obtained contain almost equal amounts of para- and meta-platinated aromatic compounds, but for different samples of one and the same complex, the m/p ratio differs somewhat. These quantitative differences in the composition of the samples are apparent not only in the intensity ratio of the methyl group signals, but also in the form of the multiplets of the aromatic protons. A change in

TABLE 3. Data on ¹⁹F NMR Spectra (ppm, with reference to fluorobenzene)^a

Complex No.	Solvent	δ_p^F	δ_m^F	σ_I	σ_R
VI	CD ₃ COCD ₃	9.44	3.87	-0.46	-0.19
VI	CD ₃ SOCD ₃	9.10	3.80	-0.45	-0.18
VI	CH ₃ OD	7.90	1.80	-0.17	-0.21
VI	D ₂ O	6.32	1.14	-0.08	-0.18
XIII	CD ₃ COCD ₃	11.90	7.35	—	—
XVI	CD ₃ COCD ₃	—	2.54	—	—

Note. Numeration corresponds to that in Table 1.

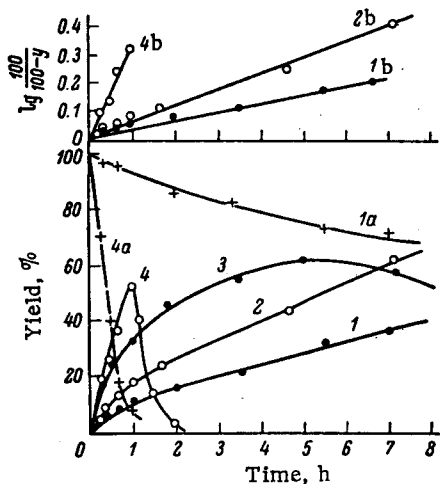


Fig. 1

Fig. 1. Kinetic curves of accumulation of Pt(IV) complex of benzene in reaction between H_2PtCl_6 and benzene in a $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ mixture (5:1 by volume). Concentration of Pt(IV) 0.074 mole/liter, C_6H_6 1.75 moles/liter. 1) 70°C ; 2) 79.5°C ; 3) 79.5°C with addition of Na_2PtCl_4 (0.007 mole/liter); 4) 86.5°C . a) Corresponding curves for the consumption of H_2PtCl_6 ; b) corresponding semilogarithmic anamorphoses of the accumulation curves of the complex.

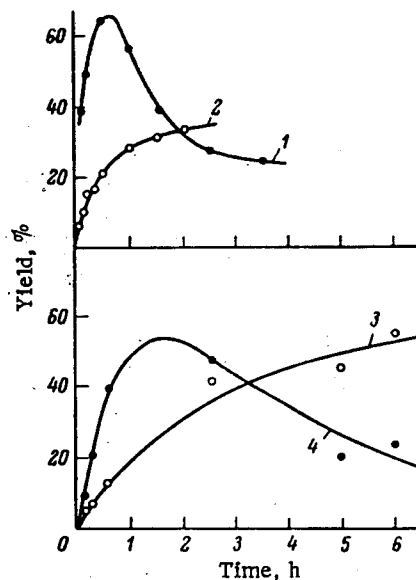


Fig. 2

Fig. 2. Kinetic curves of accumulation of σ -aryl complexes in reaction between H_2PtCl_6 (0.074 mole/liter) and anisole (2.0 moles/liter, 1), diphenyl (0.38 mole/liter); 2) chlorobenzene (1.80 moles/liter); 3) chlorobenzene (the same conditions) in the presence of Na_2PtCl_4 (0.01 mole/liter; 4) in a mixture of $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ (6:1 by volume) at 94°C .

the m/p ratio for the platinated aromatic compounds on transition from one sample to another (obtained under somewhat different conditions) can apparently be explained by the para-meta isomerization occurring simultaneously with the accumulation of the complex (see below).

No formation of the ortho-platinated aromatic derivatives is observed in the reaction compounds and hexachloroplatinic acid. This is also confirmed chemically: We were unable to isolate a significant amount of σ -aryl complex of Pt(IV) from the reaction between H_2PtCl_6 and aromatic compounds in which only the ortho positions in the ring are free (with p-xylene, p-dimethoxybenzene, p-dichlorobenzene, mesitylene, pentamethylbenzene, pentafluorobenzene). The reason for this sharply expressed steric deactivation of the ortho positions is probably the large volume of the platinum-containing entering group. We should note that, according to data of x-ray diffraction analysis [22], platinum enters into the β -position of the naphthalene ring.

The σ -aryl anionic complexes of Pt(IV) obtained in the present investigation are soluble in water, alcohol, acetone, and dimethyl sulfoxide, very sparingly soluble in chloroform, and insoluble in benzene, ether, and hexane. During recrystallization from acetone, the solvent can become included in the crystal lattice of the complexes, as apparent from the data of the PMR and IR spectra. The x-ray diffraction analysis and the IR spectrum of the σ -naphthyl complex indicate that in the crystals of this compound, for each anionic moiety containing naphthalene and platinum atom, there are two molecules of acetone oriented differently in the crystal lattice. The number of acetone molecules in the sample of a σ -aryl complex generally depends on the crystallization conditions, and can vary from 0 to 2 molecules per molecule of the complex.

The yields of complexes obtained in the present investigation vary from 10 to 80%, and it should be noted that the yield is very strongly dependent on the time

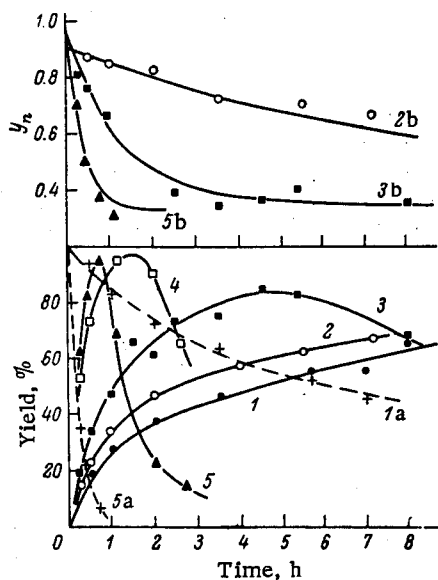


Fig. 3

Fig. 3. Kinetics of reaction between H_2PtCl_6 (0.074 mole/liter) and toluene (1.54 moles/liter) in a $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ mixture (5:1 by volume). Curves of accumulation of σ -tolyl complex: 1) 63°C ; 2) 70°C ; 3) 85°C ; 4) 93°C ; 5) 96.5°C . a) Corresponding curves for the consumption of H_2PtCl_6 ; b) corresponding theoretical curves for the change in the content of the para-isomer in the mixture.

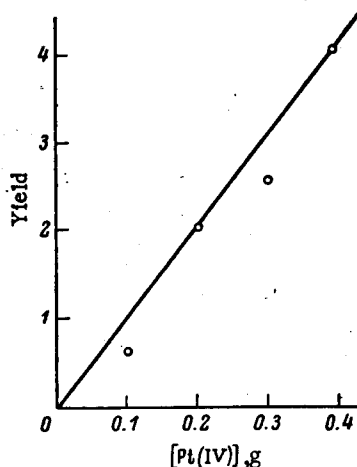


Fig. 4

Fig. 4. Dependence of yield of σ -phenyl complex of Pt(IV) on H_2PtCl_6 concentration [yield in arbitrary units; the line corresponds to a first order reaction with respect to Pt(IV)].

of the reaction. To obtain a maximum yield of the complex, we must first determine the optimal time of reaction on a kinetic curve, containing a section of accumulation of the complex, followed by rapid decomposition.

The kinetic curves for formation and decomposition of the complexes of certain aromatic compounds are shown in Figs. 1-3. It is seen that electron-donor substituents accelerate the formation of the complex, and shorten the time to the beginning of its decomposition. For example, in the case of anisole, after 30 min a noticeable decomposition of the complex is observed, while for chlorobenzene, the maximum concentration of the complex before decomposition begins corresponds to time $t > 6$ h. As shown in the case of phenyl and tolyl complexes, on the section of accumulation, the kinetic curves are satisfactorily linearized in the $[\log 100/(100 - x), t]$ coordinates, where 100 is the total amount of Pt(IV) in % and x the current yield of complex. However, it should be pointed out that at the initial sections of the semilogarithmic anamorphoses, the experimental points are located a little above the line. This can be explained by the formation of small amounts of a still unidentified Pt(IV) compound, whose absorption in the UV spectrum is superimposed on the absorption of the complexes. The presence of the unidentified compound has an effect only if the yield of the complex is low and commensurable with the amount of the unknown admixture. Figures 4 and 5 show the dependence of the yield of the Pt(IV) complex on the concentration of Pt(IV) and benzene, respectively. It is seen that the reaction is approximately first order with regard to Pt(IV) and benzene.

If small amounts of Na_2PtCl_4 are added to the reaction mixture, the yield of Pt(IV) complex increases somewhat, as shown in the case of the complex with benzene in Fig. 1, curve 3. Simultaneously, the maximum of the concentration of the complex shifts in the direction of a shorter time. Additions of $\text{Hg}(\text{OAc})_2$ have a similar effect. The dependence of the yield of the Pt(IV) complex of benzene on the amount of Pt(II) and Hg(II) salts is shown in Fig. 6. The accelerating action of the Pt(II) and Hg(II) salts can be explained by the higher electrophilicity of these compounds and the intermediate formation of σ -derivatives of Pt(II) and Hg(II), which react further with H_2PtCl_6 to form a σ -complex with Pt(IV). However, we must take into account that the Hg(II) compounds are good acceptors of the Cl^- ion, which

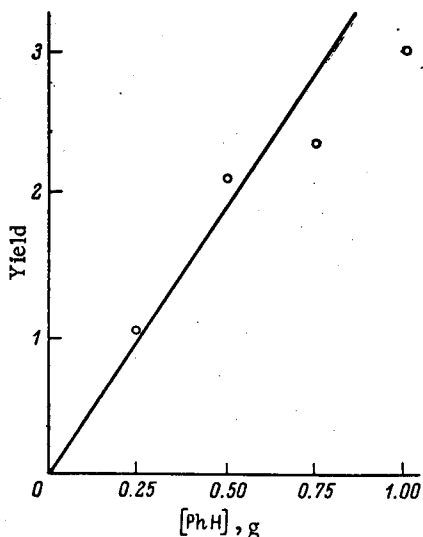
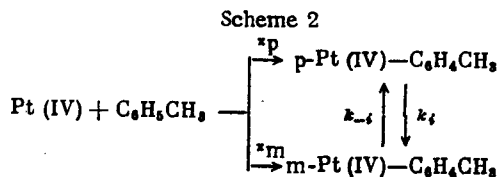


Fig. 5. Dependence of yield of σ -phenyl complex of Pt(IV) on C_6H_6 concentration (yield in arbitrary units; the line corresponds to a first order reaction with respect to C_6H_6).

slows down the reaction. In the case of a Pt(II) catalyzed reaction, the kinetic curve is not a straight line for the semilogarithmic anamorphosis. We should note that σ -aryl complexes of Pt(II) formed in the reaction between Na_2PtCl_4 and aromatic hydrocarbons in the $CF_3COOH-H_2O$ system can be detected in the reaction mixture, but these compounds are less stable than the Pt(IV) complexes.

The formation of σ -tolyl complex of Pt(IV) (Fig. 3) has been studied in greater detail. Besides the total concentration of the complex, determined spectrophotometrically, we measured at given intervals of time the relative amounts of the para- and meta-isomers of the σ -tolyl complex in the mixture of products by the PMR method. One of the signals of the methyl group in the PMR spectrum could be assigned by comparing with the spectrum of a pure p-tolyl complex obtained in the reaction between p-tolylmercury chloride and H_2PtCl_6 in aqueous acetone [23]. Figure 3 shows that simultaneously with the accumulation of the σ -tolyl complex, the content of the para-isomer in the mixture decreases. The curves corresponding to decrease in the content of the para-isomer can be extrapolated at time $t = 0$ to a value of approximately 90%. When the reaction has proceeded to a higher degree, an equilibrium mixture is obtained containing about 33% of the para-isomer. The change in the ratio between the isomers may be due to para-meta isomerization of the complex, occurring simultaneously with its accumulation



(see scheme 2). The kinetic analysis of this system (carried out by A. T. Nikitaev), assuming that $\Delta H = 0$, led to the following dependence of the fraction of the para-isomer on time:

$$y_p = \frac{[\text{p-Pt(IV)-C}_6\text{H}_4\text{CH}_3]}{[\text{p-Pt(IV)-C}_6\text{H}_4\text{CH}_3] + [\text{m-Pt(IV)-C}_6\text{H}_4\text{CH}_3]} = \frac{1}{3} + \frac{3x_p - x}{3(x - 1.5k_i)} \cdot \frac{e^{-1.5k_it} - e^{-xt}}{1 - e^{-xt}}$$

where $x = x_p + x_m$; $k_i = 2k_{-i}$. The values of x at different temperatures were calculated from the slope of the semilogarithmic accumulation anamorphosis. The best agreement between the calculated and experimental curves (Fig. 3) was attained at the following values of the constants (h^{-1}): for $70^\circ C$ $x = 0.20 \pm 0.05$, $x_p = 0.18 \pm 0.05$, $k_i = 0.18 \pm 0.02$; for $85^\circ C$ $x = 0.57 \pm 0.12$, $x_p = 0.55 \pm 0.12$, $k_i = 1.7 \pm 0.5$; for $96.5^\circ C$ $x = 4.1 \pm 0.8$, $x_p = 3.9 \pm 0.78$, $k_i = 4.6 \pm 0.5$.

To study the decomposition of the σ -aryl complexes of platinum, we carried out the following experiment. A solution of H_2PtCl_6 and toluene was heated at a $CF_3COOH-H_2O$ mixture to $96.5^\circ C$ for 45 min, which corresponds to the maximum accumulation of the complex. The temperature of the solution was decreased to $10^\circ C$, and the solution was thoroughly extracted by hexane to remove toluene. The reaction mixture was heated again to $99^\circ C$. The curves for the decomposition of the σ -complex and the para-isomer content are given in Fig. 7. Figure 7 shows that the decomposition of the complex only begins after a certain induction period. After this time the content of the para-isomer decreases somewhat, and then remains constant

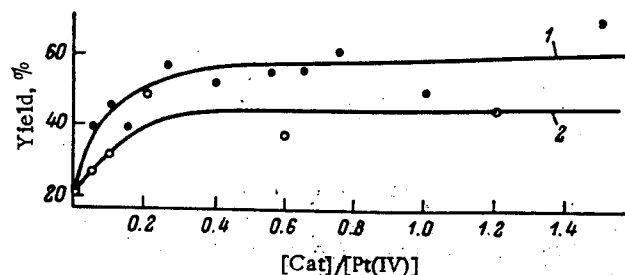
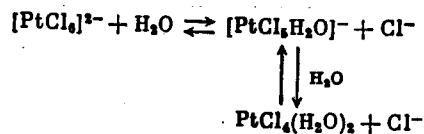


Fig. 6. Dependence of the yield of phenyl complex of Pt(IV) on the catalyst concentration (H_2PtCl_6 0.074 mole/liter, C_6H_6 2.2 moles/liter, $\text{CF}_3\text{COOH-H}_2\text{O}$ 6:1 by volume, 15 min, 84°C). 1) Na_2PtCl_4 ; 2) $\text{Hg}(\text{OCOCH}_3)_2$.

at the 20% level. It is already known [18] that the oxidation of the aromatic hydrocarbons by hexachloroplatinic acid leads to the formation of chlorinated arenes and diphenyl derivatives. We confirmed this in the case of anisole. On prolonged heating of an anisole solution and H_2PtCl_6 in a mixture of trifluoroacetic acid and water, a mixture of chloroanisole isomers and isomers of dimethoxydiphenyl is formed. We should note that the time to the beginning of the decomposition of the complex is very dependent on the concentration of the initial reagents, and the decomposition is possibly accelerated by Pt(II) salts. The decomposition is accompanied by the formation of Pt(II) derivatives. The same products were obtained by heating for 1 h the solution of a Pt(IV) complex of anisole in $\text{CF}_3\text{COOH-H}_2\text{O}$. This agrees with the assumption that the oxidation of the aromatic compounds by H_2PtCl_6 proceeds with the intermediate formation of σ -aryl complexes of Pt(IV).

By using the competing reactions method, we determined the relative reactivity of different aromatic compounds in the reaction with hexachloroplatinic acid. A solution of H_2PtCl_6 and two aromatic compounds taken in excess, was heated at $80-90^\circ\text{C}$ for 15 min. The composition of the mixture of the complexes after chromatography on silica gel, was analyzed by the PMR method. The reaction rates were calculated with respect to one hydrogen atom of benzene, taking into account the number of hydrogen atoms in the given aromatic compound which are reactive in the electrophilic substitution (5 in monosubstituted benzenes, 10 in diphenyl and diphenyl oxide, 8 in naphthalene). The relative reaction rates thus calculated are listed in Table 4. Figure 8 shows that the logarithms of the rates correlate satisfactorily with the Hammett σ constants and σ^+ electrophilic constants. For most of the substituents, the best correlation is obtained when σ_p and σ_p^+ constants are used. For the COCH_3 , Cl, and NO_2 groups, we used the σ_m and σ_m^+ constants. The better correlation obtained for these constants in the case of *m*-substituents, probably indicates that benzenes containing electron-donor substituents, with H_2PtCl_6 give considerable amounts of the meta-platinated product. However, the point for σ_m of the nitro group lies at a considerable distance from the line. A better correlation is obtained with the electrophilic constant σ_m^+ of the nitro group. The value of ρ for the correlation with σ constants is equal to -3.0 , while for the σ^+ electrophilic constants, the value of ρ^+ is smaller and equal to -1.5 . By assuming that the relative rate of substitution of hydrogen by Pt(IV) in toluene is equal to 3, and taking into account the fact that at the initial period of time about 90% of the para-isomer is formed, we can calculate the factors of the partial rates $o_f^{\text{CH}_3} = 0$, $m_f^{\text{CH}_3} = 0.9$, $p_f^{\text{CH}_3} = 16.2$. We can see that the rate of platination in the meta-position practically does not increase under the influence of the methyl group. Anomalous selectivity of the electrophilic substitution reactions was observed, for example, in the nitration of toluene by nitronium tetrafluoroborate in sulfolane [24]. The selectivity factor for the reaction between toluene and H_2PtCl_6 in $\text{CF}_3\text{COOH-H}_2\text{O}$ is $S_f = \log(p_f^{\text{CH}_3}/m_f^{\text{CH}_3}) = 1.255$.

In a discussion on the mechanism of formation of σ -aryl complexes of Pt(IV), we can assume that the first stage consists in aquation of the Pt(IV) containing ion.



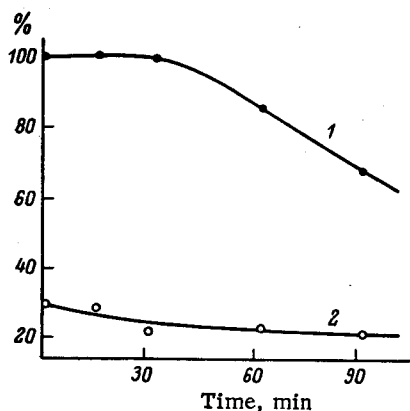


Fig. 7

Fig. 7. Decomposition of σ -tolyl complex of Pt(IV) in a $\text{CF}_3\text{COOH-H}_2\text{O}$ mixture (5:1 by volume) at 99°C . 1) Content of complex 2) content of para-isomer.

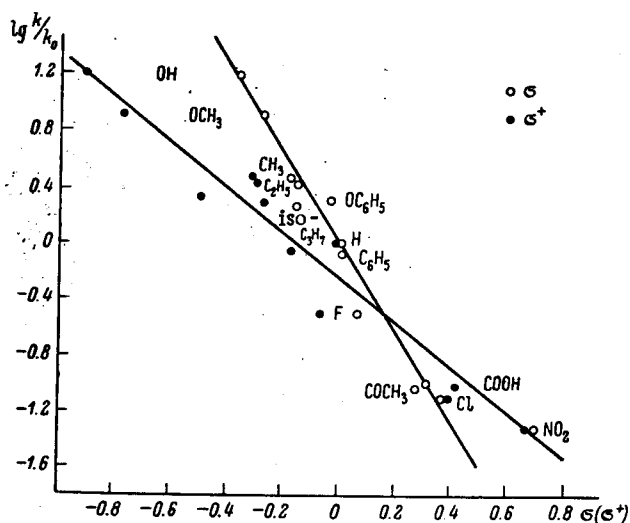
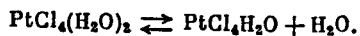


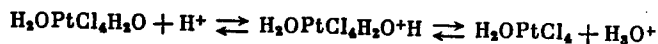
Fig. 8

Fig. 8. Correlation between relative rates of substitution of hydrogen by Pt(IV) in aromatic compounds and σ and σ^+ constants.

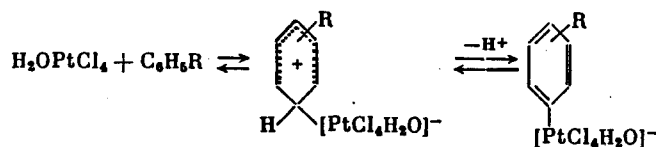
We should note that Hg(II) compounds can catalyze the equation of a chloride complex of a transition metal. The acceleration of the accumulation process of the aryl complex of Pt(IV) on addition of mercuric acetate has already been mentioned above. The neutral molecule formed in the aquation should have a higher electrophilicity than the initial anion. One molecule of water in the role of a ligand can dissociate to form a coordinationally unsaturated electrophilic particle:



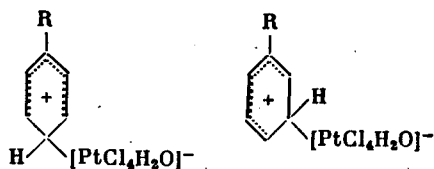
It is not improbable that trifluoroacetic acid is able to shift this equilibrium to the right, with protonation of the coordinated water molecule.



It is known that additions of strong acids sharply accelerate the electrophilic substitution reactions [9], in particular the mercuriation reaction. Mercuriation with mercury trifluoroacetate proceeds much more actively than electrophilic substitution with mercury acetate. The platinum-containing particle attacks the aromatic ring to form a Wheland σ -complex, which in this case has a zwitterion structure. The splitting of a proton leads to an anionic σ -aryl derivative.



In the zwitterion compound, the Pt(IV)-containing fragment can pass from the para-carbon atom to the m-position and vice versa.



The Wheland complex can probably also be formed in the protonation of the σ -derivative of Pt(IV) in trifluoroacetic acid. The existence of reversible protonation and migration of the organometallic fragment over the aromatic ring explains well the multiple H-D exchange in the aromatic hydrocarbons derived from platinum. During chromatography of the reaction mix-

TABLE 4. Relative Rates (W) of Reaction between H_2PtCl_6 and Aromatic Compounds

ArH	W	ArH	W
C_6H_5OH	16.00	C_6H_6	1.00
$C_6H_5OCH_3$	8.40	$C_6H_5C_6H_5$	0.85
$C_{10}H_8$	4.25	C_6H_5F	0.30
$C_6H_5CH_3$	3.00	$C_6H_5COCH_3$	0.10
$C_6H_5C_2H_5$	2.70	C_6H_5COOH	0.09
$C_6H_5OC_6H_5$	2.10	C_6H_5Cl	0.08
$C_6H_5CH(CH_3)_2$	1.90	$C_6H_5NO_2$	0.05

ture in the reaction between the aromatic hydrocarbons and H_2PtCl_6 on an ammonia-containing silica gel, ammonia substitutes water in the coordination sphere of Pt(IV).

Decomposition of the σ -aryl complexes proceeds by two paths, the first of which leads to a chlorinated arene and the second to a dimerization product. In both cases, Pt(IV) is reduced to Pt(II). The transfer of a chlorine atom from platinum to the aromatic ring can proceed both intra- and intermolecularly. At present, it is difficult to choose between these two possibilities. The dimerization probably includes the intermediate formation of a diaryl complex in the disproportionation reaction ($2 [ArPtCl_4L]^- \rightarrow [Ar_2PtCl_3L]^- + [PtCl_3L]^-$) or in an electrophilic attack by the σ -aryl complex on the molecule of free arene ($[ArPtCl_4L]^- + ArH \rightarrow [Ar_2PtCl_3L]^-$). The last variant explains the decrease in the decomposition of the complex in the absence of an aromatic compound (Fig. 7). It is probable that the path along which the oxidation, chlorination, or dimerization proceeds preferentially, depends on the reaction conditions and on the nature of the substituents in the benzene ring.

Certain chemical properties of the anionic σ -aryl complexes of Pt(IV) have also been studied. By the action of pyridine on the ionic complexes, successive substitution of the chlorine atoms takes place, and then of ammonia in the coordination sphere of platinum.



If the reaction is carried out in acetone with pyridine deficiency, there is a preferential formation of a neutral ammonia-containing complex. If the reaction is carried out in an aqueous solution with excess of pyridine, a neutral compound is formed which contains two pyridine ligands. When cesium chloride is added to the aqueous solution of the anionic complex, a cesium salt $[ArPtCl_4NH_3]Cs$, which is slightly soluble in water, separates out. Treatment of the aqueous solution of the anionic complex with sodium borohydride leads to the immediate separation of black metallic platinum, the aromatic compound and ammonia.

From the data on ^{19}F NMR spectrum of the complex with fluorobenzene (Table 3), we can estimate the electronic effect of the $[PtCl_4NH_3]^-$ fragment. The inductive σ_I and resonance σ_R constants were calculated from the Taft equations $\delta_m^F = -7.1\sigma_I + 0.6$ and $\delta_p^F = -20.5\sigma_R + \delta_m^F$. Table 3 shows that the platinum containing grouping has a donor effect in both inductive and resonance mechanisms. Transition from weakly basic solvents (acetone and dimethyl sulfoxide) to weakly acid solvents (methanol and water) leads to a decrease in the electron-donor inductive effect of the grouping.

In conclusion, we should note that the anionic complexes of Pt(IV) are also formed in the reaction between aromatic compounds and H_2PtCl_6 in acetic or formic acids. The characteristic features of the reactions in these acids are now being studied.

EXPERIMENTAL

The PMR spectra were obtained on the "Bruker HXP-4-100" apparatus with a working frequency of 90 MHz. The electronic spectra were run on the "Spekord UV-Vis" apparatus, and the IR spectra on the "UR-20" apparatus in KBr tablets. In the kinetic measurements, the reactions were carried out in open vessels with a reflux condenser, placed in a thermostat. After given periods of time, samples of the reaction solution (0.5 to 2.0 ml) were withdrawn, the solvent was evaporated in vacuo, and the residue was chromatographed on a column with silica gel. The amount of the complex formed was determined spectrophotometrically.

General Procedure for Preparation of Anionic σ -Aryl Complexes of Pt(VI). A solution of $H_2PtCl_6 \cdot 6H_2O$ and the aromatic compound taken in excess was heated in a $CF_3COOH-H_2O$ mixture (5:1 by volume) to boiling. The time of the reaction depends on the nature of the aromatic

compound and the relative concentration of the reagents, and should correspond to the maximum yield of the product on the kinetic curve. The solvent was evaporated in vacuo, and the residue was dissolved in acetone and deposited on a silica gel column treated with hexane. The hexane elutes the initial aromatic compound treated with hexane. The hexane elutes the initial aromatic compound, and then an acetone-hexane mixture (2:1) elutes a yellow or orange band of the complex. After evaporation of the solvent, the residue was purified by TLC on silica gel and recrystallized from acetone.

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CONCLUSIONS

1. The reaction between hexachloroplatinic acid and aromatic compounds in aqueous trifluoroacetic acid leads to the formation of σ -aryl complexes of Pt(IV).

2. The aromatic compounds can be arranged in a series, characteristic of electrophilic substitution.

3. Substitution in the ortho position in the phenyl ring does not take place because of steric hindrances.

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