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THE REACTION OF H_2PtCl_6 WITH AROMATIC COMPOUNDS IN CF_3COOH/H_2O AFFORDING THE ANIONIC σ-ARYL COMPLEXES OF PLATINUM(IV)

IV *. THE SYNTHESIS OF PLATINUM(IV) COMPLEXES OF FLUORINATED BENZENES AND THE ELECTRONIC INFLUENCE OF THE PLATINUM MOIETY

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Summary

The reaction of H_2PtCl_6 with fluorobenzene, *o*-chlorofluorobenzene and *m*-chlorofluorobenzene in CF_3COOH/H_2O affords anionic σ-aryl complexes of platinum(IV). The first two compounds give rise to mixtures of two isomers (*meta* and *para*), the latter forms only one isomer (1,3,5-substituted). The ^{19}F NMR spectrum shows that $[PtCl_4NH_3]^-$ group, when bound to fluorobenzene, is an electron donor in both the inductive and resonance senses.

Introduction

Recently a new route to σ-aryl derivatives of platinum(IV) was described. Refluxing of a mixture of H_2PtCl_6 and naphthalene [1], benzene, alkylbenzene, anisole, chlorobenzene [2], nitrobenzene, benzoic acid, acetophenone or diphenyl [3] in aqueous trifluoroacetic acid followed by chromatography on silica gel containing ammonia affords an ionic σ-aryl complex $[ArPtCl_4NH_3]$-NH_4. Kinetic studies of the reaction have been carried out in [4—6]. The complexes may be also prepared from arylmercury compounds and H_2PtCl_6 [7]. These σ-aryl complexes of platinum(IV) are intermediates in the dimerization and chlorination of aromatic compounds by H_2PtCl_6.

It was of interest to estimate the electronic influence of the platinum(IV) moiety. In order to calculate the σ_I and σ_R^0 constants of the platinum(IV)

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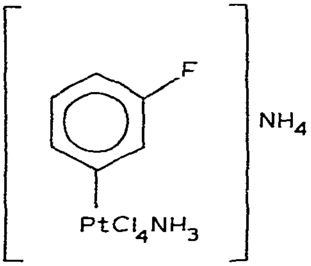
* For part III see reference 3.

group, the σ-complex of fluorobenzene was prepared and ^{19}F NMR spectra of this compound in various solvents were recorded.

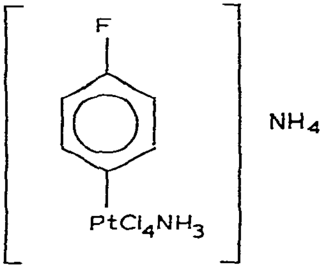
Results and discussion

The platinum(IV) complex of fluorobenzene (I) was prepared by the method described earlier [1—3]. As expected [2,3] a mixture of two isomers (*meta*- and *para*-platinated compounds IA and IB, respectively) is formed. *o*-Chlorofluorobenzene was also used as an aromatic compound for this reaction and a mixture of two isomers, IIA and IIB, of the corresponding complex was isolated. The reaction of *m*-chlorofluorobenzene with H_2PtCl_6 afforded only one isomer III.

$$RH + H_2PtCl_6 \xrightarrow[2.\ SiO_2 \cdot NH_3]{1.\ CF_3COOHH_2O} [RPtCl_4NH_3]\,NH_4$$



(IA)



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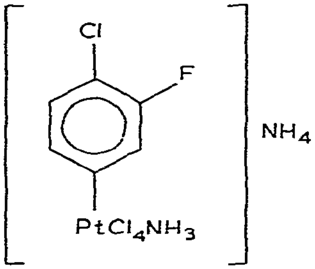
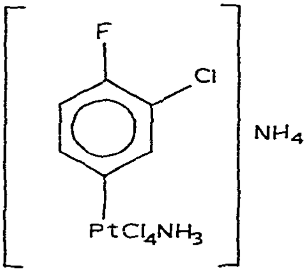
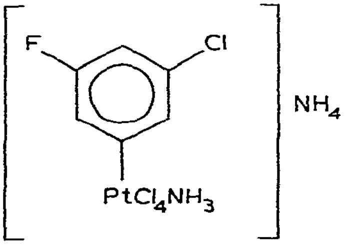


(IIA)



(IIB)



(III)

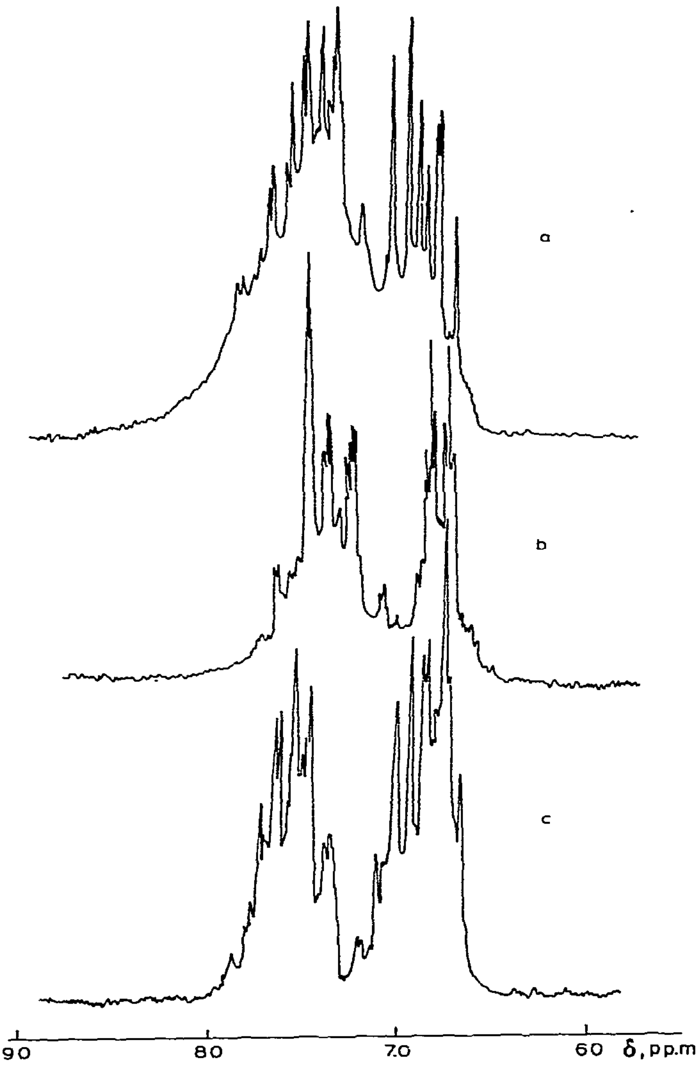


Fig. 1. ^{1}H NMR spectra (in acetone-d_6) of complexes I (a), II (c) and III (b).

In the ^{1}H NMR spectra of all the complexes the aromatic protons appear as complicated multiplets (Fig. 1). In the ^{19}F NMR spectra of complexes I and II (Fig. 2 and 3) there are two multiplets (of approximately equal intensity) which indicate the formation of two isomers. Only one multiplet was found in the ^{19}F NMR spectrum of compound III (Fig. 4). The chemical shifts of the ^{19}F signals are listed in Table 1.

The ^{19}F NMR data of fluorobenzene complex I were used to calculate σ_I and σ_R^0. The resonance σ_R^0 and inductive σ_I constants were calculated from the Taft equations [8,9]:

$$\delta_m^F = -7.1\,\sigma_I + 0.6$$

$$\delta_p^F = -29.5\,\sigma_R^0 + \delta_m^F$$

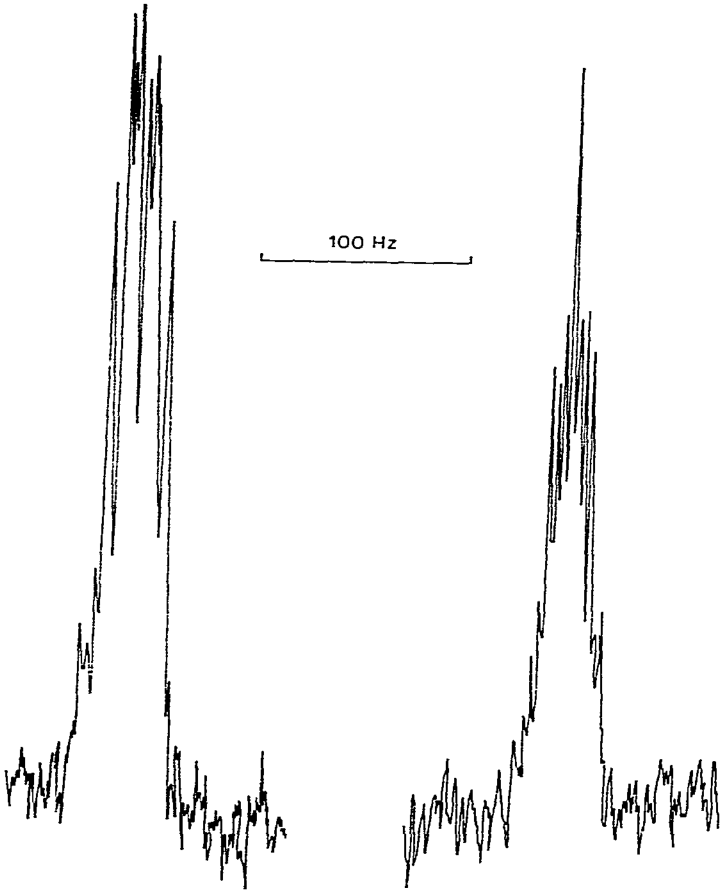


Fig. 2. ^{19}F NMR spectrum of complex I.

As follows from the data in Table 1, introducing the $[PtCl_4NH_3]^-$ fragment into the phenyl ring of fluorobenzene gives rise to a shift of the signals of the *p* and *m* isomers to high field. The shifts of the *p*-fluorine in the cases of all solvents are larger for all solvents than those of the *m* isomer. The values calculated for acetone solution of σ_I (—0.46) and σ_R^0 (—0.19) indicate that the fragment $[PtCl_4NH_3]^-$ exhibits a rather strong electron-donating influence. The inductive effect of this moiety is greater than the influence of the $—B(OH)_3^-$ group (σ_I = —0.36). The resonance effect of the platinum(IV) fragment may be compared to the donating ability of $—OCOCH_3$ (σ_R^0 = —0.20), $—CH_3$ (—0.15) and —Cl (—0.18) groups. In Table 1 ^{19}F NMR data and σ parameters for various platinum(II) derivatives are also given. The fluorobenzene complex of platinum(II) containing PEt_3 and CH_3 groups as ligands reveals the strongest donating influence in both the inductive and resonance senses. In contrast, the fragment containing platinum(IV) and PEt_3 ligands is a very weak inductive donor (σ_I = —0.01). However, the resonance constants σ_R^0 for neutral and anionic derivatives of platinum(IV) are equal.

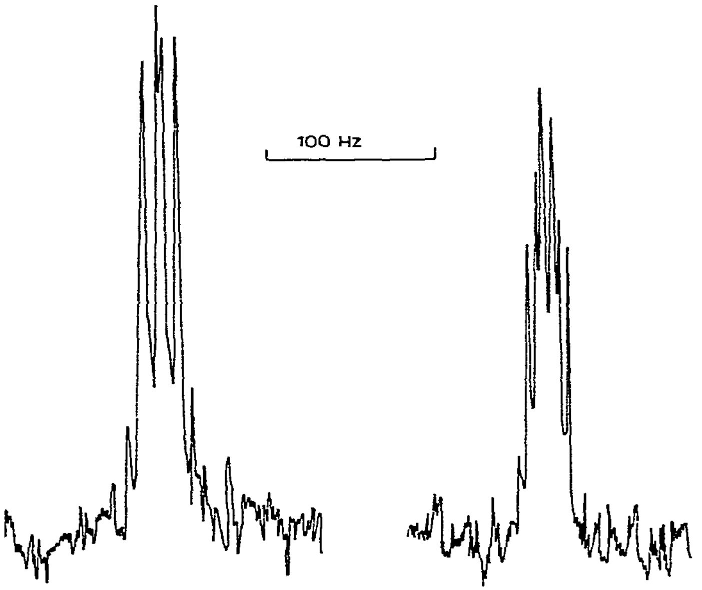


Fig. 3. ^{19}F NMR spectrum of complex II.

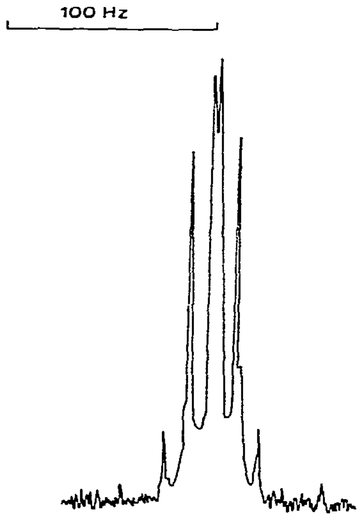


Fig. 4. ^{19}F NMR spectrum of complex III.

The ^{19}F shielding parameters for complex I are greatly affected by the nature of the solvent. On passing from acetone or dimethylsulfoxide as solvent to more acidic methanol and water, chemical shifts of signals in the spectrum of complex I decrease. For water as solvent the value of σ_I is rather small. This effect may be due to coordination of solvent molecules with the platinum(IV) fragment, possibly by a weak hydrogen bond MeOH...ClPt. Hence, donor properties of the fragment $[-PtCl_4NH_3]^-$ are not very strong pronounced in acidic solvents.

The ^{19}F NMR spectrum (in acetone-d_6) of the fluorobenzene complex was also recorded before chromatography on silica gel. There are several signals

TABLE 1

^{19}F NMR CHEMICAL SHIFTS (ppm RELATIVE TO FLUOROBENZENE) AND σ CONSTANTS OF SOME PLATINUM COMPLEXES

Compounds	Solvent	δ F_m	δ F_p	σ_I	σ_R^0	Reference
$[FC_6H_4PtCl_4NH_3]NH_4$ (I)	$(CD_3)_2CO$	3.87	9.44	–0.46	–0.19	[a]
	$(CD_3)_2SO$	3.80	9.10	–0.45	–0.18	[a]
	CH_3OD	1.80	7.90	–0.17	–0.21	[a]
	D_2O	1.14	6.32	–0.08	–0.18	[a]
$FC_6H_4PtCl_3(PEt_3)_2$	$(CH_3)_2CO$	0.64	6.06	–0.01	–0.18	10
$FC_6H_4Pt(PEt_3)_2Cl$	$(CH_3)_2CO$	2.11	10.1	–0.21	–0.27	11, 12
$FC_6H_4Pt(PEt_3)_2CH_3$	$(CH_3)_2CO$	3.93	11.70	–0.47	–0.26	11
$[o\text{-}F,ClC_6H_3PtCl_4NH_3]NH_4$ (II)	$(CD_3)_2CO$	7.35	11.9	—	—	[a]
$[m\text{-}F,ClC_6H_3PtCl_4NH_3]NH_4$ (III)	$(CD_3)_2CO$	2.54	—	—	—	[a]

[a] This work.

shifted to high field relative to fluorobenzene in this spectrum, suggesting that platinum(IV) not stabilized with NH_3 (apparently $[-PtCl_4H_2O]^-$) also exhibit donor properties.

Experimental

Hexachloroplatinic acid was purchased commercially and dissolved in distilled water as a stock solution. All procedures were carried out in air. ^1H and ^{19}F NMR spectrum were recorded on a Bruker SXP-4-100 spectrometer. IR spectra were recorded on an UR-20 spectrometer as KBr pellets.

Platinum(IV) complex of fluorobenzene (I)

A solution of 2.0 g of $H_2PtCl_6 \cdot 6\ H_2O$ and 6.0 ml of fluorobenzene in 20 ml of CF_3COOH and 6 ml of H_2O was refluxed for 2 h. The solvent was evaporated in vacuo and the residue was chromatographed on a silica gel column and then on plates of silica gel (eluent hexane/acetone 1/2). The complex I was prepared as yellow crystals (0.6 g, 35% yield). Analysis. Found: C, 15.3; H, 2.4; N, 6.0. Calcd for $[FC_6H_4PtCl_4NH_3]NH_4$: C, 15.3; H, 2.4; N, 6.0%. IR spectrum (cm^{-1}): 450m, 515m, 675m, 767m, 810w, 820m, 845s, 900w, 1000w, 1012m, 1053m, 1090w, 1160s, 1208s, 1275s, 1405s, 1435s, 1470s, 1480s, 1577s, 1590s, 1610m, 1690m, 2600—3650.

Platinum(IV) complex of o-chlorofluorobenzene (II)

Complex II (yellow crystals, 0.4 g, 35% yield) was prepared analogously from 1.0 g of H_2PtCl_6 and 2 ml of *o*-chlorofluorobenzene in 10 ml of CF_3-COOH and 2 ml of H_2O. The mixture was refluxed for 2 h. Analysis. Found: C, 21.1; H, 3.6; N, 4.5. Calcd for $[F(Cl)C_6H_3PtCl_4NH_3]NH_4 \cdot 1.5\ (CH_3)_2CO$: C, 21.4; H, 3.2; N, 4.8%. IR spectrum (cm^{-1}): 443m, 453m, 523w, 546w, 571m, 596w, 613m, 705m, 712m, 826s, 875s, 1060m, 1088s, 1150m, 1165m, 1227s, 1246s, 1270s, 1294s, 1393s, 1414s, 1490s, 1578m, 1595m, 1620m, 1695m, 1715m, 2700—3680.

Platinum(IV) complex of m-chlorofluorobenzene (III)

Complex III was obtained analogously from 1.0 g of $H_2PtCl_6 \cdot 6\ H_2O$ and 2 ml of *m*-chlorofluorobenzene in 15 ml of CF_3COOH and 3 ml of H_2O. Yield of complex III (yellow crystals) was 0.3 g (28%). Analysis. Found: C, 19.4; H, 2.9. Calcd. for $[F(Cl)C_6H_3PtCl_4NH_3]NH_4 \cdot (CH_3)_2CO$: C, 19.3; H, 2.8%. IR spectrum (cm^{-1}): 422m, 537m, 545m, 681m, 776s, 865s, 872s, 912s, 1005w, 1040w, 1051w, 1080m, 1095m, 1108m, 1130w, 1190m, 1225s, 1242s, 1280s, 1372s, 1410s, 1428s, 1443s, 1578s, 1692s, 2600—3880.

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