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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)

III *. THE SYNTHESIS OF PLATINUM(IV) COMPLEXES OF BENZENES CONTAINING ELECTRON-WITHDRAWING SUBSTITUENTS

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Summary

The reaction of H_2PtCl_6 with nitrobenzene, *o*-nitrotoluene, benzoic acid, acetophenone and diphenyl in a CF_3COOH/H_2O mixture affords the anionic σ-aryl complexes of Pt^{IV}. In the case of monosubstituted benzenes, mixtures of *meta*- and *para*-platinated isomers were prepared. *o*-Nitrotoluene also gave rise to two isomers. Electron-withdrawing substituents decrease the rate of introducing the platinum moiety into benzene ring.

Introduction

The metallation reactions of aromatic hydrocarbons with non-transition metal compounds, affording σ-aryl derivatives of these metals, are well known. Only a few examples of the preparation of σ-aryl metallated complexes directly from aromatic hydrocarbon and transition metal compounds have been described. These methods are the Kharasch auration of aromatics [1,2], photo-induced insertion of tungsten into a C—H bond [3], oxidative addition of ruthenium [4] and iron [5] to arenes. The formation of σ-bonded complex was proposed in reactions of aromatics with palladium salts (oxidative coupling [6], the Fujiwara reaction [7], carboxylation of aromatic hydrocarbons with carbon monoxide [8]) but this complex was not isolated.

Recently, we have found that heating a solution of an aromatic compound and hexachloroplatinic acid in a CF_3COOH/H_2O mixture gives rise to the for-

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[*] For part II see reference 10.

mation of a stable anionic σ-aryl complex of platinum(IV) which may be isolated after chromatography on silica gel containing ammonia as $[RPtCl_4NH_3]NH_4$. The following aromatic compounds, RH, were used: naphthalene [9], benzene, toluene, ethylbenzene, *ortho*- and *meta*-xylenes, anisole, chlorobenzene and *meta*-chlorotoluene [10]. Monosubstituted benzenes gave rise to mixtures of *meta*- and *para*-platinated isomers. The reaction of H_2PtCl_6 with *para*-disubstituted benzenes (xylene, dimethoxybenzene, dichlorobenzene), mesitylene and pentamethylbenzene did not afford any σ-aryl complexes. We have also shown that the same complexes may be isolated from the reaction of H_2PtCl_6 with various arylmercury compounds in CF_3COOH/H_2O or acetone [11]. X-ray analysis demonstrated that in the σ-naphthyl complex the platinum atom was octahedrally coordinated, with four chlorine atoms occupying the equatorial positions and a σ-aryl naphthalene and a neutral ammonia ligand occupying the axial positions [9,10].

The σ-aryl platinum(IV) complexes are intermediates in the chlorination and dimerization of aromatic compounds by H_2PtCl_6, and if the reflux time for the reaction of aromatic compounds containing electron-releasing substituents is extended, chlorobenzene and diphenyl derivatives may be obtained.

The progress of the reaction with time [12], the *para—meta* isomerisation of the σ-tolyl complex of platinum(IV) [13] and the relative rates of complex formation for various aromatics [14] have been studied. The electronic influence of the platinum(IV) moiety has also been estimated using ^{19}F NMR spectroscopy [15].

A platinum(II) salt, when added to the reaction mixture, accelerates the rate of formation of the platinum(IV) complex. This fact may be explained by the intermediate formation of a platinum(II) σ-aryl complex; the platinum(II) salt being more reactive in this interaction. Recently we have detected the formation of σ-aryl complexes of platinum(II) in the reaction of Na_2PtCl_4 with benzene or toluene [16] in CF_3COOH/H_2O.

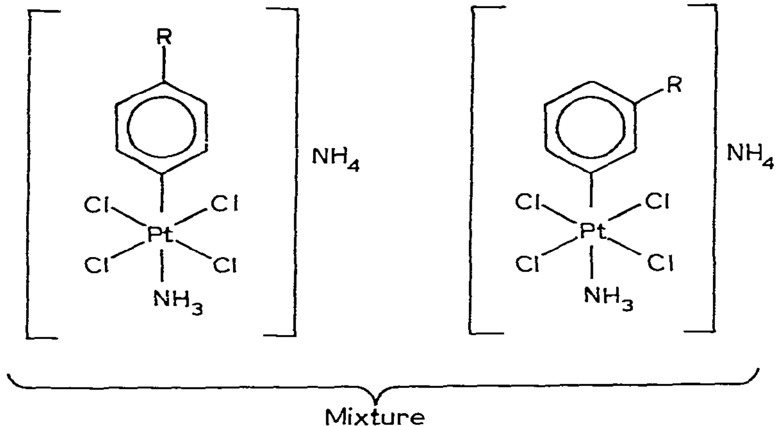
In the present paper we expand the set of aromatic ligands for which this reaction occurs, and we report the synthesis of platinum(IV) complexes of benzenes bearing electron-withdrawing substituents.

Results and discussion

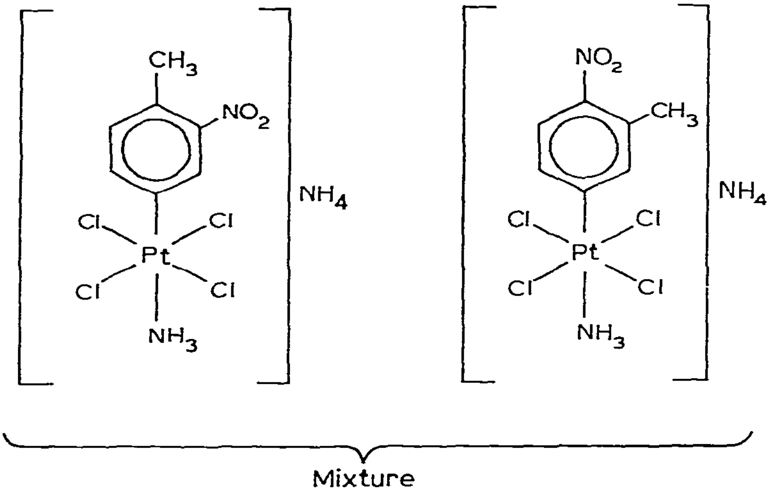
In the reaction of H_2PtCl_6 with aromatic compounds we used nitrobenzene, *ortho*-nitrotoluene, benzoic acid, acetophenone and diphenyl. The mixture of H_2PtCl_6 and aromatic compound in aqueous trifluoroacetic acid was refluxed for several hours, the solvent was evaporated under reduced pressure from the yellow or orange-red solution and the residue was chromatographed on a silica gel column. Hexane eluted unreacted aromatic compound and then acetone/hexane eluted a yellow or orange band of crude product. The complex was purified by TLC on silica gel (eluent acetone/hexane, 2/1) and following crystallization from acetone or acetone/hexane. Complexes I—V were prepared by this method.

It should be noted that the reactions of benzenes bearing electron-withdrawing substituents, in contrast to the reactions of toluene, anisole and xylenes, require prolonged refluxing (several hours). In the case of nitrobenzene, reflux-

$$ArH + H_2PtCl_6 \xrightarrow[2.\ SiO_2 \cdot NH_3]{1.\ CF_3COOH/H_2O} \left| ArPtCl_4NH_3 \right| NH_4$$



(I , R = NO_2 ;
III, R = COOH ;
IV , R = $COCH_3$;
V , R = C_6H_5)

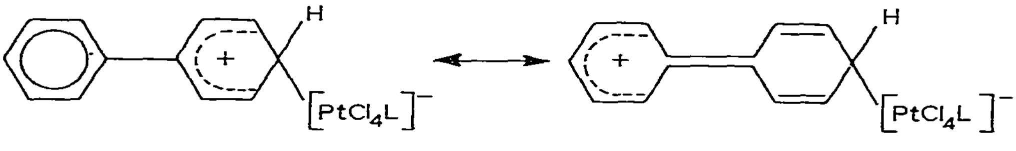


(II)

ing the mixture for 3 hours does not give rise to tar formation and the σ-aryl complex may be isolated with high yield (84%). The complexes of benzenes bearing electron-releasing groups decompose completely when refluxed for 1—2 hours. When a mixture of H_2PtCl_6 and *m*-dinitrobenzene is refluxed for 1.5 h, a sufficient amount of σ-aryl complex cannot be isolated.

Methylbenzoate in the reaction with H_2PtCl_6 in CF_3COOH/H_2O affords the platinum(IV) complex of benzoic acid.

When a mixture of H_2PtCl_6 and diphenyl in aqueous trifluoroacetic acid is refluxed for several minutes, the solution becomes blue-green. The concentration of the blue-green complex is constant during heating for 1—2 h but is decreased if NaOAc is added. This complex may be extracted from the solution with chloroform. Evaporation of the chloroform solution gives a small amount of a dark complex, which decomposes in alcohol solution during ca. 1 h (added NaOH accelerates decomposition). There is an absorption band in the visible spectrum of the complex at ν(max) 16 800 cm^{-1} (in chloroform). One of possible structures of the blue-green compound is a σ-complex of the Wheland type, the positive charge being delocalized on the two phenyl rings (VA and VB).



(VA) (VB)

However, alternative structures may be proposed for this compound. A similar green complex is formed in the reaction of H_2PtCl_6 with naphthalene.

The ^{1}H NMR spectra of complexes I—V suggest σ-bonding of the aromatic moiety with the platinum atom. The aromatic protons appear as complex multiplets in the region δ 7—8 ppm (Fig. 1). In the spectra of complexes I—IV there are triplet signals having two ^{195}Pt satellites at low field. At higher field there is a triplet signal for complex I, a doublet for II and quartets for III and IV. The relative ratio of the signals in the high and low parts of the aromatic region is not constant for products of different runs of the same reaction and these signals appear to belong to different isomers. The spectra of the methyl protons of compounds II and IV are in agreement with the presence of a mixture of *meta* and *para* isomers (two singlets are observed in each spectrum).

In the IR spectra of the complexes prepared there are strong absorption bands in the 2800—3600 cm^{-1} region which may be due to N—H vibrations. The strong bands at 1345 and 1515 cm^{-1} in the IR spectrum of complex I appear to be due to NO_2 vibrations. The corresponding bands in the spectrum of complex II are at 1358 and 1530 cm^{-1}. The strong absorptions at 1725 and 1675 cm^{-1} in the spectra of complexes III and IV, respectively, are due to C=O vibrations. Acetone in the crystals of the complexes appears as absorptions in the 1700—1720 cm^{-1} region.

We have recorded the UV-visible spectra of various platinum(IV) complexes prepared in this and previous works (Fig. 2). In all cases there is one intense absorption band in the UV region. It should be noted that the frequency of this band decreases on going from complexes bearing electron-releasing substituents (36 600 cm^{-1} of the anisole complex, 36 400 cm^{-1} for the toluene and ethylbenzene complexes) to the nitrobenzene complex (35 400 cm^{-1}). The benzene complex absorbs at 36 250 cm^{-1}. The intense band at 38 300 cm^{-1} in the spectrum of the diphenyl complex appears to be due to superimposed absorptions of the unsubstituted phenyl ring. Chlorobenzene and fluorobenzene complexes absorb at 36 300 and 36 650 cm^{-1}, respectively. In the spectra of all the com-

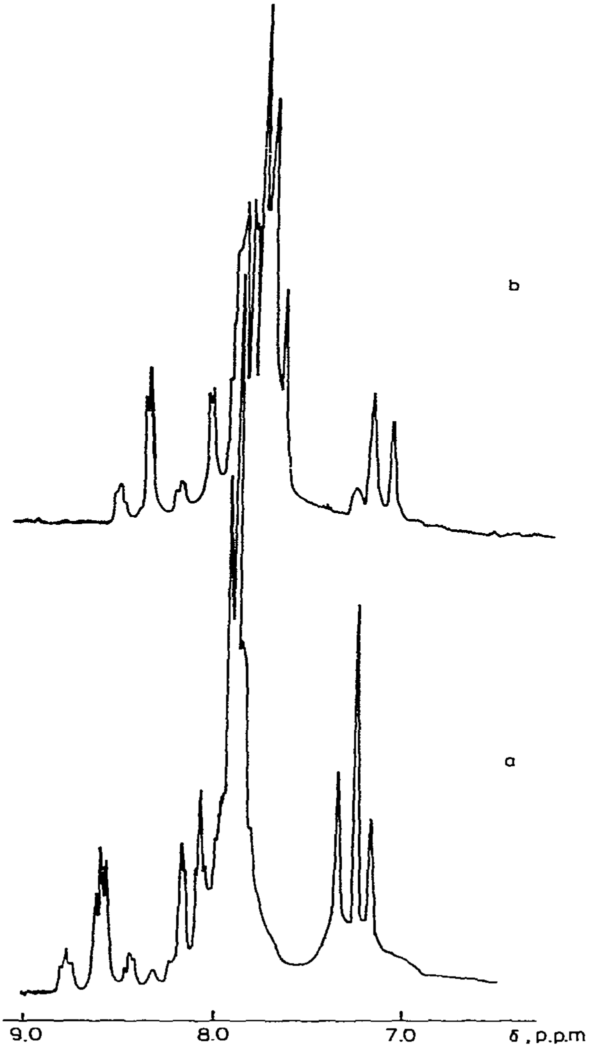


Fig. 1. ^{1}H NMR spectra of nitrobenzene (I, a) and o-nitrotoluene (II, b) complexes of platinum(IV).

plexes there is a second band in the visible region at approximately 21 000 cm^{-1}. The intensity of this band decreases on going from the anisole complex to the benzene and especially the nitrobenzene complexes. In accordance with the spectra, the solution of the anisole complex is orange-brown and the solution of the nitrobenzene complex is pale yellow.

The complexes prepared are soluble in alcohol, acetone, water, sparingly soluble in chloroform and insoluble in benzene, ether and hexane. We have found that when treated with cesium chloride an aqueous solution of an anionic platinum(IV) complex deposits a yellow precipitate of the cesium salt.

$$[RPtCl_4NH_3]NH_4 \begin{cases} \xrightarrow{CsCl} [RPtCl_4NH_3]Cs \\ \xrightarrow{NaBH_4} RH + Pt + NH_3 \end{cases}$$

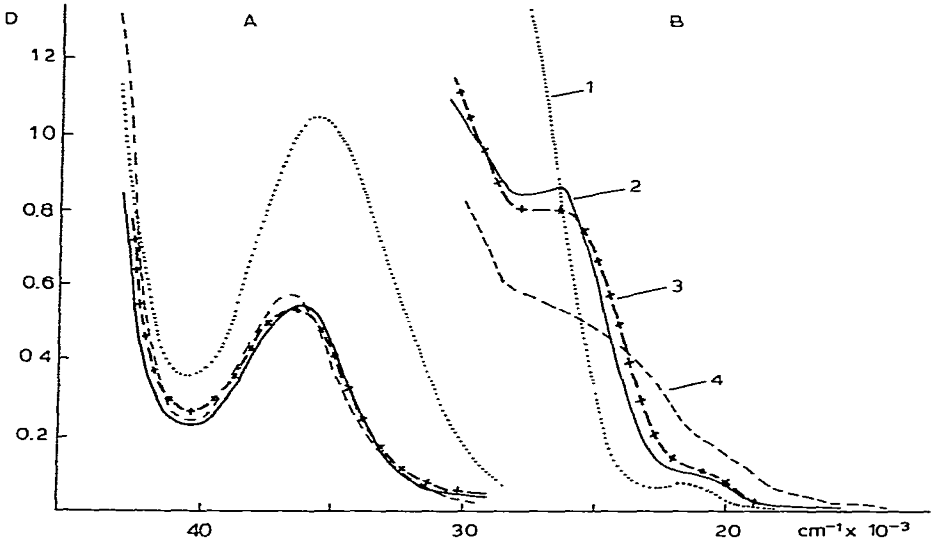


Fig. 2. UV (A) and visible (B) spectra of nitrobenzene (1), benzene (2), ethylbenzene (3) and anisole (4) complexes of platinum(IV) (in ethanol, 10^{-4} *M* for A and 2×10^{-3} *M* for B).

Under the action of sodium borohydride in water, the platinum(IV) complex decomposes with precipitation of platinum black and evolution of hydrocarbon and ammonia.

The crystal and molecular structures of the *o*-nitrotoluene complex (II) will be published elsewhere.

Experimental

Hexachloroplatinic acid was purchased commercially and dissolved in distilled water as a stock solution. All procedures were carried out in air. Proton NMR spectra were recorded on a Bruker SXP-4-100 spectrometer at 90 MHz (δ in ppm relative TMS). Infrared spectra were recorded on an UR-20 instrument as KBr pellets. UV-visible spectra were recorded on a Specord UV-VIS instrument.

Platinum(IV) complex of nitrobenzene (I)

A solution of 1.0 g of $H_2PtCl_6 \cdot 6\ H_2O$ and 2.0 ml of nitrobenzene in 15 ml of CF_3COOH and 3 ml of H_2O was refluxed for 3 h. The solvent was removed in vacuo from orange-red solution. The residue was chromatographed as an acetone solution on a silica gel column made up in hexane. Hexane eluted nitrobenzene and then a solution of acetone/hexane (2/1) eluted a yellow band which when dried became a yellow oil. The complex was purified by TLC on silica gel plates (eluent acetone/hexane, 2/1) yielding 0.8 g (84% yield) of I as yellow crystals. The complex may be recrystallized from a mixture acetone/hexane (2/1). Analysis. Found: C, 14.9; H, 2.6; N, 8.4. Calculated for $[NO_2C_6H_4PtCl_4\text{-}NH_3]NH_4$: C, 14.6; H, 2,2; N, 8.5%. ^1H NMR spectrum (in acetone-d_6): 7.27 t, 7.80—8.30 m, 8.63 t (t = triplet, m = multiplet). Protons NH: 3.85. IR spectrum: 480m, 675w, 720s, 738m, 804m, 840m, 854m, 862m, 883w, 995w, 1012w, 1058m, 1105m, 1232s, 1275m, 1345s, 1415m, 1515s, 1570w, 1625s, 2800—3650 cm^{-1} (w = weak, m = medium, s = strong).

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

A solution of 1.0 g of $H_2PtCl_6 \cdot 6\ H_2O$ and 2.0 ml of *o*-nitrotoluene in 15 ml CF_3COOH and 3 ml of H_2O was refluxed for 2.5 h. The red-brown solution was worked-up as in the case of the nitrobenzene complex. The orange-yellow complex II (0.45 g, 41% yield) was recrystallized from acetone. Analysis. Found: C, 21.3; H, 3.3; N, 8.2%. Calculated for $[NO_2(CH_3)C_6H_3PtCl_4NH_3]NH_4 \cdot (CH_3)_2CO$: C, 21.2; H, 3.3; N, 7.4%. ^1H NMR spectrum (in acetone-d_6): 7.08 d, 7.55—8.10 m, 8.32 d, 2.54 s, 2.56 s (s = singlet, d = doublet). Protons NH: 3.78. IR spectrum: 543m, 710m, 767s, 810w, 838s, 888s, 1040w, 1055w, 1085w, 1110m, 1080m, 1214s, 1246s, 1285s, 1316m, 1358s, 1420s, 1458s, 1488m, 1530s, 1575s, 1610s, 1720s, 2700—3680 cm^{-1}.

Platinum(IV) complex of benzoic acid (III)

Complex III was prepared analogously from 2.0 g of $H_2PtCl_6 \cdot 6\ H_2O$, 1.0 g of benzoic acid in 20 ml of CF_3COOH and 4 ml of H_2O. The mixture was refluxed for 2 h. Complex III (0.6 g, 30% yield) forms orange-yelow crystals: Analysis. Found: C, 20.9; H, 3.1; N, 4.0. Calculated for $[(COOH)C_6H_4PtCl_4NH_3]NH_4 \cdot (CH_3)_2CO$: C, 21.8; H, 3.3; N, 5.0%. ^1H NMR spectrum (in D_2O): 7.22 q, 7.40—8.07 m, 8.20 t, 2.02 s (acetone) (q = quartet). IR spectrum: 498m, 545m, 650w, 695m, 770s, 805w, 828w, 865m, 925w, 1010w, 1025m, 1065w, 1077m, 1110m, 1135m, 1195m, 1215m, 1260s, 1270s, 1300s, 1315m, 1425s, 1485m, 1580m, 1598s, 1630s, 1710s, 1725s, 2300—3690 cm^{-1}.

Platinum(IV) complex of acetophenone (IV)

Complex IV (yellow crystals, 0.6 g, 30% yield) was prepared analogously from 2.0 g of $H_2PtCl_6 \cdot 6\ H_2O$, 2 ml of acetophenone in 20 ml of CF_3COOH and 4 ml of H_2O. The mixture was refluxed for 45 min. Analysis. Found: C, 22.0; H, 3.3; N, 4.8. Calculated for $[CH_3COC_6H_4PtCl_4NH_3]NH_4 \cdot (CH_3)_2CO$: C, 21.6; H, 3.3; N, 5.4%. ^1H NMR spectrum (in D_2O): 6.26 q, 7.53—8.20 m, 2.61 s, 2.62 s (CH_3), 2.20 s (acetone). IR spectrum: 475m, 500w, 605s, 660m, 700s, 750w, 775w, 803s, 835m, 905m, 980m, 997m, 1005m, 1021m, 1065m, 1076s, 1095m, 1130w, 1155w, 1205s, 1273s, 1290s, 1380s, 1425s, 1470w, 1570s, 1590s, 1675s, 1710m, 2200—2530, 2700—3650 cm^{-1}.

Platinum(IV) complex of diphenyl (V)

Complex V (orange crystals, 0.5 g, 42% yield) was prepared from 1.0 g of $H_2PtCl_6 \cdot 6\ H_2O$, 1.0 g of diphenyl in 15 ml of CF_3COOH and 2 ml of H_2O. The mixture was refluxed for 2 h. Analysis. Found: C, 32.3; H, 3.9%. Calculated for $[C_6H_5C_6H_4PtCl_4NH_3]NH_4 \cdot 1.5\ (CH_3)_2CO$: C, 32.4; H, 4.1%. ^1H NMR spectrum (in D_2O): 7.10—7.90 m, 2.13 s (acetone). IR spectrum: 480w, 504m, 515w, 558m, 715s, 734w, 765m, 780s, 837m, 929m, 941m, 1019s, 1030m, 1055w, 1085m, 1105m, 1255m, 1288s, 1385s, 1428s, 1490s, 1570w, 1597m, 1612m, 1704s, 1712m, 2680m, 2790m, 2500—3670 cm^{-1}.

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