

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, ALKYL BENZENES AND CHLORINATED BENZENES **

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Summary

The reaction of H_2PtCl_6 with benzene, toluene, ethylbenzene, xylenes, anisole and chlorobenzene affords the new anionic σ -aryl complexes of Pt^{IV} . In the cases of monosubstituted benzenes mixtures of *meta*- and *para*-platinated isomers were prepared. No examples of the *ortho*-isomer were found. These complexes are intermediates in the chlorination and dimerization of aromatic compounds by H_2PtCl_6 .

Introduction

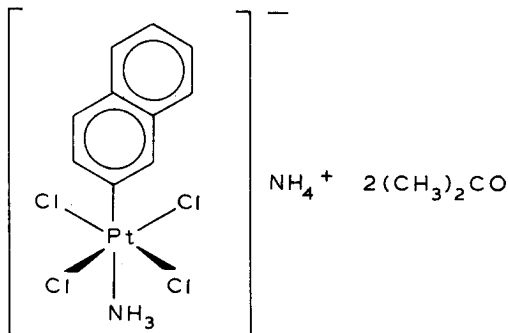
Although σ -methyl complexes of platinum(IV) were the first σ -derivatives of a transition metal, only a few σ -aryl complexes of platinum(IV) are known [2—5].

Recently, we have reported the first example of a σ -aryl complex of Pt^{IV} which does not contain two phosphine or amine ligands [1]. A solution of naphthalene and H_2PtCl_6 in $CF_3COOH-H_2O$ was refluxed for 10 min, after which the ionic complex was isolated by chromatography on silica gel, which contained ammonia (see below). The molecular structure, determined by X-ray analysis, showed that the platinum atom was octahedrally coordinated with four chlorine atoms occupying the equatorial positions and a σ -bonded naphthal-

* For part I see ref. 1.

** Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

ene and a neutral ammonia (see below) ligands occupying the axial positions [1]:



This result was important not only for synthetic organometallic chemistry but also for the elucidation of the mechanism of chlorination and dimerization of aromatic compounds by chloroplatinic acid. The formation of σ -aryl and σ -alkyl intermediates had been proposed earlier for the oxidation reaction of hydrocarbons with Pt^{IV} compounds [6–9].

In the present paper we show the generality of the reaction by reporting the synthesis of the Pt^{IV} complexes of benzene and its derivatives.

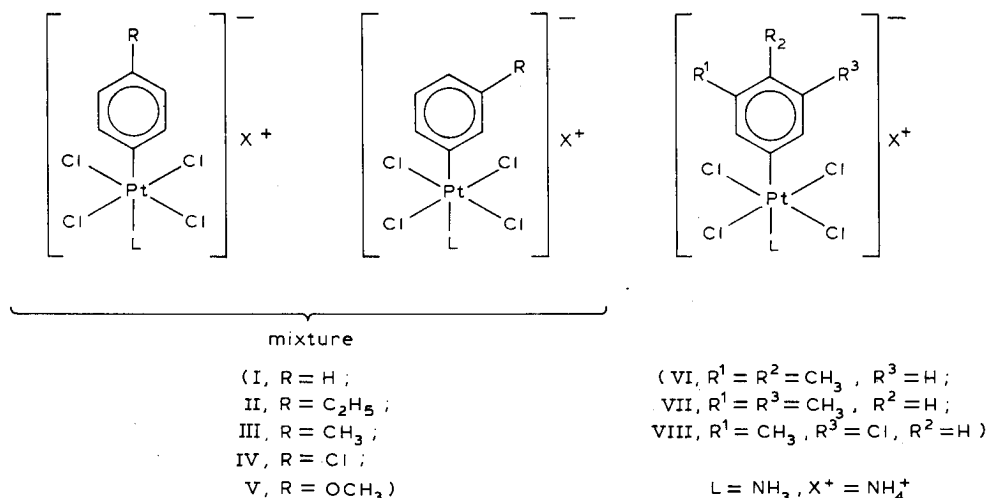
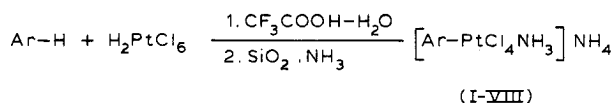
Results and discussion

When a mixture of H_2PtCl_6 and an aromatic compound in aqueous trifluoroacetic acid is refluxed, a σ -bonded aromatic complex of Pt^{IV} is formed. The reaction time varies from a few minutes for alkylated benzene and anisole to several hours for chlorobenzene. If the reaction time is extended, decomposition occurs as evidenced by the dark brown color of the solution and tar formation.

The complexes are isolated from the reaction mixture by column chromatography on silica gel and purified by thin layer chromatography on silica gel. Crystallization from acetone produces yellow or yellow-orange crystalline complexes (I–VIII). The yields range from 10 to 60%. These complexes are air stable, soluble in acetone, alcohol or water and insoluble in chloroform, ether, benzene or hexane. Water may replace trifluoroacetic acid as the solvent in the reaction, however, the product yield is greatly reduced.

The structure of the complexes may be proposed on the basis of spectral data, analytical results and the molecular structure of the analogous naphthalene complex [1]. The ^1H NMR spectra of the complexes are in agreement with the σ -bonding of the aromatic moiety with platinum atom. Thus, in the ^1H NMR spectrum of the benzene complex I the aromatic protons appear as two multiplets in the region δ 7–8 ppm. The spectra of the trisubstituted benzene complexes VII and VIII are rather simple with only a singlet having two ^{195}Pt satellites for the two ring protons and other singlet for the *para*-proton. The aromatic protons of compounds II–V appear as complex multiplets which indicates the presence of *meta*- and *para*-isomers. In the aliphatic region, the relative intensity of the CH_3 and CH_2 resonances for complexes III and II, respectively, indicate that the *meta/para* ratio is approximately 1 : 1. A singlet is ob-

served for the methyl groups in II and V since these groups are not sensitive to



the different shielding influence of the platinum moiety in the *meta* and *para*-isomers. It should be noted that the *meta/para* ratio varied in different runs of the same reaction. Thus, various peaks in the complex aromatic multiplet of V had different intensities for two samples prepared independently. Unfortunately, the isomers could not be separated by TLC.

It is interesting to note that no *ortho*-isomers were observed. Apparently a pronounced *ortho* steric deactivation effect is present in these reactions. We were unable to isolate any σ -aryl complexes from the reaction of H₂PtCl₆ with *para*-xylene, mesitylene, pentamethylbenzene, *para*-dimethoxybenzene and *para*-dichlorobenzene. As we showed earlier, Pt replaced only the β -hydrogen atom of naphthalene [1]. This fact is in good agreement with the experiments of Garnett on chlorination and H-D exchange of aromatics in the presence of H₂PtCl₆ [10]. Recently, the strong *ortho* steric deactivation effect was observed in the oxidative addition reaction of aromatic compounds with complexes of Fe⁰ [11].

Elemental analysis showed that all the complexes prepared contained two atoms of nitrogen per one aromatic moiety and one platinum atom. These two atoms of nitrogen belong to the two molecules of ammonia present in the complex. One ammonia appears to be the neutral ligand L = NH₃ and the other is the cation, X⁺ = NH₄⁺. IR and NMR spectra are consistent with this interpretation. A strong absorption band is observed in the 2800–3650 cm⁻¹ region in the IR spectra of all the complexes, which is the result of the N-H vibrations. In the ¹H NMR spectra, the N-H protons appear as broad signals at δ 3–5 ppm.

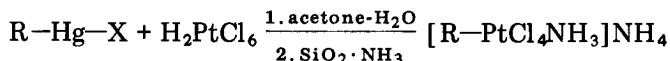
The source of ammonia is silica gel. Analysis * showed that 1 g of silica gel

* The quantitative determination of ammonia present in silica gel was carried out by Dr. L.A. Nikonova.

contained 1–2 mg of ammonia. Nitrogen was detected in the naphthyl complex of Pt^{IV} , described in previous paper [1], and the structure of this complex must be reformulated. Analysis. Found: C, 31.0; H, 4.3; N, 4.3. Calcd. for $[\text{C}_{10}\text{H}_7\text{PtCl}_4\text{NH}_3]\text{NH}_4 \cdot 2(\text{CH}_3)_2\text{CO}$: C, 31.2; H, 4.3; N, 4.4%. In the absence of ammonia, water molecules may play the role of the ligand and the cation.

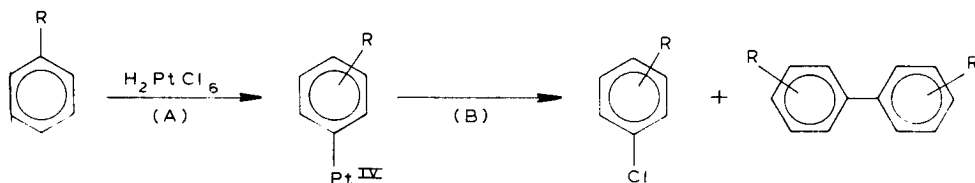
Elemental analysis and IR and ^1H NMR spectra indicated the presence of acetone molecules within the crystals, as all complexes were recrystallized from acetone (see also ref. 1). The number of acetone molecules present depended on the recrystallization conditions.

Recently, we prepared the same ionic σ -aryl complexes of Pt^{IV} by the interaction of H_2PtCl_6 with arylmercury compounds [12]:



In order to prove the proposal that the aromatic σ -complexes of Pt^{IV} are intermediates in the oxidation reaction of aromatic compounds by hexachloroplatinic acid, the following experiments were carried out. The reflux time for the reaction of anisole with H_2PtCl_6 was extended from 7 to 15 minutes. A colorless crystalline solid was isolated from the reaction residue. The ^1H NMR spectrum showed that this solid was a mixture of at least two isomers of dianisole. Dianisole was also prepared by the oxidative coupling [13–15] of anisole [16] with PdCl_2 in CH_3COOH in the presence of CH_3COONa . According to the ^1H NMR spectrum, only the *p,p*-dimethoxydiphenyl isomer was isolated after recrystallization from hexane. Comparison of the ^1H NMR spectra of the products isolated from these two reactions indicates that the *p,p*-dimethoxydiphenyl isomer is predominant in the mixture resulting from the reaction of anisole with H_2PtCl_6 . The second isomer appears to be the 3,4'-derivative. Refluxing of the pure anisole complex V in an aqueous CF_3COOH solution for 1 hour yielded a complex mixture of organic products. The ^1H NMR spectrum of this mixture showed the presence of the 4,4'-, 3,4'- and possibly 3,3'-isomers of dianisole as well as isomers of chloroanisole.

The results of this work show that σ -complex formation does occur in the oxidation reaction of aromatic hydrocarbons with H_2PtCl_6 . The reaction consists of two steps. The first step (A) is the formation of a stable σ -derivative of Pt^{IV} . The second step (B) is the degradation of this complex and formation of the organic products.



The relative rates for different aromatic compounds in the reaction with H_2PtCl_6 will be published in subsequent papers [17–19].

Experimental

Hexachloroplatinic acid was purchased commercially and dissolved in distilled water as a stock solution. All procedures were carried out in air. Proton and ^{13}C NMR spectra (δ (ppm) relative to TMS) were recorded on a Bruker SXP-4-100 spectrometer using 90 MHz and 22.63 MHz frequencies for proton and ^{13}C , respectively. Infrared spectra (in cm^{-1}) were recorded on a UR-20 spectrometer as KBr pellets.

Platinum(IV) complex of benzene (I)

A solution of 2.0 g of $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ and 10 ml of benzene in 20 ml of CF_3COOH and 6 ml of H_2O was refluxed for 2.5 h. The solvent was removed under reduced pressure. The residue was chromatographed as an acetone solution on a silica gel column made up in hexane. A mixture of acetone-hexane (2 : 1) eluted an orange band which when dried became an orange oil. The complex was purified by TLC on silica gel (eluent acetone-hexane 2 : 1) yielding 0.8 g (41% yield) of I as a yellow solid. The complex may be recrystallized from acetone, m.p. 186°C (dec.). Analysis. Found: C, 21.7; H, 3.1; Cl, 28.3; Pt, 39.2; N, 5.9%. Calcd. for $[\text{C}_6\text{H}_5\text{PtCl}_4\text{NH}_3]\text{NH}_4 \cdot (\text{CH}_3)_2\text{CO}$: C, 21.3; H, 3.6; Cl, 28.0; Pt, 38.5; N, 5.5%. ^1H NMR spectrum (in CD_3OD): 6.93–7.11m, 7.42–7.80m (C_6H_5), 2.13s (acetone) (m, multiplet; s, singlet). Protons N–H (in acetone- d_6): 3.00–3.35. ^{13}C NMR spectrum (in CH_3OD) 126.6, 127.2, 128.1, 139.1. IR spectrum (KBr pellet): 470w, 490w, 620w, 698m, 746s, 838m, 908w, 1000w, 1026m, 1066w, 1240s, 1260m, 1275m, 1400s, 1470m, 1570m, 1610m, 1660m, 1685m, 2800–3650s (w, weak; m, medium; s, strong).

Platinum(IV) complex of ethylbenzene (II)

A solution of 1.0 g of $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ and 1 ml of ethylbenzene in 15 ml of CF_3COOH and 3 ml of H_2O was refluxed for 45 min. The solvent was removed under reduced pressure and the residue was developed as in the case of benzene complex. Complex II was obtained as a yellow solid (0.27 g, 28% yield) which was recrystallized from acetone-chloroform (1 : 1). Analysis. Found: C, 23.3; H, 3.9; N, 5.5%. Calcd. for $[\text{C}_6\text{H}_4\text{C}_2\text{H}_5\text{PtCl}_4\text{NH}_3]\text{NH}_4 \cdot \frac{1}{2}(\text{CH}_3)_2\text{CO}$: C, 22.3; H, 3.9; N, 5.5%. ^1H NMR spectrum (in D_2O): 1.11t (CH_3), 2.40–2.80 two quartets (CH_2), 2.15s (acetone), 6.85–7.55m (C_6H_4). Protons N–H (in acetone- d_6): 3.22–3.96. IR spectrum: 422s, 470s, 702m, 790m, 822s, 1016m, 1070m, 1272s, 1375m, 1405s, 1490w, 1570w, 1585m, 1610m, 1685w, 2875w, 2935m, 2968m, 3180s, 3260s, 3330s, 2850–3640.

Platinum(IV) complex of toluene (III)

Complex III (orange-yellow crystals, 0.13 g, 14% yield) was prepared analogously from 1.0 g of $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$, 3 ml of toluene, 15 ml of CF_3COOH and 3 ml of H_2O . The mixture was refluxed for 15 min. ^1H NMR spectrum (in D_2O): 2.33s, 2.41s (CH_3), 6.95–7.55m (C_6H_4). IR spectrum: 428s, 440s, 510s, 583w, 615w, 700m, 788s, 810s, 735m, 887w, 1000m, 1021m, 1045w, 1069m, 1115w, 1130w, 1150w, 1195m, 1215m, 1221m, 1245s, 1270s, 1330m, 1410s, 1438s, 1478m, 1490s, 1570m, 1590s, 1610s, 1670m, 2400–3690.

Platinum(IV) complex of chlorobenzene (IV)

A solution of 1.0 g of $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ and 1 ml of chlorobenzene in 15 ml of CF_3COOH and 3 ml H_2O was refluxed for 2 h. The solvent was removed in vacuo and the residue was purified by column and thin layer chromatography on silica gel (eluent acetone-hexane 2 : 1). The complex was obtained as a yellow crystalline solid (0.20 g, 20% yield). Analysis. Found: C, 18.4; H, 3.0%. Calcd. for $[\text{ClC}_6\text{H}_4\text{PtCl}_4\text{NH}_3]\text{NH}_4 \cdot \frac{1}{2}(\text{CH}_3)_2\text{CO}$: C, 17.8; H, 2.7%. ^1H NMR spectrum (in CD_3OD): 6.85–7.20m, 7.35–7.80m (C_6H_4), 2.16 (acetone). Protons N–H (in acetone- d_6): 3.62. IR spectrum: 505m, 548w, 687m, 740s, 775s, 813m, 860w, 880w, 994m, 1009s, 1062s, 1090s, 1238s, 1255s, 1274s, 1370s, 1400s, 1418s, 1458s, 1475s, 1568s, 1610s, 1693s, 2600–3680.

Platinum(IV) complex of anisole (V)

A solution of 2.0 g of $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ and 4 ml of anisole in 15 ml of CF_3COOH and 6 ml of H_2O was refluxed for 7 min. After column and thin layer chromatography the complex was obtained as a red-brown crystalline solid (0.45 g, 49%). Analysis. Found: C, 18.1; H, 2.6; N, 6.3. Calcd. for $[\text{CH}_3\text{OC}_6\text{H}_4\text{PtCl}_4\text{NH}_3]\text{NH}_4$: C, 17.5; H, 2.9; N, 5.8%. ^1H NMR spectrum (in CD_3OD): 6.50–7.72m (C_6H_4), 3.82s (CH_3). IR spectrum: 425m, 575w, 600m, 633w, 770w, 790w, 820s, 853w, 1005m, 1012m, 1073w, 1110w, 1182s, 1240s, 1280s, 1405s, 1442m, 1488s, 1584s, 1620m, 1650w, 2700–3630.

When $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ and anisole in a solution of $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ was refluxed for 15 min, colorless crystals were obtained from the reaction residue. This substance was purified by column chromatography on silica gel and recrystallized from hexane (0.025 g). The ^1H NMR spectrum (in CDCl_3) showed the compound to be a mixture of isomers of dimethoxydiphenyl: 6.74–7.16m, 7.34–7.65m (C_6H_4), 3.78s, 3.69s (CH_3). The ^1H NMR spectrum of dimethoxydiphenyl prepared according to the method of [16]: 6.85–7.00m, 7.40–7.58m (C_6H_4), 3.78s (CH_3).

Platinum(IV) complex of o-xylene (VI)

A solution of 1.0 g of $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ and 2 ml of *o*-xylene in 15 ml of CF_3COOH and 3 ml of H_2O was refluxed for 12 min. After removing the solvent, the residue was purified by column and thin layer chromatography; complex VI was obtained as an orange-yellow crystalline solid (0.27 g, 27% yield). M.p. 160°C (after crystallization from acetone-chloroform, 1 : 1). Analysis. Found: C, 22.6; H, 4.1. Calcd. for $[(\text{CH}_3)_2\text{C}_6\text{H}_3\text{PtCl}_4\text{NH}_3]\text{NH}_4 \cdot \frac{1}{2}(\text{CH}_3)_2\text{CO}$: C, 22.2; H, 3.9%. ^1H NMR spectrum (in D_2O): 6.64–7.40m (C_6H_3), 2.17s, 2.26s (CH_3), 2.17s (acetone). IR spectrum: 425m, 810m, 860m, 880w, 1000w, 1020w, 1134m, 1152w, 1188w, 1260s, 1408s, 1430s, 1445m, 1590m, 1614m, 1705w, 2600–3650.

Platinum(IV) complex of m-xylene (VII)

Complex VII was prepared according to the procedure used for the *o*-xylene complex VI. The product was obtained as yellow crystals (0.30 g, 32% yield), m.p. $>250^\circ\text{C}$ (acetone-chloroform, 1 : 1). Analysis. Found: C, 20.3; H, 3.5; Cl, 29.2; N, 5.9%. Calcd. for $[(\text{CH}_3)_2\text{C}_6\text{H}_3\text{PtCl}_4\text{NH}_3]\text{NH}_4$: C, 20.0; H, 3.3; Cl, 29.6; N, 5.8%. ^1H NMR spectrum (in D_2O): 7.13 broad s, 6.84 broad s (C_6H_3), 2.25s (CH_3). Protons N–H appear at 3.53 ppm (in acetone- d_6). ^{13}C NMR spectrum (in

CH₃OD): 135.3 (*ortho*, 2 C), 127.2 (*para*, 1 C), 113.2, 134.1, 20.3 (CH₃). IR spectrum: 404m, 695m, 800m, 845s, 882w, 908w, 992w, 1035w, 1238s, 1400s, 1568m, 1595m, 2700–3380.

Platinum(IV) complex of m-chlorotoluene (VIII).

Complex VIII was prepared according to the procedure for the *o*-xylene complex VI. The product was obtained as yellow crystals (0.65 g, 62% yield). Analysis. Found: C, 22.0; H, 3.7; Pt, 35.2%. Calcd. for [(CH₃)ClC₆H₃PtCl₄NH₃]₂NH₄ · (CH₃)₂CO: C, 22.0; H, 3.5; Pt, 35.7%. ¹H NMR spectrum (in D₂O): 7.33 broad s, 7.08 broad s (C₆H₃), 2.28s (CH₃), 2.17 (acetone). IR spectrum: 545m, 685m, 750s, 850s, 880m, 992w, 1040w, 1091w, 1109m, 1160w, 1220m, 1240s, 1410s, 1555s, 1583s, 1612s, 1695m, 2350w, 2398w, 2448w, 2495w, 2700–3650.

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