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# Synthesis, structure and reactivity of stable dianionic organometallic complexes of Pt(IV). Crystal structure of $[PEtPh_3]_2[cis\text{-}Pt(C_6F_5)_2Cl_4]$ and $[NBu_4][mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]$ ☆

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## Abstract

The stable dianionic complexes $Q_2[cis\text{-}Pt(C_6F_5)_2Cl_4]$ ($Q=NBu_4^+$, **1**; $PEtPh_3^+$, **2**) have been obtained from reaction of the corresponding $Q_2[trans\text{-}Pt(C_6F_5)_2Cl_2]$ complexes with $Cl_2$ in $CCl_4$ solution. $[PEtPh_3]_2[cis\text{-}Pt(C_6F_5)_2Cl_4]$ is the first dianionic organometallic complex of Pt(IV) structurally characterized by X-ray diffraction. It crystallizes with two $CH_2Cl_2$ solvent molecules per complex molecule. The crystal system is monoclinic and the space group is $C2/c$ (No. 15), $a=23.648(5)$, $b=13.895(3)$, $c=17.651(4)$ Å, $\beta=106.42(3)°$, $V=5563(2)$ Å$^3$, $Z=4$ (20 °C). $[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2Cl_4]$ has been used as starting material in the synthesis of $[NBu_4][mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]$, **3**. The crystal structure of this new stable Pt(IV) compound has been determined. It crystallizes in the monoclinic system, space group $P2_1/n$ (No. 14), $a=11.122(3)$, $b=23.150(3)$, $c=16.086(3)$ Å, $\beta=105.79(3)°$, $V=3985(2)$ Å$^3$, $Z=4$ (20 °C). The disposition of the two $C_6F_5$ groups is very similar in both molecules. This is a consequence of steric constraints imposed by the octahedral coordination of the platinum atom.

*Keywords:* Platinum(IV) complexes; Crystal structures; Pentafluorophenyl groups; Anionic complexes

## 1. Introduction

Organometallic compounds of Pt(IV) have been known since 1909 [1] when $[Pt(CH_3)_3I]_4$ was isolated. Since then, other organometallic Pt(IV) complexes have been characterized, a large number of which were neutral methyl derivatives. Few anionic organometallic compounds are known [2–7], although only the mono-anionic $[NH_4][PtRCl_4(NH_3)]$ (R = naphtyl, *o*-nitrotolyl) [3] and $[NBu_4][Pt(C_6F_5)_2(C_5H_4NS)(CN\text{-}t\text{-}C_4H_9)Br_2]$ [5] complexes have been studied by X-ray methods.

The use of the pentafluorophenyl group has allowed us to develop an interesting line of stable anionic organometallic compounds of Pt(II). The latter appeared to be possible precursors for stable anionic Pt(IV) complexes, especially since an oxidation process must be favored because of their anionic character. Some studies have already been conducted in this direction, yielding varying results. The homoleptic pentafluorophenyl compound of Pt(II), $[NBu_4]_2[Pt(C_6F_5)_4]$, reacts with halogens giving rise to other anionic complexes of Pt(II) through a reaction sequence comprising oxidative addition to Pt(IV) compounds, followed by reductive elimination back to Pt(II). The intermediate Pt(IV) species were not stable under the reaction conditions used [8]. However, the reaction of another anionic pentafluorophenyl complex with $CCl_4$ solutions of $Cl_2$ or $Br_2$ affords the stable anionic organometallic complexes of Pt(IV), $[NBu_4][Pt(C_6F_5)_2(C_5H_4NS)X_2]$ (X = Cl, Br). In this complex, Pt(II) is coordinated to a chelating ligand in order to favor the stability of the resulting compounds [5].

This paper presents the results of reactions of other anionic pentafluorophenyl complexes of Pt(II) with $Cl_2$, leading to stable mono- and dianionic organometallic complexes of Pt(IV).

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☆ Dedicated to Professor F. Albert Cotton on the occasion of his 65th birthday.

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## 2. Results and discussion

### *2.1. Synthesis and structure of [cis-Pt($C_6F_5$)$_2$Cl$_4$]$^{2-}$*

The yellow air-stable compounds, $Q_2$[*cis*-Pt($C_6F_5$)$_2$Cl$_4$] (Q = $NBu_4^+$, **1**; $PEtPh_3^+$, **2**), were obtained by reaction of $Q_2$[*trans*-Pt($C_6F_5$)$_2$Cl$_2$] (Q = $NBu_4^+$, $PEtPh_3^+$) with a $CCl_4$ solution of $Cl_2$.

Both compounds have been studied by IR spectroscopy. The pentafluorophenyl absorption that appears at 950 cm$^{-1}$ in the starting materials is shifted to a higher value (**1**: 965 cm$^{-1}$; **2**: 969 cm$^{-1}$) in both compounds, in accordance with the higher oxidation state of the platinum atom [9]. Pentafluorophenyl groups also present absorptions between 820 and 740 cm$^{-1}$, although the absorptions that appear in this zone are not the $\nu$(Pt–C). They arise rather from an X-sensitive mode of the $C_6F_5$ group that behaves similarly to $\nu$(Pt–C) [10]. Therefore, the number and shape of these absorptions are related to the number of these groups and their disposition in the complex. The theory of X-sensitive vibrations indicates that two absorptions should be present for complexes with two mutually *cis* $C_6F_5$ groups. A broad absorption at 782 cm$^{-1}$ for complex **1** is likely the result of these two absorptions, with a small separation in frequency between them. The IR spectrum of the $PEtPh_3^+$ salt presents several absorptions in this zone due to the cation, and no useful information can be obtained from that part of the spectrum. On the other hand, several absorptions corresponding to $\nu$(Pt–Cl) appear between 350 and 250 cm$^{-1}$ (**1**: 322, 282, 270, 256 cm$^{-1}$; **2**: 330, 288, 280, 258 cm$^{-1}$). If these complexes were the *trans* isomers, a simpler pattern would have been expected. In fact, the X-ray diffraction study of complex **2** verifies that the complexes obtained are the *cis* isomers.

The positional parameters of complex **2** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2. Fig. 1 shows the structure of the anion [*cis*-Pt($C_6F_5$)$_2$Cl$_4$]$^{2-}$.

The asymmetric unit contains a $PEtPh_3^+$ cation, a $CH_2Cl_2$ solvent molecule and only one half anion. The platinum atom lies on a crystallographic two-fold axis. (Symmetry-generated atoms are indicated by the 'a' appended to atom names in Fig. 1.) The platinum atom exhibits octahedral coordination, which is typical for Pt(IV) compounds, and is bonded to two pentafluorophenyl groups in *cis* positions (92.4(2)°), which are related to each other by the two-fold axis. The coordination sphere is completed by four chlorine atoms, two in mutually *cis* positions (86.4(1)°), related again by the two-fold axis and in the same plane as the *ipso*-C of the pentafluorophenyl groups, and two more chlorine atoms in *trans* positions (177.1(1)°), perpendicular to the Pt($C_6F_5$)$_2$Cl$_2$ plane and which are related by the diad symmetry element.

Table 1
Atomic coordinates (×$10^4$) and equivalent isotropic displacement coefficients (Å$^2$×$10^3$) for [PEtPh$_3$]$_2$[Pt($C_6F_5$)$_2$Cl$_4$]·2CH$_2$Cl$_2$

| | *x* | *y* | *z* | $U_{eq}$[a] |
|---|---|---|---|---|
| Pt | 0 | 2719(1) | 2500 | 37(1) |
| Cl(1) | 940(1) | 2676(1) | 3429(1) | 43(1) |
| Cl(2) | 351(1) | 1452(1) | 1811(1) | 49(1) |
| C(1) | 306(2) | 3744(3) | 1873(2) | 39(1) |
| C(2) | 253(2) | 3662(3) | 1068(2) | 47(1) |
| C(3) | 507(2) | 4290(3) | 665(2) | 54(2) |
| C(4) | 821(2) | 5064(3) | 1038(3) | 60(2) |
| C(5) | 871(2) | 5199(3) | 1816(3) | 57(2) |
| C(6) | 613(2) | 4547(3) | 2220(2) | 47(1) |
| F(2) | −58(1) | 2942(2) | 626(1) | 61(1) |
| F(3) | 455(1) | 4149(2) | −106(2) | 75(1) |
| F(4) | 1075(2) | 5679(2) | 645(2) | 88(1) |
| F(5) | 1165(2) | 5972(2) | 2194(2) | 82(1) |
| F(6) | 681(1) | 4780(2) | 2986(1) | 58(1) |
| P(1) | 1684(1) | 9270(1) | 2831(1) | 41(1) |
| C(7) | 1465(2) | 9170(3) | 1771(2) | 42(1) |
| C(8) | 1395(2) | 8256(3) | 1430(3) | 54(2) |
| C(9) | 1175(2) | 8158(4) | 618(3) | 63(2) |
| C(10) | 1010(2) | 8983(4) | 161(3) | 66(2) |
| C(11) | 1077(2) | 9865(4) | 492(3) | 66(2) |
| C(12) | 1313(2) | 9977(3) | 1303(2) | 54(2) |
| C(13) | 674(2) | 9333(4) | 3333(2) | 53(2) |
| C(14) | 1120(2) | 8753(3) | 3204(2) | 43(1) |
| C(15) | 1114(2) | 7764(3) | 3328(3) | 54(2) |
| C(16) | 672(3) | 7374(4) | 3586(3) | 69(2) |
| C(17) | 240(2) | 7931(5) | 3736(3) | 71(2) |
| C(18) | 235(2) | 8921(4) | 3603(3) | 66(2) |
| C(19) | 3261(2) | 7903(3) | 3146(3) | 62(2) |
| C(20) | 2729(2) | 8374(3) | 2793(3) | 52(2) |
| C(21) | 2357(2) | 8619(3) | 3246(2) | 44(1) |
| C(22) | 2521(2) | 8426(4) | 4049(3) | 56(2) |
| C(23) | 3055(2) | 7955(4) | 4382(3) | 66(2) |
| C(24) | 3412(2) | 7699(3) | 3935(4) | 64(2) |
| C(25) | 1799(2) | 10494(3) | 3155(3) | 55(2) |
| C(26) | 2367(2) | 10936(4) | 3067(3) | 75(2) |
| C(27) | 1877(3) | 4594(6) | 4355(5) | 106(3) |
| Cl(3) | 2201(1) | 5551(2) | 3947(1) | 120(1) |
| Cl(4) | 2371(1) | 3704(2) | 4719(2) | 142(1) |

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 2
Selected bond distances and angles[a] for [PEtPh$_3$]$_2$[*cis*-Pt($C_6F_5$)$_2$Cl$_4$] (**2**)

| | | | |
|---|---|---|---|
| Bond distances (Å) | | | |
| Pt–Cl(1) | 2.361(1) | Pt–C(2) | 2.417(4) |
| Pt–C(1) | 2.056(4) | | |
| Angles (°) | | | |
| Cl(1)–Pt–Cl(2) | 86.6(1) | Cl(1)–Pt–C(1) | 89.2(1) |
| Cl(2)–Pt–C(1) | 90.6(1) | Cl(1)–Pt–Cl(1a) | 177.1(1) |
| Cl(2)–Pt–Cl(1a) | 91.2(1) | C(1)–Pt–Cl(1a) | 92.8(1) |
| C(1)–Pt–Cl(2a) | 177.0(1) | Cl(2)–Pt–Cl(2a) | 86.4(1) |
| C(1)–Pt–C(1a) | 92.4(2) | | |

[a] Atoms labelled 'a' are generated by the symmetry operation: $-x$, $y$, $0.5-z$.

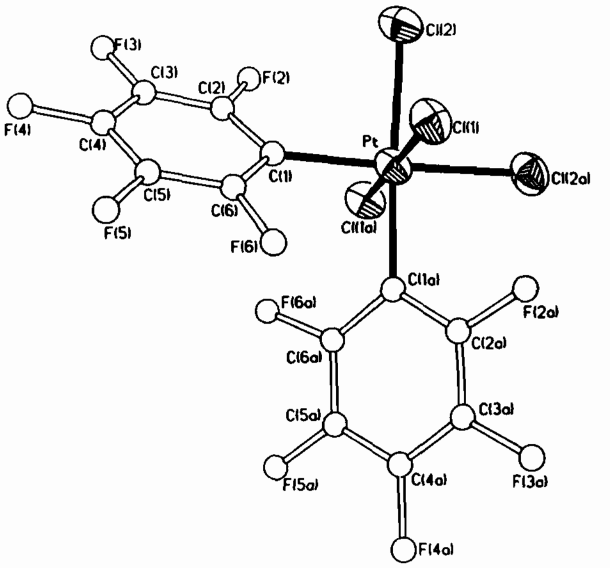


Fig. 1. View of the $[cis\text{-}Pt(C_6F_5)_2Cl_4]^{2-}$ anion with atom numbering scheme.

The Pt–C(1) distance, where C(1) is the *ipso*-C of the $C_6F_5$ group, is 2.056(4) Å, in the range found for pentafluorophenyl complexes of Pt(II) [11]. As mentioned before, the structure of another pentafluorophenyl complex of Pt(IV), although monoanionic, has been studied previously by X-ray diffraction [5]. That compound presents two pentafluorophenyl groups in *cis* positions, one of them *trans* to a bromine atom (Pt–C, 1.994(8) Å) and the other one *trans* to a nitrogen atom (Pt–C, 2.051(8) Å). The Pt–C distance (2.056(4) Å) in complex **2**, in which the $C_6F_5$ group is *trans* to a chlorine atom, is longer than the Pt–C distance *trans* to the bromine atom. In addition to the different *trans* influences of chlorine and bromine, the different charge of the anion must be considered.

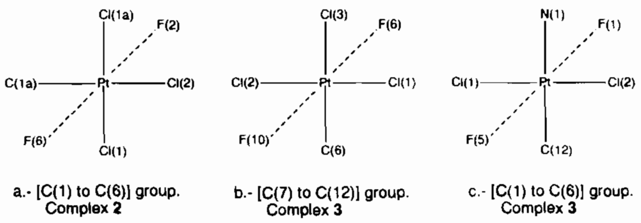
The Pt–Cl distances are different: Pt–Cl(1) (where Cl(1) is *trans* to chlorine) is 2.361(1) Å, while the Pt–Cl(2) (where Cl(2) is *trans* to a $C_6F_5$ group) is 2.417(1) Å. This difference shows the different *trans* influences of the chlorine atom and the pentafluorophenyl group. In keeping with this, the pentafluorophenyl group would have a stronger *trans* influence than the chlorine atom, as already observed in Pt(II) complexes [12].

The Pt–Cl distance for the chlorine *trans* to chlorine (Cl(1)) would be an interesting value for comparing with other dianionic organometallic complexes with two chlorines in a *trans* arrangement so no *trans* influence would have to be considered; however, the only structural data available for the *trans*-Cl–$Pt^{IV}$–Cl unit in anionic complexes are for non-organometallic compounds. The most similar anionic complexes are those with the $[PtCl_6]^{2-}$ anion. It could be thought at first glance that the Pt–Cl distances should be equal in all these complexes; however, the influence of the counterion or solvent molecules mainly through hydrogen interactions modifies these Pt–Cl distances. The minimum Pt–Cl distance found in $[PtCl_6]^{2-}$ is 2.293(4) Å [13] when the counterion is $NMe_4^+$. There is a $Cl\cdots C_{methyl}$ distance of 3.719 Å. This distance is approximately the sum of the van der Waals radii and, therefore, hydrogen interactions must be very weak if present. The largest Pt–Cl distance is 2.332(3) Å in $[AsPh_4]_2[PtCl_6]$ [14]. (We exclude from consideration the compound $[H_3N(CH_2)_3NH_3]_2[PtCl_6]$ [15] (Pt–Cl = 2.349(3) Å), in which the errors in the distances and displacement parameters of all chlorine atoms are suspiciously high as compared to the light atoms.) $[AsPh_4]_2[PtCl_6]$ presents shorter $Cl\cdots C$ distances (3.539, 3.489 Å) than $[NMe_4]_2[PtCl_6]$, with $Cl\cdots H$ distances of 2.796, 2.866 and 2.864 Å.

Thus, complex **2** presents the longest Pt–Cl distance observed for a chlorine atom *trans* to a chlorine atom in complexes of Pt(IV); and, as do many of the chlorine atoms of the $[PtCl_6]^{2-}$ anions, it presents hydrogen interactions, in this case with a $CH_2Cl_2$ solvent molecule, since the $C(27)\cdots Cl(1)$ distance is 3.555(7) Å and $Cl(1)\cdots H(27a)$ is 2.738(8) Å.

The angle formed by the pentafluorophenyl group (C(1) to C(6)) and the plane that contains the two *ipso*-C atoms (C(1), C(1a), Cl(2), Cl(2a)) is 43.0(2)°. Fig. 2(a) shows the projection of this pentafluorophenyl group on the coordination plane (Cl(1), Cl(2), Cl(1a), C(1a)) of the platinum atom, which is perpendicular to the $C_6F_5$ group. Thus, the view is the projection of the pentafluorophenyl group in the *ipso* C(1)–Pt direction. As can be seen, the corresponding *ortho*-F atoms are located almost at the same distance from the nearest chlorine atoms: $F(2)\cdots Cl(2)$, 2.908(3) Å; $F(2)\cdots Cl(1a)$, 3.031(3) Å; $F(6)\cdots Cl(1)$, 3.041(3) Å. A rotation around the $Pt–C_{ipso}$ bond will change this situation, shortening at least one of these distances, which are already shorter than the sum of the van der Waals radii (3.15 Å).

The $^{19}F$ NMR spectrum of complex **1** in $CD_2Cl_2$ (complex **2** is not sufficiently soluble) shows two signals for the *ortho*-F atoms at −112.63 (d) and −116.23 (d) ppm, with the corresponding $^{195}Pt$ satellites: $^3J(^{195}Pt–F) = 74.4$ Hz and 113.0 Hz, respectively. The



a.- [C(1) to C(6)] group. Complex 2

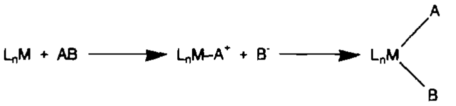
b.- [C(7) to C(12)] group. Complex 3

c.- [C(1) to C(6)] group. Complex 3

Fig. 2. Cores of the anionic complexes **2** and **3**. They are projected in the $Pt–C_{ipso}$ ($C_{ipso}$ of a $C_6F_5$ group) direction. The $C_6F_5$ group is represented by thick dashed lines and only the *ortho*-F atoms of that group are shown.

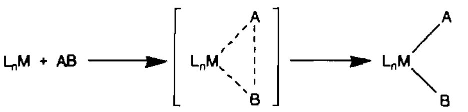
$Pt^{IV}$–*o*-F coupling constants are in the range observed for other $Pt^{IV}$–*o*-F systems [5]. The signals at −166.59 (m) and −167.27 (m) ppm correspond to the *meta*-F atoms, while the *para*-F atoms only present a signal at −164.53 (t) ppm. While some pentafluorophenyl complexes of Pt(II) with planar Pt(II) environments, like $[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]^{2-}$ [16], present only one signal for the $o\text{-}F_{terminal}$ or $o\text{-}F_{bridges}$ atoms, due to the possibility of movement around the $Pt\text{–}C_{ipso}$ bond, octahedral pentafluorophenyl Pt(IV) complexes, with the two apical positions occupied by atoms, seem to have a strong limitation for this movement [5]. The number of signals observed for complex **1** is consistent with the structure in the solid state ($C_{2v}$ symmetry) and with the limited mobility of these groups in Pt(IV) complexes. This limited mobility has to be a consequence of the short F···Cl distances that we have just mentioned. Since these distances are within the anion, they remain present in solution, preventing the $C_6F_5$ group from moving enough to make the two *ortho*-F (and the two *meta*-F) atoms chemically equivalent, on the NMR time scale.

Since complexes **1** and **2** have been obtained from the corresponding $[trans\text{-}Pt(C_6F_5)_2Cl_2]^{2-}$ complexes, an isomerization process must have occurred. The $S_N2$ mechanism (Eq. (1)) is the one most widely accepted for this kind of reaction in Pt(II) complexes.



(1)

A five-coordinate platinum(IV) intermediate would be involved in this process and a rearrangement of this intermediate would render the final *cis* isomer, as has been proposed in the synthesis of $[NBu_4][Pt(C_6F_5)_2(C_5H_4NS)Br_2]$ [5] where an isomerization is also observed. However, a concerted addition (Eq. (2)) cannot be dismissed, since this mechanism could also afford the *cis* isomer. A radical-type mechanism is less likely since it can afford both *cis* and *trans* AB products.



(2)

Complex **1**, which is air stable and easy to prepare from the corresponding Pt(II) compound, is an appropriate starting material for obtaining other Pt(IV) compounds.

### 2.2. Synthesis of $[NBu_4][Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]$

The reaction of complex **1** with $AgClO_4$ and *p*-toluidine (Eq. (3)) gives rise to AgCl precipitation and formation of the monoanionic $[NBu_4][mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]$ complex, **3**.

$$[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2Cl_4] + AgClO_4 + NH_2\text{-}p\text{-}C_6H_4CH_3 \longrightarrow AgCl + NBu_4ClO_4 + [NBu_4][mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)] \qquad (3)$$

Complex **3** is an air-stable solid and no signs of Pt(II) compounds are observed by IR spectroscopy.

There are several possible isomers for this stoichiometry. The X-ray diffraction study of a single crystal of complex **3** shows it to be the *mer* isomer. The chlorine atom that has been substituted is one of the two chlorine atoms *trans* to the pentafluorophenyl groups, proving these groups to have a stronger *trans* effect than the chlorine atoms.

### 2.3. Crystal structure of $[NBu_4][mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]$

The atomic coordinates of complex **3** are presented in Table 3. Selected bond lengths and angles are given in Table 4. Fig. 3 shows the crystal structure of the anion.

The platinum atom is coordinated to three chlorine atoms, two pentafluorophenyl groups and a *p*-toluidine ligand in an octahedral fashion, typical for Pt(IV) complexes. Two chlorine atoms (Cl(1), Cl(2)) are in mutually *trans* positions (Pt–Cl(1) distance, 2.312(2) Å; Pt–Cl(2), 2.327(2) Å; Cl(1)PtCl(2) angle, 174.6(1)°). The third chlorine atom -Cl(3)- makes the following angles with Cl(1) and Cl(2): Cl(1)PtCl(3), 92.0(1)°; Cl(2)PtCl(3), 85.7(1)°. The Pt–Cl(3) distance is 2.391(2) Å.

The Pt–Cl distances for the chlorine atoms *trans* to each other are very similar to each other and shorter than those found in complex **2** (2.361(1) Å). This difference agrees with the different ionic characters of these anions. Thus, complex **2**, which is dianionic, exhibits a longer Pt–Cl distance than the monoanionic complex **3**. However, the charge may not be the only reason for the observed shortening. As mentioned before, the chlorine atoms in mutually *trans* positions in complex **2** present interactions with $CH_2Cl_2$ molecules through a hydrogen atom, which could conceivably elongate the Pt–Cl distances and which do not exist in complex **3**.

The long Pt–Cl(3) distance (2.391(2) Å) is a consequence of the *trans* influence of the pentafluorophenyl group. This distance is slightly shorter than the analogous Pt–Cl distance in complex **2** (2.417(1) Å), thus showing less sensitivity to the different anionic character of the complex than does the chlorine *trans* to chlorine. The Pt–C distances are 2.046(5) Å for Pt–C(6) and 2.044(6) Å for Pt–C(12). These distances and the Pt–C distances in complex **2** are equal within experimental error, showing no variation either with the change of the anionic character or with the change of the group in the *trans* position.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[NBu_4][Pt(C_6F_5)_2Cl_3(C_7H_9N)]$

| | $x$ | $y$ | $z$ | $U_{eq}$ [a] |
|---|---|---|---|---|
| Pt | 2079(1) | 3846(1) | 2544(1) | 44(1) |
| Cl(1) | 2835(1) | 3117(1) | 3531(1) | 59(1) |
| Cl(2) | 1143(2) | 4531(1) | 1513(1) | 64(1) |
| Cl(3) | 1828(2) | 3198(1) | 1352(1) | 72(1) |
| F(1) | 107(3) | 4739(1) | 3039(2) | 63(1) |
| F(2) | 265(3) | 5397(2) | 4383(2) | 79(2) |
| F(3) | 2360(4) | 5414(2) | 5736(2) | 94(2) |
| F(4) | 4351(3) | 4756(2) | 5652(2) | 78(2) |
| F(5) | 4305(3) | 4138(1) | 4288(2) | 61(1) |
| F(6) | 4505(3) | 3114(2) | 2383(3) | 83(2) |
| F(7) | 6693(4) | 3433(2) | 2263(3) | 116(2) |
| F(8) | 7335(4) | 4560(3) | 2284(3) | 126(2) |
| F(9) | 5648(4) | 5379(2) | 2425(3) | 114(2) |
| F(10) | 3447(4) | 5089(2) | 2600(2) | 77(2) |
| N(1) | 172(4) | 3568(2) | 2471(3) | 60(2) |
| C(1) | 1211(5) | 4725(2) | 3660(3) | 49(2) |
| C(2) | 1260(6) | 5067(3) | 4365(4) | 56(2) |
| C(3) | 2301(7) | 5077(3) | 5034(4) | 61(3) |
| C(4) | 3306(6) | 4754(3) | 4997(3) | 54(2) |
| C(5) | 3249(5) | 4419(2) | 4279(3) | 46(2) |
| C(6) | 2195(5) | 4383(2) | 3573(3) | 44(2) |
| C(7) | 4714(6) | 3686(3) | 2396(4) | 60(3) |
| C(8) | 5869(6) | 3844(4) | 2334(4) | 81(3) |
| C(9) | 6194(7) | 4397(5) | 2334(4) | 80(3) |
| C(10) | 5367(7) | 4812(3) | 2417(4) | 74(3) |
| C(11) | 4188(6) | 4657(3) | 2494(3) | 58(3) |
| C(12) | 3811(5) | 4096(3) | 2473(3) | 49(2) |
| C(13) | −23(6) | 2622(3) | 3085(4) | 76(3) |
| C(14) | −294(7) | 2286(3) | 3744(5) | 90(4) |
| C(15) | −671(7) | 2535(4) | 4402(5) | 92(4) |
| C(16) | −802(7) | 3122(4) | 4401(5) | 91(4) |
| C(17) | −542(6) | 3465(3) | 3771(4) | 76(3) |
| C(18) | −146(5) | 3213(3) | 3120(4) | 57(2) |
| C(19) | −953(8) | 2164(4) | 5093(5) | 139(5) |
| N(2) | 4896(5) | 1369(2) | 3130(3) | 60(2) |
| C(20) | 3744(6) | 1174(3) | 2431(5) | 76(3) |
| C(21) | 2866(8) | 1645(4) | 1979(6) | 116(4) |
| C(22) | 1837(9) | 1397(4) | 1257(8) | 150(6) |
| C(23) | 1097(16) | 1731(6) | 725(12) | 283(12) |
| C(24) | 4530(6) | 1711(3) | 3822(4) | 72(3) |
| C(25) | 3729(7) | 1388(3) | 4292(5) | 86(3) |
| C(26) | 3320(8) | 1778(4) | 4914(5) | 101(4) |
| C(27) | 2563(9) | 1469(5) | 5409(6) | 128(5) |
| C(28) | 5698(6) | 1762(3) | 2752(4) | 68(3) |
| C(29) | 6238(8) | 1491(3) | 2063(5) | 92(3) |
| C(30) | 6959(8) | 1907(4) | 1680(6) | 105(4) |
| C(31) | 7512(9) | 1637(5) | 1022(6) | 145(6) |
| C(32) | 5589(7) | 820(3) | 3495(4) | 71(3) |
| C(33) | 6794(7) | 900(3) | 4183(4) | 75(3) |
| C(34) | 7307(8) | 323(4) | 4520(5) | 101(4) |
| C(35) | 8532(10) | 356(5) | 5151(6) | 147(6) |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 4
Selected bond distances and angles for $[NBu_4][mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]$, **3**

| | | | |
|---|---|---|---|
| Bond distances (Å) | | | |
| Pt–Cl(1) | 2.312(2) | Pt–Cl(2) | 2.327(2) |
| Pt–Cl(3) | 2.391(2) | Pt–N(1) | 2.189(5) |
| Pt–C(6) | 2.046(5) | Pt–C(12) | 2.044(6) |
| Angles (°) | | | |
| Cl(1)–Pt–Cl(2) | 174.6(1) | Cl(1)–Pt–Cl(3) | 92.0(1) |
| Cl(2)–Pt–Cl(3) | 85.7(1) | Cl(1)–Pt–N(1) | 89.3(1) |
| Cl(2)–Pt–N(1) | 85.6(1) | Cl(3)–Pt–N(1) | 82.7(1) |
| Cl(1)–Pt–C(6) | 87.5(1) | Cl(2)–Pt–C(6) | 94.6(1) |
| Cl(3)–Pt–C(6) | 176.6(2) | N(1)–Pt–C(6) | 93.9(2) |
| Cl(1)–Pt–C(12) | 94.2(2) | Cl(2)–Pt–C(12) | 90.7(2) |
| Cl(3)–Pt–C(12) | 92.2(2) | N(1)–Pt–C(12) | 173.9(2) |
| C(6)–Pt–C(12) | 91.2(2) | | |

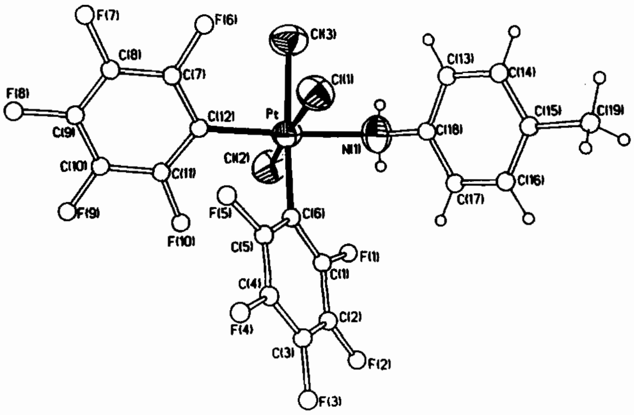


Fig. 3. View of the $[mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]^-$ anion with atom numbering scheme.

The Pt–N distance is 2.189(5) Å. This distance is equal within experimental error to those found in the complexes $[NH_4][PtRCl_4(NH_3)]$ (R = naphthalene, *o*-nitrotoluene) [3]. In these complexes the nitrogen atoms are *trans* to Pt–C σ-bonds too, and the complexes are monoanionic like complex **3**. These Pt–N distances are all longer than the Pt–N distances in complexes in which the nitrogen atom is *trans* to a chlorine atom (1.961 [17] to 2.083 [18] Å), in agreement again with the stronger *trans* influence of the $C_6F_5$ group versus Cl atoms.

The two pentafluorophenyl groups (C(1) to C(6) and C(7) to C(12)) form angles of 43.0(2)° and 47.0(2)°, respectively, with the C(6)C(12)PtNCl(3) plane. These orientations locate the *ortho*-F atoms almost equidistant from the nearest chlorine atoms, as can be seen in Fig. 2(b) and (c). The distances *ortho*-F···Cl are the following: F(1)···Cl(2), 3.020(4) Å; F(5)···Cl(1), 2.942(4) Å; F(6)···Cl(1), 2.954(5) Å; F(6)···Cl(3), 2.994(4) Å; F(10)···Cl(2) 2.976(4) Å. If the angle of 47.0(2)° were different for the $C_6F_5$ *trans* to N(1) (C(7)–C(12), Fig. 2(b)) one of the F(6)···Cl(3) or F(6)···Cl(1) distances would become shorter, thus giving rise to steric problems since the present distances are already quite short. Fig. 2(c) shows that for the group C(1)–C(6) both F···Cl distances can become longer at the same time by a rotation of the $C_6F_5$ group around the corresponding Pt–$C_{ipso}$ bond. However, in that case, the F(1)···N(1) or F(5)···C(12) distance would have become shorter than the present values of 2.868(6) and 2.822(6) Å, respectively, and would again create steric problems, since the sum of the van der Waals radii are: F–N, 2.85; F–C, 3.1 Å.

As can be seen from Fig 2, the dispositions of the $C_6F_5$ groups in both structures are almost the same, with each group bisecting two of the angles in the plane perpendicular to the corresponding Pt–C bond, thus giving rise to F···Cl distances in the range of 2.908(3) to 3.031(3) Å and showing a very restricted location for these groups in these kinds of octahedral environments.

## 3. Experimental

### 3.1. General methods

C, H and N analyses were made with a Perkin-Elmer 240B microanalyzer. The IR spectra were recorded over the 4000–200 $cm^{-1}$ range on a Perkin-Elmer 883 or a Perkin-Elmer 1730 FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. The $^{19}F$ NMR spectra were recorded on a Unity 300 instrument in $CDCl_3$ solutions.

### 3.2. Synthesis of $[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2Cl_4]$, 1

To a solution of 0.170 g (0.157 mmol) of $[NBu_4]_2[trans\text{-}Pt(C_6F_5)_2Cl_2]$ [10] in $CH_2Cl_2$ (30 ml) was added an excess of a solution of $Cl_2$ in $CCl_4$. After a few minutes of stirring at room temperature the solution was evaporated to dryness and the oily residue was washed with water and n-hexane. The residue was dissolved again in $CH_2Cl_2$ and $MgSO_4$ was added; the suspension was stirred for a few minutes and filtered off. The resulting solution was evaporated to dryness, the residue was treated with $OEt_2$ (40 ml) and stirred until a yellow solid corresponding to $[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2Cl_4]$ was obtained; the solid was filtered off and washed with n-hexane (0.091 g, 50% yield).

*Anal.* Calc.: C, 45.67; H, 6.22; N, 2.42. Found: C, 45.40; H, 5.97; N, 2.36%. IR (Nujol) $\nu$ ($cm^{-1}$) $C_6F_5$: 1624 m, 1594 w, 1497 vs, 1062 s, 998 m, 965 vs; X-sensitive mode: 782 (br) s; Pt–Cl: 322 s, 282 m, 270 s, 256 m. NMR data ($CDCl_3$, room temperature) $^{19}F$ NMR: $\delta = -112.63$ (d, 2F, $^3J(^{195}Pt\text{–}F) = 74.4$ Hz, o-F), $-116.23$ (d, 2F, $^3J(^{195}Pt\text{–}F) = 113.0$ Hz, o-F), $-164.53$ (t, 2F, p-F), $-166.59$ ($m_c$, 2F, m-F), $-167.27$ ($m_c$, 2F, m-F).

### 3.3. Synthesis of $[PEtPh_3]_2[trans\text{-}Pt(C_6F_5)_2Cl_2]$

To a solution of 0.700 g (0.547 mmol) of $[NBu_4]_2[trans\text{-}Pt(C_6F_5)_2Cl_2]$ in MeOH (25 ml) was added 0.957 g (2.580 mmol) (ratio 1:4) of $PEtPh_3Br$. After 15 min of stirring at room temperature, 20 ml of $H_2O$ were added dropwise and a pale-yellow solid corresponding to $[PEtPh_3]_2[trans\text{-}Pt(C_6F_5)_2Cl_2]$ was precipitated; the solid was filtered off and washed with $H_2O$, $^iPrOH$ and n-hexane (0.616 g, 81% yield).

*Anal.* Calc.: C, 52.83; H, 3.41. Found: C, 52.83; H, 3.80%. IR (Nujol) $\nu$ ($cm^{-1}$) $C_6F_5$: 1589 m, 1490 vs, 1055 s, 1042 s, 996 m, 950 vs; X-sensitive mode: 768 s; Pt–Cl: 318 m.

### 3.4. Synthesis of $[PEtPh_3]_2[cis\text{-}Pt(C_6F_5)_2Cl_4] \cdot 2CH_2Cl_2$, 2

To a solution of 0.100 g (0.085 mmol) of $[PEtPh_3]_2[trans\text{-}Pt(C_6F_5)_2Cl_2]$ in 10 ml of a mixture of $CH_2Cl_2/OC(CH_3)_2$ (50%) was added an excess of a solution of $Cl_2$ in $CCl_4$. After 12 h of stirring at room temperature a pale-yellow solid corresponding to $[PEtPh_3]_2[cis\text{-}Pt(C_6F_5)_2Cl_4] \cdot 2CH_2Cl_2$ was filtered off, washed with $CHCl_3$ and dried in the air (0.090 g, 75% yield).

*Anal.* Calc.: C, 45.46; H, 3.11. Found: C, 45.45; H, 3.05%. IR (Nujol) $\nu$ ($cm^{-1}$) $C_6F_5$: 1635 m, 1587 m, 1509 vs, 1069 s, 997 m, 969 vs; X-sensitive mode: 790 s, 780 s; Pt–Cl: 330 s, 288 s, 280 s, 258 m.

### 3.5. Synthesis of $[NBu_4][mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]$, 3

To a solution of 0.373 g (0.322 mmol) of $[NBu_4]_2[mer\text{-}Pt(C_6F_5)_2Cl_4]$ in $(CH_3)_2CO$ (10 ml) was added 0.067 g (0.322 mmol) of $AgClO_4$, and the AgCl instantaneously precipitated as a white solid. After filtration of the AgCl, 0.035 g (0.322 mmol) $NH_2\text{-}p\text{-}C_6H_4CH_3$ (1:1 ratio) was added to the solution. After 10 min of stirring at room temperature the solution was evaporated to dryness. To the oily residue 4×30 ml of $OEt_2$ were added and after vigorously stirring a pale-yellow solution was separated from a white solid corresponding to $NBu_4ClO_4$. The pale-yellow solution was concentrated to about 10 ml and a pale-yellow solid which corresponds to $[NBu_4][mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]$ was obtained, filtered off and dried in the air (0.282 g, 90% yield).

*Anal.* Calc.: C, 42.62; H, 4.56; N, 2.84. Found: C, 42.23; H, 4.05; N, 2.93%. IR (Nujol) $\nu$ ($cm^{-1}$) $C_6F_5$: 1636 m, 1604 w, 1510 vs, 1092 s, 1070 vs, 970 vs; X-sensitive mode: 797 s, 791 s; Pt–Cl: 345 s, 330 m, 282 (sh) s; $NH_2\text{-}p\text{-}C_6H_4CH_3$: 1581 m, 1121 m, 814 s, 543 m, 465 w, 430 w.

### 3.6. Crystal structure determination

General crystallographic information for compounds **2** and **3** is collected in Table 5. Data were collected

Table 5
Crystallographic data for complexes $[PEtPh_3]_2[cis\text{-}Pt(C_6F_5)_2Cl_4]$, **2**, and $[NBu_4][mer\text{-}Pt(C_6F_5)_2Cl_3(NH_2\text{-}p\text{-}C_6H_4CH_3)]$, **3**

| | Complex **2** | Complex **3** |
|---|---|---|
| Formula | $PtCl_4P_2F_{10}C_{52}H_{40}\cdot 2CH_2Cl_2$ | $PtCl_3F_{10}N_2C_{35}H_{45}$ |
| Molecular weight | 1422.6 | 984.35 |
| Crystal system | monoclinic | monoclinic |
| Space group | *C2/c* | *P2₁/n* |
| $a$ (Å) | 23.648(5) | 11.122(3) |
| $b$ (Å) | 13.895(3) | 23.150(3) |
| $c$ (Å) | 17.651(4) | 16.086(3) |
| $\beta$ (°) | 106.42(3) | 105.79(3) |
| $V$ (Å$^3$) | 5563(3) | 3985(3) |
| $Z$ | 4 | 4 |
| Crystal dimens. (mm) | 0.30 × 0.30 × 0.15 | 0.20 × 0.15 × 0.70 |
| $\mu$ (Mo K$\alpha$) (cm$^{-1}$) | 30.3 | 38.0 |
| Diffractometer | Siemens/STOE AED2 | Siemens/STOE AED2 |
| Radiation | Mo K$\alpha$ ($\lambda_\alpha$ 0.71073 Å) | Mo K$\alpha$ ($\lambda_\alpha$ 0.71073 Å) |
| Temperature (°C) | 20 ± 1 | 20 ± 1 |
| Scan method | $\omega$–$\theta$ | $\omega$–$\theta$ |
| Data collection range (°) | $3 < 2\theta < 50$ | $3 < 2\theta < 50$ |
| No. data with $F_o^2 > 3\sigma(F_o^2)$ | 4320 | 4191 |
| Absorption correction | 12$\psi$ scan | 13$\psi$ scan |
| No. refined parameters | 339 | 461 |
| $R$ [a] | 0.0293 | 0.0259 |
| $R_w$ [b] | 0.0430 | 0.0279 |
| $g$ | 0.001300 | 0.000250 |
| GOF | 1.0089 | 1.0019 |
| Largest shift/error | 0.011 | 0.007 |
| Final difference Fourier max. peak (e Å$^{-3}$) | 1.01 | 0.42 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$.

on a Siemens STOE/AED-2 four-circle diffractometer. Intensity data were corrected for Lorentz and polarization effects. Absorption corrections based on $\Psi$ scans were applied. The intensities of three standard reflections were checked every 45 min and no decay was observed. The structures were solved by the use of Patterson and Fourier methods. All the non-hydrogen atoms, even those of the $CH_2Cl_2$ solvent molecule (complex **2**), were refined with anisotropic displacement parameters.

*Complex 2*: All hydrogen atoms were introduced at calculated positions (C–H bond distance 0.96 Å) except those of the methyl group. For each methyl group, one or two hydrogen atoms were located in a difference map; their positions along with that of the neighboring carbon atom of the $CH_2$ group were used as the basis for calculating the position(s) of the other methyl hydrogen atom(s). A common fixed displacement parameter ($U = 0.08$ Å$^2$) was assigned.

*Complex 3*: Some hydrogen atoms were located in the difference Fourier map and the remaining hydrogen atoms were introduced at calculated positions. Only the common displacement parameter was refined ($U = 0.11$ Å$^2$).

Both structures were solved by calculations carried out on a Local Area VAXcluster (VAX/VMS V5.5) with the program REDU4 Rev. 7.03 (Stoe) for data reduction and with the commercial package SHELXTL-PLUS [19].

## 4. Supplementary material

Tables of calculated and observed structure factors, hydrogen positions, anisotropic displacement parameters and the full list of bond distances and angles may be obtained from the authors upon request.

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