Ligand structural factors in the establishment of intramolecular Pt···H hydrogen-bridging interactions in pentafluorophenyl complexes of platinum

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Anionic complexes with molecular formula $[Q][Pt(C_6F_5)_3L]$ [$Q = NBu_4^+$, L = diphenyl-2-pyridylmethane **1**, 2-benzylpyridine **2**, 2-(hydroxymethyl)pyridine **3** or 2-hydroxyaniline **4**; $Q = PPh_3Me^+$, L = 2-isopropylaniline **5**] were prepared by cleavage of the pentafluorophenyl bridging system in $[Q]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ with L. The analogous complex $[NBu_4][Pt(C_6F_5)_3(2\text{-}Ph_2PC_6H_4CHO)]$ **6** was prepared by substitution of the chloride ion by the ligand L in $[NBu_4]_2[Pt(C_6F_5)_3Cl]$. The ligands L contain hydrogen atoms which are suitable, from the point of view of both their structure and acidic properties, for establishing hydrogen-bridging interactions with the platinum centre. Proton NMR spectra of some of these complexes show displacement of the signal corresponding to the hydrogen atom towards higher frequencies but no Pt–H coupling. The structure of complex **1** was determined by single crystal X-ray diffraction (Pt···H distance 2.65 Å). The decisive factors for the existence of Pt···H hydrogen-bridging interactions in solution and in the solid state are discussed.

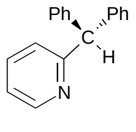
The platinum centre in perhalogenophenyl anionic complexes has basic character, and it is thus able to donate electron density to establish types of bonds or interactions. The vast majority of these bonds reported to date are formed with other metallic centres, such as Ag^{I},[1] Sn^{II},[2] Pb^{II},[3] Hg^{I}[4] or Tl^{I},[5] having acidic properties, giving rise to the preparation of heteropolynuclear complexes containing donor–acceptor Pt→M bonds.

In recent work[6] we have investigated the behaviour of the basic platinum centre in these anionic pentafluorophenyl starting materials with the aim of achieving the syntheses of complexes containing similar Pt→H interactions in which the hydrogen atom is part of a nitrogen-donor ligand. These kind of interactions are of the 'hydrogen bonding' type and have only recently been described.[7] The electron density of the metal centre is donated to the hydrogen atom with more or less acidic properties (three-centre, four-electron model). These Pt→H hydrogen-bonding interactions are substantially different from the well known 'agostic interactions',[8] in which the electron pair of the C–H bond is donated to the metal centre (three-centre, two-electron model). In our work we have concluded that the correct choice of the kind of hydrogen atoms which could interact is very important. The key characteristics are a certain electropositive character for the hydrogen atom and rigidity of the ligand containing it. In this paper we continue this study by using other ligands in which the hydrogen atoms are different from both a structural and electropositive point of view.

Results and Discussion

Synthesis of complexes $[Q][Pt(C_6F_5)_3L]$ ($Q = NBu_4^+$, L = diphenyl-2-pyridylmethane 1, 2-benzylpyridine 2, 2-(hydroxymethyl)pyridine 3 or 2-hydroxyaniline 4; $Q = PPh_3Me^+$, L = 2-isopropylaniline 5)

The addition of compound L to a yellow solution of $[Q]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ in CH_2Cl_2 in a 2:1 molar ratio results in decolouration after 3 h of stirring, thus indicating cleavage of the $\mu\text{-}C_6F_5$ system and co-ordination of L. Evaporation of the solvent leads to a solid the analytical and spectroscopic data of which are in accord with the formulation $[Q][Pt(C_6F_5)_3L]$ [equation (1)]. Whereas for complexes **1–4** we have used tetrabutylammonium as counter ion, for solubility reasons methyltriphenylphosphonium has been employed in the preparation of **5**.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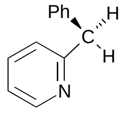
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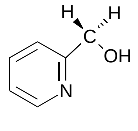
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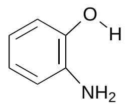
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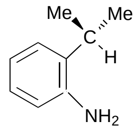
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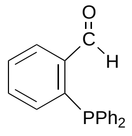
2-diphenylphosphino-benzaldehyde

$$[Q]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4] + 2\,L \xrightarrow{CH_2Cl_2} 2\,[Q][Pt(C_6F_5)_3L] \quad (1)$$

Preparation of $[NBu_4][Pt(C_6F_5)_3(2\text{-}Ph_2PC_6H_4CHO)]$ 6

Complex **6** is obtained by substitution of the halide in $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ by 2-(diphenylphosphino)benzaldehyde. The addition of $AgClO_4$ to a solution of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ and L in tetrahydrofuran (thf) (molar ratio 1:1:1) resulted in precipitation of AgCl. After removal of the AgCl, the solution was evaporated to dryness rendering complex **6** in 40% yield [equation (2)].

$$[NBu_4]_2[Pt(C_6F_5)_3Cl] + L + AgClO_4 \xrightarrow{thf} [NBu_4][Pt(C_6F_5)_3L] + AgCl + NBu_4ClO_4 \quad (2)$$

NMR studies of complexes 1–3

The diphenyl-2-pyridylmethane, 2-benzylpyridine and 2-(hydroxymethyl)pyridine ligands comprise a pyridine ring with a substituent in the 2 position which contains a hydrogen atom able to establish some kind of interaction with the platinum centre. The skeleton of each ligand is less rigid than the condensed double aromatic ring system of the quinoline-type ligands used in our previous work.[6] Here, the C−C σ bond between the carbon atom at position 2 of the ring and the carbon atom of the substituent allows its rotation.

In complex **1** it is reasonable to expect that the hydrogen atom of the tertiary carbon atom is located over the platinum co-ordination plane due to the bulkiness of the two phenyl rings bonded to this carbon. The ^{1}H NMR spectrum of **1** [$(CD_3)_2CO$, room temperature] shows signals corresponding to the diphenyl-2-pyridylmethane ligand and the NBu_4^+ cation. The most important feature is the downfield shift with respect to free L of the signal corresponding to the hydrogen atom bonded to the only non-aromatic carbon. This signal is a singlet at δ 7.55, whereas for free L it appears at δ 5.69. The displacement of a signal to higher frequencies has sometimes been invoked as an indication of the existence of a Pt···H interaction in solution. One of the characteristics of the M→H hydrogen bond is the displacement of the signal of the interacting hydrogen to higher frequencies in the ^{1}H NMR spectrum.[7] The displacement seems to be due to the deshielding of the proton produced by the electron density of the metal centre that is donated to the hydrogen atom. In the case of Pt^{II} this electron density is located in the d_{z^2} orbital, perpendicular to the square plane. This behaviour in the ^{1}H NMR spectrum differentiates the M→H hydrogen bond from the agostic model in which the signal of the hydrogen involved moves to lower frequencies.[8] Nevertheless, the mere shift of the signal to higher frequencies does not provide enough evidence of the existence of Pt→H interaction in solution, but rather is evidence of the location of the hydrogen atom over the platinum co-ordination plane, where some electron density from the metal atom is found. More conclusive proof is obtained when a coupling between the platinum centre and the hydrogen atom is observed in the ^{1}H NMR spectrum. Despite this the magnitude of the signal displacement in the spectrum of **1** is significant, no coupling is observed, and thus there is no evidence of a Pt→H interaction existing in solution for complex **1**. We do, however, observe ^{195}Pt–H coupling (27 Hz) in the signal corresponding to the hydrogen atom bonded to the carbon atom in *ortho* position with respect to the nitrogen in the pyridine ring of **1**. However, this coupling is transmitted through the Pt–N and the N−C bonds and is always found for this kind of platinum–pyridine complex.[6,9] In the ^{13}C NMR spectrum [$(CD_3)_2CO$, room temperature] the signal corresponding to the aliphatic C displays platinum satellites with a coupling constant of 40 Hz. Again this is not proof of any kind of Pt···H interaction since coupling of this magnitude has been found previously for analogous C atoms in other platinum complexes containing 2-substituted pyridines in which no Pt→H interaction can occur. This coupling is transmitted through the ligand skeleton [^3J(Pt−H)] and is, on some occasions, larger than that observed for pyridine carbon atoms nearer to the platinum centre.[10]

In complex **2** one of the phenyl rings of the diphenyl-2-pyridylmethane ligand has been replaced by a hydrogen atom in the 2-benzylpyridine ligand. Thus, the steric constraint of placing the hydrogen atoms close to the metal centre is less pronounced. In the ^{1}H NMR spectrum ($CDCl_3$, room temperature) of **2** only a singlet is observed for both methylene hydrogen atoms. This observation together with the AA′MM′X spin system observed for the phenyl group indicate the existence of a mirror plane in the molecule on the NMR time-scale. The plane could arise either by a static, symmetric disposition of the molecule in solution, or, as is more likely, by a dynamic behaviour in solution, probably involving swinging of the 2 substituent about the C_{py}–CH_2Ph bond (a full rotation around this bond seems unlikely due to the size of the phenyl group and the presence of the fluorine atoms of the C_6F_5 ligands). The CH_2 hydrogen atoms appear at δ 5.06, 0.94 ppm higher than for free L, and no ^{195}Pt−H coupling is observed. The magnitude of the downfield displacement is less significant than for **1** (1.86 ppm). Again, from the ^{1}H NMR spectrum we cannot conclude the existence of any Pt···H interaction; besides, the smaller displacement of the signal to higher frequencies seems to indicate that, due to the structural characteristics of the ligand chosen for **2**, which allow greater movement, the hydrogen atoms are not so rigidly located over the platinum plane. Once again the ^{13}C NMR spectrum of **2** [$(CD_3)_2CO$, room temperature] shows platinum satellites on the signal due to the CH_2 carbon atom [J(Pt−C) = 52 Hz]. As commented above, this coupling is transmitted through the bond system and no Pt···H interaction need be invoked.[10]

The 2-(hydroxymethyl)pyridine ligand present in complex **3** has a less bulky substituent in the 2 position. In addition, two possibilities for Pt···H interaction could be established here: (*i*) interaction of the hydroxy hydrogen or (*ii*) interaction of one or both hydrogens bonded to the C atom. In previous work we found that Pt→H interactions have a strong electrostatic component and thus their existence is favoured by a moderate electrophilic character of the hydrogen. Consequently, in **3**, the hydroxy hydrogen should interact with the platinum centre more easily than the aliphatic hydrogen atoms. Nevertheless, in the ^{1}H NMR spectrum [$(CD_3)_2CO$, room temperature] neither the signal corresponding to the OH nor that corresponding to the CH_2 shows platinum satellites and hence no Pt···H interaction can be inferred. The OH hydrogen signal appears at δ 4.99 as a triplet due to coupling with the CH_2 hydrogen atoms. This represents an *upfield* shift of 0.18 ppm. There is only one doublet signal for the CH_2 at δ 5.53 whereas this signal appears 0.80 ppm lower for the free L. The equivalence of these two protons can be explained in a similar way as for complex **2**. Given these data it seems that in this case not only is there no Pt···H interaction with the OH hydrogen atom, but the latter is not even located above the co-ordination plane, suffering anisotropic deshielding. The ^{1}H NMR data seem to indicate that the CH_2 hydrogen atoms occupy this position. Also in this case the ^{13}C NMR spectrum ($CDCl_3$, room temperature) shows platinum satellites [J(Pt−C) = 31 Hz] on the signal corresponding to the aliphatic carbon atom. This coupling, as previously mentioned, is propagated through the bond system.[10]

The ^{19}F NMR spectra of complexes **1–3** show signals for two types of pentafluorophenyl groups in a 1 : 2 intensity ratio. These correspond to the *trans* and *cis* groups respectively. Only in the spectrum of complex **1** there are some peculiarities, since the resonance due to the *o*-fluorine atoms of the *cis* C_6F_5 group appears split into two signals. The inequivalence of these fluorine atoms may indicate that the bulkiness of the 2 substituent precludes rotation of the pyridine ligand and/or the pentafluorophenyl rings.

Crystal structure of $[NBu_4][Pt(C_6F_5)_3(NC_5H_4CHPh_2\text{-}2)]$ 1

The structure of the anion of complex **1** with the atom numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. As expected, Pt lies at the centre of a square-planar environment. The Pt−C and Pt−N distances are within the range found for other similar compounds.[1,6,9,11] The three C_6F_5 rings are not perpendicular to the molecular plane (dihedral angles 64.3, 67.4 and 69.5°). Once all the heavy atoms of the structure had been located and their positions refined, the hydrogen atoms of the diphenyl-2-pyridylmethane ligand were located as peaks in the difference density maps and refined without constraints. We thus found a C(24)−H(24) distance of 0.90(7) Å and H(24)−C(24)−C angles ranging from 102(4) to 107(4)°. The Pt···C(24) distance was 3.344(9) Å. The C(24)−H(24) vector was directed towards the platinum atom and the Pt···H(24) distance was 2.65(7) Å. This distance is the range in which M···H interactions have been reported.[7,9] The Pt−H(24)−C(24) angle was 135(5)°.

Table 1 Selected bond distances (Å) and angles (°) and their estimated standard deviations for $[NBu_4][Pt(C_6F_5)_3(NC_5H_4CHPh_2\text{-}2)]\cdot 0.5C_6H_5Me$

Pt–C(1)	2.045(8)	Pt–C(7)	2.039(9)
Pt–C(13)	1.986(9)	Pt–N(1)	2.117(7)
Pt ··· C(24)	3.344(9)	Pt ··· H(24)	2.65(7)
C(24)–H(24)	0.90(7)		
C(1)–Pt–C(7)	175.6(3)	C(1)–Pt–C(13)	88.3(3)
C(1)–Pt–N(1)	92.7(3)	C(7)–Pt–C(13)	92.7(3)
C(7)–Pt–N(1)	86.4(3)	C(13)–Pt–N(1)	178.6(3)
Pt–N(1)–C(19)	126.5(5)	Pt–N(1)–C(23)	115.0(6)
Pt ··· H(24)–C(24)	135(5)		

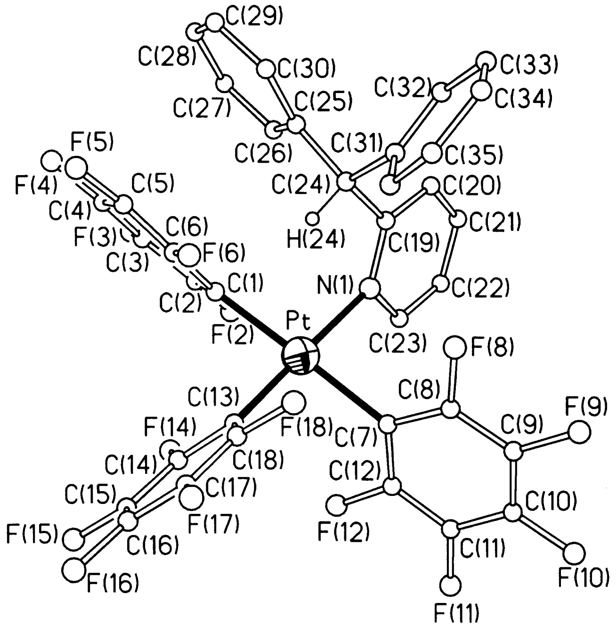

Fig. 1 Crystal structure of the anion of $[NBu_4][Pt(C_6F_5)_3(NC_5H_4CHPh_2\text{-}2)]\cdot 0.5C_6H_5Me$, showing the atom labelling scheme. Heavy atoms are represented by their 50% probability ellipsoids

NMR studies on complexes 4–6

The 2-hydroxyaniline, 2-isopropylaniline and 2-(diphenylphosphino)benzaldehyde ligands are less rigid than those used for the syntheses of complexes **1–3**. In this case, the donor atom of the ligand, N or P, is not part of the aromatic ring system. Hence, rotation about the N–C or P–C bond as well as rotation of the 2 substituent could take place.

The ^1H NMR spectrum of complex **4** [$(CD_3)_2CO$, room temperature] was poorly resolved. This was not improved at lower temperatures. The hydroxy hydrogen atom appears at δ 8.34 as a relatively broad signal without platinum satellites. In the case of free L, the analogous signal appears at about δ 7 as a very broad resonance. The two protons bonded to the nitrogen donor atom appear at δ 5.59 with platinum satellites [$J(\text{Pt–H}) = 30$ Hz]. There is therefore no evidence of a Pt ··· HO interaction.

For complex **5** the signal corresponding to the $NH_2C_6H_4\text{-}C\mathit{H}Me_2$ hydrogen in the ^1H NMR spectrum [$(CD_3)_2CO$, room temperature] appears as a multiplet at δ 3.87 which represents a downfield shift of 0.88 ppm with respect to the analogous signal of free L and no platinum satellites are observed. The methyl groups appear at δ 1.21, practically at the same chemical shift as for the free L (δ 1.23). These data suggest that the hydrogen bonded to the tertiary carbon atom of the isopropyl group is located over the co-ordination plane (and thus the methyl groups are in the opposite direction). This is a logical disposition in order to avoid steric hindrance. Despite the fact that the situation seems to be optimal, from a geometric point of view, for establishing some kind of Pt ··· H interaction, it is not possible to conclude its existence due to the absence of coupling with the ^{195}Pt nucleus.

The 2-(diphenylphosphino)benzaldehyde ligand present in complex **6** has a similar skeleton to the aniline ligands used for **4** and **5**. It has a hydrogen atom in a suitable position to interact with the platinum centre. In addition, this hydrogen atom belongs to an aldehyde fragment and thus it has a certain electropositive character. Nevertheless, in the ^1H NMR spectrum ($CDCl_3$, room temperature) of **6** the only remarkable fact is that the signal caused by this hydrogen atom shifts from δ 10.47 for free L to δ 11.42. No coupling with the platinum centre is observed. Again, there is no evidence of any Pt ··· H interaction.

The ^{19}F NMR spectra of complexes **4–6** are similar. In all three cases the pentafluorophenyl ligands appear as AA′MM′X spin systems, the mutually *trans* being magnetically equivalent. Thus two sets of three signals, one for each type of fluorine atoms (*ortho*, *meta* and *para*), with 2 : 1 relative intensities are observed.

Conclusion

The synthesis of $[Q][Pt(C_6F_5)_3L]$ complexes containing ligands L with hydrogen atoms located in such a way that Pt ··· H interactions could be present has been achieved. We have carefully studied their ^1H NMR spectra in solution and in most cases have detected a significant displacement towards higher frequency of the signal due to the hydrogen that could be involved in a Pt ··· H interaction. However, the shift in the signal is not sufficient proof of a significant interaction since it could, in principal, also be caused by the anisotropic deshielding effect of the $5d_{z^2}$ orbital electron density. The presence of coupling between the metal centre and the hydrogen atoms would be much more conclusive. We did not find such coupling for any of the complexes studied. In previous work,[6] in which we found Pt ··· H bridging interactions, it was concluded that there are several factors which are decisive for such interactions to exist. One is the existence of electron density at the metal which can be donated to the hydrogen atom. Another is a certain electropositive character of the contacting hydrogen atom. Finally, the rigidity of the ligand skeleton seems to be very important in fixing the hydrogen atom in a suitable position.

The chief difference between the ligands used in complexes **1–6** and the quinoline-type ones in our previous work[6] is the rigidity of their skeletons. Whereas the three aromatic, condensed rings of the quinolines restrain the freedom of the potentially interacting hydrogen, the present pyridine or aniline and phosphine ligands have single σ C–C or C–N bonds which allow rotation or twisting of the substituents containing the hydrogen atom. This probably precludes that any stable Pt ··· H interaction in solution which can be detected by ^1H NMR spectroscopy. Thus, the ligand structural features are a decisive factor in the establishment of Pt ··· H interactions.

In the solid state we have found a Pt ··· H distance of 2.65(7) Å for complex **1**, in the range reported for this kind of Pt ··· H interactions,[7,9] *i.e.* such an interaction in the solid state could be present. Nevertheless, it is necessary to be cautious since the geometry of the ligand has been chosen precisely to enforce the proximity of the hydrogen atoms to the metal. We consider that with the data available it is not possible either to confirm nor to discard the presence of a Pt ··· H interaction in **1**.

Experimental

General procedures

Analyses C, H and N were carried out with a Perkin-Elmer 240B microanalyser. Infrared spectra were recorded over the range 4000–200 cm^{-1} on a Perkin-Elmer 883 or 1710 FTIR spectrophotometer using Nujol mulls between polyethylene sheets, ^{1}H, ^{13}C and ^{19}F NMR spectra on a Varian XL-200 or a Unity-300 spectrometer in $CDCl_3$ or $(CD_3)_2CO$ solutions and were referenced externally to $SiMe_4$ (^{1}H and ^{13}C) and $CFCl_3$ (^{19}F). The complexes $[NBu_4]_2[Pt(C_6F_5)_3Cl]$[12] and $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$[13] were prepared as described elsewhere; $[PPh_3Me]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ was prepared using $[PPh_3Me]_2[Pt(C_6F_5)_3Cl]$ as starting material in the same way as the tetrabutylammonium salt. The N-donors were obtained from commercial sources and used as delivered. All the reactions in which a silver reagent was used were carried out with exclusion of light.

Preparations

$[NBu_4][Pt(C_6F_5)_3L]$ (L = diphenyl-2-pyridylmethane 1, 2-benzylpyridine 2, 2-(hydroxymethyl)pyridine 3 or 2-hydroxyaniline 4). To a solution of $[NBu_4]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (0.278 g, 0.148 mmol) in CH_2Cl_2 (20 cm^3) was added 0.296 mmol of L (**1**, 0.073 g; **2**, 48.5 μl; **3**, 30.0 μl; **4**, 0.032 g). The mixture was stirred at room temperature for 3 h and then the solvent was evaporated to dryness. The residue was treated with Pr^iOH rendering complexes **1–4**. Yields 71, 79, 90 and 71% respectively.

$[PPh_3Me][Pt(C_6F_5)_3(H_2NC_6H_4Pr^i\text{-}2)]$ 5. To a solution of $[PPh_3Me]_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (0.274 g, 0.141 mmol) in CH_2Cl_2 (20 cm^3) was added 2-isopropylaniline (41.2 μl, 0.282 mmol). The mixture was stirred at room temperature for 2 h and then the solvent was evaporated to dryness. The white residue was treated with Pr^iOH rendering complex **5** in 77% yield.

$[NBu_4][Pt(C_6F_5)_3(2\text{-}Ph_2PC_6H_4CHO)]$ 6. To a solution of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ (0.250 g, 0.205 mmol) in CH_2Cl_2 (20 cm^3) was added 2-(diphenylphosphino)benzaldehyde (0.060 g, 0.205 mmol) and $AgClO_4$ (0.043 g, 0.205 mmol), precipitating AgCl instantaneously. The mixture was stirred at room temperature for 20 min. The precipitated AgCl was filtered off and the resulting solution evaporated to dryness. The oily residue was washed with Pr^iOH (15 cm^3) giving complex **6** as a white solid. Yield: 40%.

Crystals of 1: structure determination. Suitable crystals for X-ray purposes were obtained by slow evaporation of a saturated $CHCl_3$ solution of complex **1** in a toluene atmosphere at 4 °C.

Analytical and spectroscopic data

Complex **1** [Found (Calc.): C, 52.95 (52.75); H, 4.8 (4.35); N, 2.15 (2.35)%]. IR 802s, 787m, 771s (C_6F_5 X-sensitive); 1635m, 1601m, 1495vs, 1056vs, 954vs (C_6F_5 others); 1608m, 1277m, 1173m, 1161m, 766s, 753m, 740s, 698s, 675w, 628w, 617m, 609m (L); 886m cm^{-1} (NBu_4^+). NMR [$(CD_3)_2CO$, room temperature]: ^{1}H, diphenyl-2-pyridylmethane, δ 6.98 (several signals, 4 H), 7.14 (several signals, 6 H), 7.25 (several signals, 2 H), 7.55 (s, 1 H), 7.77 (td, 1 H), 9.37 [d, 1 H, J(Pt–H) = 27]; NBu_4^+, 0.96 (t, 12 H, CH_3), 1.44 (m, 8 H, α-CH_2), 1.82 (m, 8 H, β-CH_2), 3.46 (m, 8 H, γ-CH_2); ^{19}F, δ −116.60 and −117.86 (overlapped signals, 6 F, o-F), −167.66 (4 F, m-F), −168.19 (2 F, p-F), −170.07 (2m-F + 1p-F); ^{13}C, diphenyl-2-pyridylmethane, δ 164.09, 153.98, 143.46, 137.02, 129.65, 128.25, 127.51, 126.59, 122.83 [J(Pt–C) = 29], 55.20 [J(Pt–C) = 40 Hz]; NBu_4^+, 59.08, 24.10, 20.08, 13.54.

Complex **2** [Found (Calc.): C, 49.45 (49.85); H, 4.35 (4.3); N, 2.5 (2.5)%]. IR 805s, 787m, 770s (C_6F_5 X-sensitive); 1633m, 1604m, 1498vs, 1056vs, 956vs (C_6F_5 others); 1568m, 1277m, 1161m, 762s, 747m, 705m, 621w (L); 883m cm^{-1} (NBu_4^+). NMR (room temperature): ^{1}H ($CDCl_3$), 2-benzylpyridine, δ 5.06 (s, 1 H), 6.71 (d, 1 H), 6.92 (d, 2 H), 7.25 (several signals, 3 H), 7.39 (t, 1 H), 9.13 [d, 1 H, J(Pt–H) = 27]; NBu_4^+, 0.91 (t, 12 H, CH_3), 1.36 (m, 8 H, α-CH_2), 1.57 (m, 8 H, β-CH_2), 3.07 (m, 8 H, γ-CH_2); ^{19}F ($CDCl_3$), δ −117.81 [2 o-F, J(Pt–F) = 570.4], −118.72 [4 o-F, J(Pt–F) = 373.4], −166.0 and −168.0 (complex signals due to overlapping of m- and p-F); ^{13}C [$(CD_3)_2CO$], 2-benzylpyridine, δ 163.59, 153.29, 139.25, 137.10, 129.81, 128.92, 126.84, 125.75, 122.45 [J(Pt–C) = 40], 45.10 [J(Pt–C) = 52 Hz]; NBu_4^+, 59.15, 24.11, 20.10, 13.54.

Complex **3** [Found (Calc.): C, 46.25 (45.85); H, 4.25 (4.15); N, 2.65 (2.65)%]. IR 805s, 787m, 771s (C_6F_5 X-sensitive); 1633m, 1608m, 1498vs, 1055vs, 956vs (C_6F_5 others); 1568m, 1277m, 1161m, 762s, 747m, 705m, 621w (L); 885m cm^{-1} (NBu_4^+). NMR (room temperature): ^{1}H [$(CD_3)_2CO$], 2-(hydroxymethyl)pyridine, δ 4.99 (t, 1 H), 5.53 (d, 2 H), 7.40 (t, 1 H), 7.83 (br, 1 H), 7.98 (t, 1 H), 9.32 [d, 1 H, J(Pt–H) = 32]; NBu_4^+, 1.09 (t, 12 H, CH_3), 1.62 (m, 8 H, α-CH_2), 1.99 (m, 8 H, β-CH_2), 3.65 (m, 8 H, γ-CH_2); ^{19}F [$(CD_3)_2CO$], δ −116.19 [2 o-F, J(Pt–F) = 563.1], −116.99 [4 o-F, J(Pt–F) = 379.5], −166.5 and −168.6 (complex signals due to overlapping of m- and p-F); ^{13}C ($CDCl_3$), 2-(hydroxymethyl)pyridine, δ 161.08, 153.12, 136.76, 124.15, 123.06 [J(Pt–C) = 27], 65.41 [J(Pt–C) = 31 Hz]; NBu_4^+, 58.66, 23.67, 19.46, 13.30.

Complex **4** [Found (Calc.): C, 45.55 (45.85); H, 4.0 (4.15); N, 2.45 (2.65)%]. IR 807s, 789m, 774s (C_6F_5 X-sensitive); 1634m, 1605m, 1500vs, 1059vs, 957vs (C_6F_5 others); 3328m, 1573s, 1347m, 1279s, 1225s, 1126s, 1002m, 860m, 753s, 741m, 451m (L); 880m cm^{-1} (NBu^+). NMR ($CDCl_3$, room temperature): ^{1}H, 2-hydroxyaniline, δ 5.59 [br, 2 H, J(Pt–H) = 30], 6.59 (br, 2 H), 6.66 (br, 1 H), 7.17 (br, 1 H), 8.34 (br, 1 H); NBu_4^+, 0.96 (br, 12 H, CH_3), 1.41 (br, 8 H, α-CH_2), 1.82 (br, 8 H, β-CH_2), 3.44 (br, 8 H, γ-CH_2); ^{19}F, δ −118.87 [2 o-F, J(Pt–F) = 553.0], −119.56 [4 o-F, J(Pt–F) = 361.6 Hz], −164.36 (2 p-F), −165.55 (4 m-F), −167.21 (1 p-F).

Complex **5** [Found (Calc.): C, 49.8 (49.85); H, 3.15 (2.8); N, 1.25 (1.25)%]. IR 806s, 786m, 769s (C_6F_5 X-sensitive); 1634m, 1605m, 1497vs, 1057vs, 957vs (C_6F_5 others); 3372m, 3306m, 1598m, 948s, 903s, 818m, 535m (L); 1595m, 1278m, 1113s, 1045s, 998m, 897s, 761s, 747s, 690s, 508s, 502s, 488s, 443m cm^{-1} (PPh_3Me^+). NMR [$(CD_3)_2CO$, room temperature]: ^{1}H, 2-isopropylaniline, δ 1.21 (d, 6 H), 3.87 (q, 1 H), 5.59 [br, 2 H, J(Pt–H) = 45], 6.86 (overlapped signals, 2 H), 6.98 (overlapped signals, 2 H); PPh_3Me^+, 3.85 (d, 3 H, CH_3), 7.82 (overlapped signals, 15 H); ^{19}F, δ −115.85 [2 o-F, J(Pt-F) = 568.8], −115.94 [4 o-F, J(Pt–F) = 370.6 Hz], −166.67 (overlapped signals, 6 F), −168.80 (overlapped signals, 4 F).

Complex **6** [Found (Calc.): C, 51.55 (51.8); H, 4.3 (4.2); N, 0.9 (1.15)%]. IR 797s, 774s (C_6F_5 X-sensitive, partially masked by phosphine); 1636m, 1606m, 1497vs, 1056vs, 956vs (C_6F_5 others); 1695s, 1588m, 1200m, 1097m, 823m, 704s, 541s, 520s, 509m (L); 882m cm^{-1} (NBu^+). NMR (room temperature): ^{1}H ($CDCl_3$), 2-(diphenylphosphino)benzaldehyde, δ 6.94 (t, 1 H), 7.3 (overlapped signals, 12 H), 7.84 (br, 1 H), 11.42 (br, 1 H); NBu_4^+, 0.93 (t, 12 H, CH_3), 1.34 (m, 8 H, α-CH_2), 1.64 (br, 8 H, β-CH_2), 3.18 (br, 8 H, γ-CH_2); ^{19}F [$(CD_3)_2CO$], δ −115.73 [4 o-F, J(Pt–F) = 315.6], −117.34 [2 o-F, J(Pt–F) = 413.4 Hz], −165.92 (overlapped signals, 9 F).

Crystallography

Crystal data. $C_{52}H_{51}F_{15}N_2Pt\cdot0.5C_6H_5CH_3$ **1**, M = 1230.0, triclinic, space group $P\bar{1}$ (no. 2), a = 9.880(2), b = 11.934(3), c = 23.931(6) Å, α = 94.32(2), β = 91.82(2), γ = 111.61(2)°, U = 2610.4(10) Å^3 (by least-squares refinement of diffractometer angles from 72 centred reflections including Friedel pairs, $20.5 < 2\theta < 28.3°$), T = 223 K, graphite-monochromated Mo-Kα radiation, λ = 0.710 73 Å, Z = 2, D_c = 1.55 Mg m^{-3}, F(000) = 1212, colourless prism with dimensions 0.74 × 0.16 × 0.16 mm, μ(Mo-Kα) = 2.8 mm^{-1}.

Semiempirical absorption correction based on Ψ scans, transmission factors 0.70–0.82; Siemens AED2/STOE diffractometer with Oxford Cryogenics low-temperature attachment, ω–2θ scans, data collection range $4 < 2\theta < 47°$, $+h$, $\pm k$, $\pm l$, three standard reflections showed no significant variation in intensity; 7847 reflections measured, 7633 unique ($R_{int} = 0.033$), 6474 of which had $F_o^2 \geqslant 4\sigma(F_o^2)$.

The structure was solved by direct methods and developed and refined in series of alternating Fourier-difference maps and least-squares analyses using all data and the program SHELXL 93.[14] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the diphenyl-2-pyridylmethane ligand were located from electron-density maps and their coordinates and thermal parameters refined with no constraints. Those of NBu_4^+ were constrained to idealised geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their attached carbon (1.5 times for the methyl hydrogen atoms). In the unit cell there is a toluene solvent molecule disordered over two sets of positions. One of the six membered rings is formed by atoms C(60), C(61), C(62), C(63), C(60′) and C(64′), C(62′) being the methyl carbon atom. The other molecule is generated by the centrosymmetric carbon atoms related by an inversion centre at ($\frac{1}{2}$, 0, $\frac{1}{2}$). The bond distances within the toluene molecule were constrained and a common set of thermal anisotropic parameters was used for all the carbon atoms. The weighting scheme was $[\sigma_c^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [0.333\max(F_o^2,0) + 0.667F_c^2]$, $\sigma_c^2(F_o^2)$ is the variance in F_o^2 due to counting statistics, and $a = 0.053$, $b = 19.18$ were chosen to minimise the variation in σ as a function of $|F_o|$. Full-matrix least-squares refinement of this model against F^2 converged to final residual indices $R1$ 0.047 and $wR2(F)$ 0.111 (R factors defined in ref. 14), goodness of fit 1.05. Final electron-density difference maps showed three peaks above 1 e Å^{-3} (1.48, 1.30, 1.09; largest difference hole −1.31) lying 1.18 Å from the platinum atom.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/452.

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