The Synthesis by Decarboxylation Reactions and Crystal Structures of 1,n−Bis(diphenylphosphino)alkane(pentafluorophenyl)-platinum(II) Complexes

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Abstract. Decarboxylation reactions between the complexes *cis*−[$PtCl_2L$] (L = 1,n−bis(diphenylphosphino)−ethane (n = 2, dppe), −propane (n = 3, dppp) or −butane (n = 4, dppb)) and thallium(I) pentafluorobenzoate in pyridine give *cis*−[$PtCl(C_6F_5)L$] and *cis*−[$Pt(C_6F_5)_2L$] complexes in high yields with short reaction times. X−ray crystal structures of *cis*−[$PtCl(C_6F_5)$(dppe)] · 0.5 C_5H_5N, *cis*−[$PtCl(C_6F_5)$(dppp)], *cis*−[$PtCl(C_6F_5)$(dppb)] · C_3H_6O, *cis*−[$Pt(C_6F_5)_2L$] (L = dppe, dppp and dppb) and the reactants *cis*−[$PtCl_2$(dppp)] (as a CH_2Cl_2 solvate) and *cis*−[$PtCl_2$(dppb)] show monomeric structures with chelating diphosphine ligands in all cases rather than dimers with bridging diphosphines. ^{31}P NMR data are consistent with these structures in solution.

Keywords: Platinum; Diphosphine; Chelates; Decarboxylation; Pentafluorophenyl; Crystal structures

Introduction

Decarboxylation reactions of metal carboxylates can provide useful syntheses of organometallic compounds [1−5]. Thermally induced reactions are effective for molecules with electron withdrawing substituents in the organic group, particularly polyfluorphenyl compounds [1, 4, 5], where the method is competitive with Grignard and organolithium routes and simpler to carry out. Radical induced decarboxylation has enjoyed considerable success in the synthesis of organomercurials [1−4], and has limited extensions to cobalt [6] and platinum [7]. Thermal decarboxylation has mainly been used to give main group organometallics [1−4, 8], but some transition metal compounds can be accessed [1−5], the most recent application being to iridium compounds [9]. The method should be particularly suited to organoplatinum compounds, which are relatively robust, but so far it has been used only to give polyfluoroaryls with heterocyclic nitrogen donors [10] and a number of hemidecarboxylated tetrafluorophthalates [11] (see [7] for hydrocarbon analogues via radical decarboxylation).

We now present syntheses of mono− and bispentafluorphenylplatinum(II) complexes with 1,n−bis(diphenylphosphino)alkanes (n = 2 (dppe), 3 (dppp) and 4 (dppb)) by decarboxylation, together with crystal structures of the products. This establishes the generality of the method for pentafluorophenylplatinum(II) complexes with chelating diphosphines. With the largest chain phosphine $Ph_2P(CH_2)_4PPh_2$, it is of interest as to whether the ligand is chelating with a seven membered ring or whether bridging to give a dimer is preferred. Chelating has been proposed for [$PtCl_2L$] (L = dppe, dppp, dppb) in both solid state and solution on the basis of NMR measurements [12] and is supported by X−ray crystallography for L = dppe [13] or dppp [14], but not for L = dppb, and the structure of *cis*−[$PtCl_2$(dppb)] is now reported.

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Results and Discussion

Syntheses

Both *cis*−[$PtCl(C_6F_5)L$] (**1**−**3**) and *cis*−[$Pt(C_6F_5)_2L$] (**4**−**6**) (L = dppe (**1**, **4**), dppp (**2**, **5**), dppb (**3**, **6**)) complexes can be prepared in high yields with short reaction times by decarboxylation (eq. (1) and (2)), if platinum to thallium ratios of 1:1 and 1:3.0−3.5 respectively are employed (Table 1). An attempted synthesis of *cis*−[$Pt(C_6F_5)_2$(dppp)] (**5**) using a 1:2 ratio gave a mixture of this compound (major product) and *cis*−[$PtCl(C_6F_5)$(dppp)] (**2**). Whilst they can be readily separated by chromatography (column or TLC), this step is avoidable with appropriate stoichiometric control. In general shorter reaction times can be used for *cis*−[$PtCl(C_6F_5)L$] than *cis*−[$Pt(C_6F_5)_2L$]. Some of the former have been obtained at temperatures below reflux, one even at room temperature, but use of boiling pyridine is needed to give *cis*−[$Pt(C_6F_5)_2L$] in high yields. Given that $TlO_2CC_6F_5$ is readily prepared in bulk amounts and can be stored indefinitely [15], the short reaction time and simple procedure make decarboxylation a far more convenient preparative method for these complexes than the corresponding synthesis from C_6F_5Li (or from the Grignard reagent), which has been used to give **4** [16] and **1** [17].

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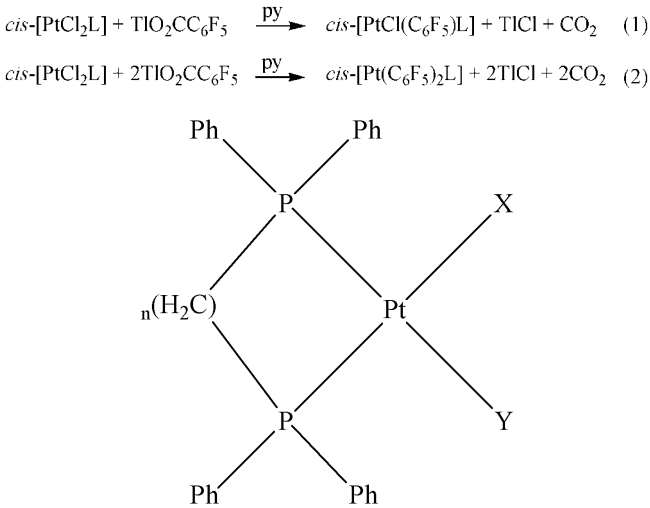
Table 1 Syntheses of organodiphosphineplatinum(II) complexes by decarboxylation

Platinum complex	n [mmol]	n($TlO_2CC_6F_5$) [mmol]	t [min]	Organoplatinum(II) Products	Yield %	CO_2 %
cis−[$PtCl_2$(dppe)]	0.55	0.55	10	*cis*−[$PtCl(C_6F_5)$(dppe)]	72	100
cis−[$PtCl_2$(dppe)]	0.43	0.43	ON RT	*cis*−[$PtCl(C_6F_5)$(dppe)]	75	–
cis−[$PtCl_2$(dppe)]	0.45	0.45	4 h 60 °C	*cis*−[$PtCl(C_6F_5)$(dppe)]	94	98
cis−[$PtCl_2$(dppe)]	0.55	1.70	10(30)	*cis*−[$Pt(C_6F_5)_2$(dppe)]	83(90)	96(90)
cis−[$PtCl_2$(dppp)]	0.50	0.50	15	*cis*−[$PtCl(C_6F_5)$(dppp)]	82	99
cis−[$PtCl_2$(dppp)]	0.73	0.73	120	*cis*−[$PtCl(C_6F_5)$(dppp)][a]	97	99
cis−[$PtCl_2$(dppp)]	0.50	1.00	15	*cis*−[$Pt(C_6F_5)_2$(dppp)] / *cis*−[$PtCl(C_6F_5)$(dppp)][b]	71/ 17	100
cis−[$PtCl_2$(dppp)]	0.59	1.83	120	*cis*−[$Pt(C_6F_5)_2$(dppp)]	99	86
cis−[$PtCl_2$(dppp)]	0.91	3.18	120	*cis*−[$Pt(C_6F_5)_2$(dppp)]	99	100
cis−[$PtCl_2$(dppb)]	0.79	0.79	60	*cis*−[$PtCl(C_6F_5)$(dppb)]	87	93
cis−[$PtCl_2$(dppb)]	0.55	1.70	30	cis−[$Pt(C_6F_5)_2$(dppb)]	83	92

[a] At 80 °C. Similar yield at boiling point.
[b] Separated by preparative TLC.



X	Y	n = 2	n = 3	n = 4
C_6F_5	Cl	**1**	**2**	**3**
C_6F_5	C_6F_5	**4**	**5**	**6**
Cl	Cl		**7**	**8**

Characterization

All complexes were obtained microanalytically pure, **3** being obtained as an acetone solvate (confirmed by IR, NMR and X−ray crystallography, below). The acquisition of C_6F_5 ligands was evident from IR absorption bands at ca. 1500 (ν(CC)), 1060−1055 and 960−955 cm^{-1} (ν(CF)) for all compounds. Whilst the *cis*−[$PtCl(C_6F_5)$L] complexes exhibit a single band at 785 cm^{-1} attributable to a mode involving platinum−carbon stretching [18, 19], two bands at 795−775 cm^{-1} for each of the *cis*−[$Pt(C_6F_5)_2$L] complexes is indicative of *cis*-C_6F_5 ligands. In the ^{1}H NMR spectra, the ortho hydrogen atoms of *cis*−[$PtCl(C_6F_5)$L] complexes are split into two groups, one similar to values for *cis*−[$Pt(C_6F_5)_2$L] and one similar to *cis*−[$PtCl_2$L]. The ^{19}F NMR chemical shifts of each class are little affected by change in diphosphine ring size with the chloride ligands at slightly lower frequencies. Larger ^{3}J(Pt,F) coupling constants are observed for **4**−**6** than **1**−**3**, consistent with *cis*−C_6F_5 groups in each and opposite to the trend for compounds with *trans*−C_6F_5 groups [18]. There is a marginal increase in ^{3}J(PtF) for *cis*−[$PtCl(C_6F_5)$L] species with increasing ring size, but for the *cis*−[$Pt(C_6F_5)_2$L] complexes the largest coupling is observed for **5**. For the ^{31}P NMR spectra, the chemical shifts are closely similar to those of the corresponding *cis*−[$PtCl_2$L] complexes, except for **3** where the two resonances are separated by 21 ppm, but the average corresponds to the chemical shift of the dichloro complex. As *cis* stereochemistry in both solid state and solution has been established by NMR spectroscopy for *cis*−[$PtCl_2$L] [12], supported by our determination of the missing X−ray structure of **8** (Tables 2 and 3), *cis* monomeric structures for **1**−**6** in solution are clearly indicated. For P *trans* to Cl of *cis*−[$PtCl(C_6F_5)$L], the ^{1}J(Pt,P) coupling constants are similar to those of *cis*−[$PtCl_2$L] [12] though the values are somewhat larger for the monochlorides with the difference increasing (ca. 100, 200, 300 Hz) with increasing ring size. Likewise, the values for P *trans* to C_6F_5 are in general agreement with P *trans* to an aryl carbon atom including fluorocarbon groups [7, 11, 17] with larger values for **4**−**6** than **1**−**3**, paralleling the behaviour of ^{3}J(Pt,F). Again the difference increases with increasing ring size (ca. 50, 100, 200 Hz). On the other hand for both groups of complexes the smallest ^{1}J(Pt,P) value in any sequence is observed with the dppp complexes **2** and **5**.

Electron impact mass spectra of representative complexes show monomer parent ions and appropriate derived ions, but the intensities of the former are low presumably due to poor volatility. Electrospray mass spectra give high intensity $[M(monomer)+Na]^+$ and/or $[M(monomer)+X]^-$ (X = Cl, O_2CH, CO_2CCF_3, etc.) peaks, but are complicated by significant cluster ions ($[2M+Na]^+$, $[2M+Cl]^-$). These decline in intensity on dilution and presumably arise through Cl^-

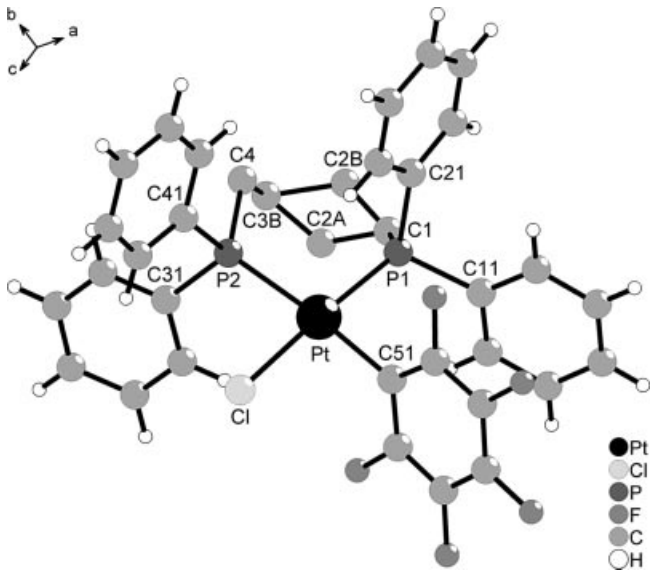


Fig. 1 Molecular structure of *cis*-[PtCl(C_6F_5)(dppb)] (**3**), showing disorder of C2A/B of the bridging carbon chain, hydrogen atoms for the bridge have not been shown for simplicity.

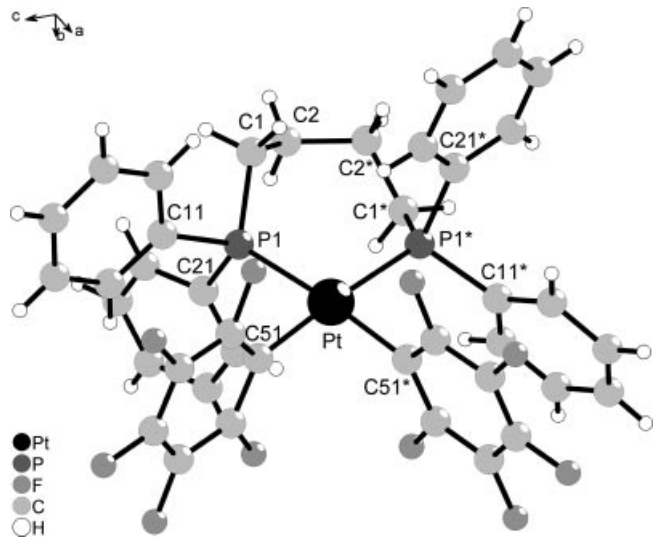


Fig. 2 Molecular structure of *cis*-[Pt(C_6F_5)$_2$(dppb)] (**6**); symmetry related atoms (x, 0.5−y, z) indicated by *.

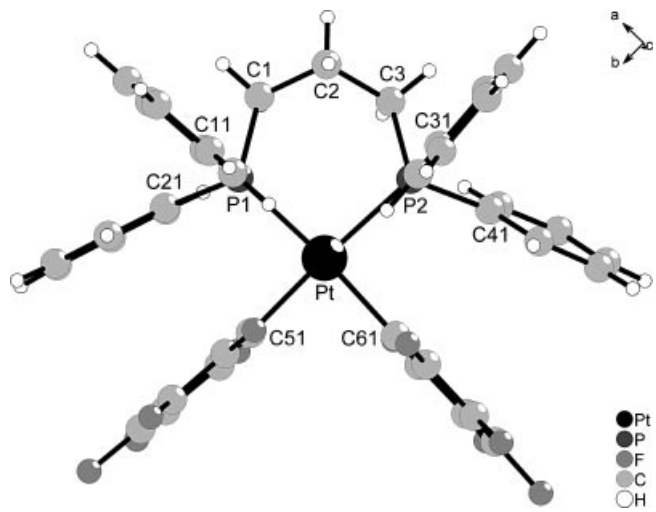


Fig. 3 Molecular structure of *cis*-[Pt(C_6F_5)$_2$(dppp)] (**5**).

or Na^+ linking two monomers. It is unlikely that diphosphine bridged dimers are present at the very high dilution of ESMS measurements, given the strong evidence from ^{31}P NMR spectra above for *cis*−monomeric complexes as single species at much higher concentrations.

X−ray crystal structures

X-ray crystal structures have been determined for **1**−**6** as well as *cis*-[$PtCl_2$(dppp)] · CH_2Cl_2 (**7**) and *cis*-[$PtCl_2$(dppb)] (**8**). Single crystals of **1** and **3** were obtained as solvates, **1** 0.5 pyridine and **3** C_3H_6O, although the bulk sample of **1** was obtained pyridine free. Representative structures **3**, **5** and **6** are shown in Figures 1−3, selected bond distances and angles for **1**−**6** are listed in Table 2 and corresponding data for *cis*−[$PtCl_2$L] have been deposited.

In the solid state, all complexes are monomeric with *chelating* diphosphines and *cis* anionic ligands. Specifically, dppb, which is the most likely ligand to bridge, gives seven membered chelate rings in all three complexes **3**, **6** and **8**. In the light of these results, it is likely that [Pt(C_6Cl_5)$_2$(dppb)], which has not been structurally characterized [20], has a similar arrangement. There is some deviation from square planar stereochemistry, most notably seen in the increase in the P1−Pt−P2 bite angle with increasing ring size, and this is compensated by a sterically disfavoured decrease in C51−Pt−C61 angles for **4**−**6** and in P2−Pt−Cl angles for **1**−**3**. Analogous effects are seen between the dichlorides **7** and **8**. There is little displacement (0−10.9(3) pm) of donor atoms and platinum from the best fit plane of the five atoms, the deviation being greatest with L = dppp complexes (**2** and **5**). All corresponding Pt−donor atom bond distances of **1**−**3** are similar to each other and to those of *cis*−[PtCl(C_6F_5)(dppm)] (dppm = $Ph_2PCH_2PPh_2$) [21], hence they are unaffected by changes in ring size from n = 1−4 and even differences in solvation. In the case of the dichlorides, one Pt−P distance increases slightly (outside the 3 esd limit) from a six membered (**7**) to a seven membered ring (**8**). The Pt−Cl and Pt−P1 (*trans* to Cl) distances are not affected by replacement of one Cl by C_6F_5. However the Pt−P2 (*trans* to C_6F_5) distances of **1**−**3** are longer (6−8 pm) then those *trans* to Cl, well outside error limits, consistent with known *trans* influences [22]. With **4**−**6**, there are slight Pt−(P,C) bond length increases from L = dppe (**4**) to L = dppp (**5**), corresponding with the largest increase in bite angle, perhaps arising from greater crowding, though the comparison is made less clear by there being two crystallographically different molecules of **4** in the unit cell. Surprisingly, the change from a six− to a seven−membered ring has little effect also on the bite

Table 2 Selected bond distances and angles in complexes **1**−**8** /pm, °

	1	**2**	**3**		**4** Mol. A	Mol. B	**5**	**6**		**7**	**8**
Pt−C51	208(1)	209.4(6)	206.8(7)	Pt−C51	203(1)	201(1)	207.4(7)	206.5(8)	Pt−Cl1	235.9(2)	236.2(1)
Pt−Cl	236.8(3)	237.0(1)	235.9(2)	Pt−C61	200(1)	202(1)	205.9(7)		Pt−Cl2		235.9(2)
Pt−P1	221.9(3)	222.9(2)	224.5(2)	Pt−P1	228.1(3)	227.4(3)	230.4(2)	231.0(2)	Pt−P1	223.9(2)	225.0(1)
Pt−P2	227.8(3)	231.4(1)	230.8(2)	Pt−P2	227.0(3)	227.4(3)	229.9(2)		Pt−P2		225.4(1)
P1−C1	183(1)	183.1(6)	183.9(8)	P1−C1	181.8(9)	183(1)	185.3(7)	186.5(5)	P1−C1	182.2(7)	183.4(5)
P1−C11	180(1)	182.1(5)	182.3(7)	P1−C11	179(1)	178(1)	181.8(8)	182.8(5)	P1−C11	179.8(7)	182.3(6)
P1−C21	181(1)	182.0(6)	183.3(7)	P1−C21	180(1)	178(1)	181.2(7)	182.5(6)	P1−C21	181.6(7)	181.3(6)
P2−C2/3/4	182.5(9)	181.3(6)	182.2(7)	P2−C2/3	183(1)	185.7(9)	182.9(7)		P2−C4		186.2(6)
P2−C31	180(1)	181.9(6)	182.0(7)	P2−C31	179(1)	178(1)	180.7(9)		P2−C31		181.8(6)
P2−C41	182(1)	181.3(6)	183.2(7)	P2−C41	182(1)	180(1)	182.7(6)		P2−C41		182.6(6)
C1−C2	154(1)	153.0(8)	151(2)	C1−C2	152(1)	152(2)	152(1)	151.5(8)	C1−C2	153.5(7)	154.3(9)
C2−C3		152.3(9)	146(2)	C2−C3/2[a]			154(1)	153(1)	C2−C3		150.4(9)
C3−C4			152(1)	C1[a]−C2[a]				151.5(8)	C3−C4		149.3(8)
C51−Pt−P1	90.4(3)	90.8(2)	90.9(2)	C51−Pt−P1	91.8(2)	92.1(3)	88.9(2)	88.6(2)	P1−Pt−Cl1	90.05(7)	85.59(5)
C51−Pt−P2	174.0(3)	173.5(2)	172.9(2)	C51−Pt−P2/1[a]	176.7(3)	176.8(3)	176.7(2)	175.1(2)	P1[b]2−Pt−Cl1	175.86(7)	179.04(5)
P1−Pt−P2	85.8(1)	93.79(5)	95.66(6)	P1−Pt−P2/1[a]	85.1(1)	85.2(1)	94.07(6)	96.3(1)	P1−Pt−P2	91.91(9)	95.37(5)
C51−Pt−Cl	90.7(3)	85.8(2)	86.0(2)	C51−Pt−C61/51[a]	90.5(3)	87.7(4)	87.2(2)	86.6(4)	Cl1−Pt−Cl2/1[b]	87.8(1)	87.83(5)
P1−Pt−Cl	178.3(1)	173.21(6)	176.88(7)	C61−Pt−P1	177.5(3)	178.8(4)	174.2(2)		P1−Pt−Cl2		170.17(6)
P2−Pt−Cl	93.0(1)	90.11(5)	87.45(6)	C61−Pt−P2	92.5(3)	95.0(3)	90.0(2)		P2−Pt−Cl2		91.21(5)
C1−P1−Pt	108.8(4)	116.4(2)	117.5(2)	C1−P1−Pt	107.2(3)	107.2(3)	117.1(3)	119.3(2)	C1−P1−Pt	116.6(2)	118.3(2)
C2/3/4−P2−Pt	107.2(4)	115.0(2)	120.0(2)	C2/3/1[a]−P2/1[a]−Pt	107.2(3)	107.6(3)	115.9(2)	119.3(2)	C4−P2−Pt		116.6(2)
C2−C1−P1	107.9(7)	113.8(4)	119.4(8)	C2−C1−P1	108.5(7)	108.1(7)	114.4(5)	117.8(4)	C2−C1−P1	115.3(6)	113.9(4)
C1/2/3−C2/3/4−P2	108.1(7)	117.8(4)	115.4(5)	C1/2/2[a]−C2/3/1[a]−P2/1[a]	107.7(7)	106.9(7)	112.7(5)	117.8(4)	C3−C4−P2		119.2(4)
C1−C2−C3		113.1(5)	120(1)	C1−C2−C3/2[a]			114.1(6)	116.8(5)	C1−C2−C1/3	114.4(9)	115.0(5)

[a] Transformations of the asymmetric unit: 1−x, y, −z
[b] Transformations of the asymmetric unit: x, 0.5−y, z

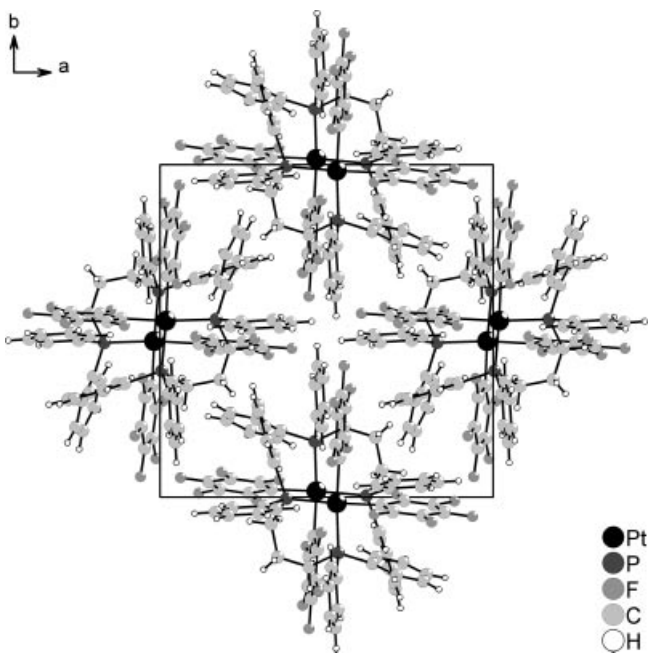


Fig. 4 Unit cell *cis*-[Pt(C_6F_5)$_2$(dppp)] (**5**), view along [001].

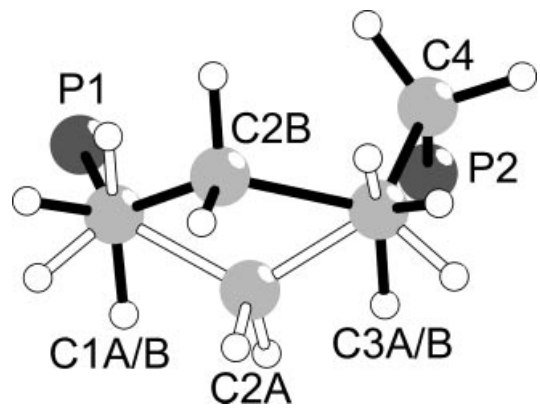


Fig. 5 Disordered carbon chain of *cis*-[PtCl(C_6F_5)(dppp)] (**3**).

angle and is evidently accommodated by the flexibility of the alkane chain.

Bond lengths of **4**−**6** are similar to corresponding reported distances for *cis*−[Pt(C_6F_5)$_2$P$_2$] complexes including bridged dimers [23−25]. Apart from the dppe complexes, the Pt−C distances are unaffected by the number of C_6F_5 groups.

With respect to intra− and inter−molecular packing, there is a tendency for the phenyl rings of the $Ph_2P(CH_2)_nPPh_2$ (n = 2−4) ligands and the C_6F_5 groups to cut the coordination plane at a similar angle (Fig. 4). For the dichlorides *cis*−[$PtCl_2$L] (L = dppe [13], dppp [14]), **7** and **8**, 3, 4 and 4 groups respectively meet this criterion. With **4**−**6** new motifs appear. Not only are all six rings orthogonal to the coordination plane but two near linear Ph−P−Pt−C_6F_5 alignments are evident in each, with the structural regularity least for **4**. This pattern is also found in **1**−**3**, where **1** has two rings orthogonal, **2** has three, and **3** has five rings cutting the coordination plane though not at 90° but at 70°. There is evidence that solvation upsets the regularity of the structures. For example in the pairs **5** and **5** · 2 C_3H_6O and *cis*−[$PtCl_2$(dppp)] and **7**, less rings are

orthogonal for the solvates than the unsolvated species. Thus, the unusual intersection angles of **3** may arise from solvation. Evidence of steric stress in **2**, **3**, **5** and **6** is provided by one or two close *ipso*−C(Ph) ··· *ipso*−C(C_6F_5) approaches (306−326 pm), which are well within the sum of two aryl van der Waals radii (346 pm) [26]. The corresponding values for **1** and **4** are larger (334−362 pm) as the aromatic rings are laterally displaced from each other. In the closest approach (**3**) the two rings are adjacent but divergent. In **1**−**6** phenyl rings are located above and below different Pt−P bonds such that *ortho*−hydrogen atoms (calculated positions) are situated above and below the platinum atom at 288−306 pm, essentially corresponding to the sum of the van der Waals radii of platinum and hydrogen (295 pm) [26, 27]. Uniquely in **6**, the C2−C2* bond lies aligned with the coordination plane.

There are close intermolecular contacts between hydrogen atoms (in calculated positions) and fluorine (227 pm) and chlorine (278 pm) respectively, which are smaller than the sum of the van der Waals radii (290 pm and 320 [26]) and are not sufficiently close to be indicative of possible H−bonding interactions. The alignment of phenyl rings extend through the crystal structure, quite spectacularly so for **5** (Fig. 4).

Conclusions

Pentafluorphenyl substituted diphosphine platinum(II) complexes *cis*−[PtXYL] (X = Cl or C_6F_5, Y = C_6F_5, L = dppe, dppp, dppb) are obtained in high yields with short reaction times by decarboxylation reactions. The X−ray crystal structures of these compounds and the reported dichloro substituted precursors show monomeric chelating complexes with *cis* geometry indicating that a seven membered chelate ring is preferred over a bridging dimeric arrangement for all three dppb complexes.

Experimental Part

General

All reactions were carried out under dry nitrogen using standard Schlenk techniques. Pyridine was dried by distillation from potassium hydroxide. Commercial $Ph_2P(CH_2)_2PPh_2$(dppe), $Ph_2P(CH_2)_3PPh_2$(dppp) and $Ph_2P(CH_2)_4PPh_2$(dppb) of >95 % purity were from Strem. The dichlorophosphine complexes were prepared as reported [28] and worked up by treatment with boiling ethanol−hydrochloric acid [29]. $TlO_2CC_6F_5$ was prepared as described [15]. Elemental analyses (C, H, F, Cl) were determined by the Australian Microanalytical Service, Melbourne, Australia and (C, H) by the Institut für Anorganische Chemie der Universität zu Köln, Germany. Infrared spectra were recorded with a Bruker IFS 66v/S instrument within the range of 4000−400 cm^{-1}. The spectra were obtained with KBr discs of the compounds. Weak and very weak IR bands have been omitted. Electrospray mass spectra were obtained using a Micromass Platform benchtop QMS with electrospray source or Bruker BioApec 47e FTMS with 4.7 T superconducting magnet and fitted with an Analytica electrospray source. Electron impact spectra were obtained on a VG Micromass 7070F spectrometer. NMR spectra were obtained on a Bruker DPX300 spectrometer. The complexes were dissolved in deuterochloroform. ^1H and ^{19}F NMR spectra are referenced to internal TMS and $CFCl_3$ respectively; the chemical shifts for the ^{31}P spectra are relative to external H_3PO_4 and P atoms are numbered as in the X−ray diagrams.

Decarboxylation procedure

The dichlorobisdiphenylphosphinealkane platinum(II) complexes and thallium(I) pentafluorobenzoate were mixed in 10 ml of dry pyridine and heated under reflux. The reactions were carried out under a slow nitrogen stream which was passed through a saturated barium hydroxide solution. The extent of decarboxylation (%CO_2) was gravimetrically determined as precipated barium carbonate and expressed as a percentage of total available CO_2. On completion of reaction, the pyridine was removed under vacuum at room temperature and the resultant residue washed with hexane (~30 ml). Extraction of the residue with boiling acetone (100 ml), filtration to remove thallium(I) chloride or insoluble impurities, and evaporation of the filtrate to dryness gave the organoplatinum complex. Amounts of reagents and yields are given in Table 1. The mixture of *cis*−[Pt(C_6F_5)$_2$ (dppp)] and *cis*−[PtCl(C_6F_5)(dppp)] (Table 1) was separated by preparative TLC on Kieselgel with $CHCl_3/CCl_4$ as eluent; column chromatography on Al_2O_3 with acetone/hexane (1:3.5) as eluent is also possible. TLC on neutral Al_2O_3 with the same eluent was used after all reactions to determine whether a single product was obtained.

***cis*−[PtCl(C_6F_5)(dppe)] (1):** $C_{32}H_{24}ClF_5P_2Pt$ (796.0 g/mol); M.p.: 251−253 °C; C 48.3 (calc. 48.3); H 2.9 (3.0); Cl 4.1 (4.5); F 12.2 (11.9) %.

IR cm^{-1}: 1499 vs, 1483 m(sh), 1454 vs, 1437 vs, 1354 m, 1105 s, 1067 m, 1053 s, 955 vs, 881 m, 824 m, 785 m, 748 m, 716 s, 706 s, 690 vs, 536 vs, 490 s, 440 m. **MS** (*m/z*) (%): **ESMS**(+): 1614 (40) [2M−Cl+C_3H_6O / 2M+Na]$^+$, 1210 (15), 877 (20) [M+Na+C_3H_6O]$^+$, 853 (20) [M+K+H_2O]$^+$, 835 (15) [M+K]$^+$, 818 (100) [M−Cl+C_3H_6O]$^+$, 804 (20) [Pt$O_2CC_6F_5$ (dppe)]$^+$, 760 (15) [M−Cl]$^+$; **MS**(EI): 796 (10) [M$^+$], 761 (10) [PtH(C_6F_5)dppe$^+$], 629 (45) [PtCldppe$^+$], 593 (100) [Ptdppe$^+$], 565 (20) [Pt(Ph_2P)$_2^+$], 303 (40) [Pt(PhP)$^+$]. **^1H NMR**: δ = 2.03−2.16 (m, 1 H, CH_2), 2.18−2.30 (m, 1 H, CH_2), 2.31−2.61 (m, 2 H, CH_2), 7.30−7.41 (m, 4 H, Ph), 7.43−7.62 (m, 12 H, Ph), 7.84−8.03 (m, 4 H, Ph). **^{19}F NMR**: δ = −119.3 (m with ^{195}Pt satellites ^{3}J(Pt,F) 268 Hz, 2 F, F(2,6)), −162.3 (m, 1 F, F(4)), −164.3 (m, 2 F, F(3,5)). **^{31}P NMR**: δ = 39.78 (d, J(P,P) 7 Hz, with ^{195}Pt satellites ^{1}J(Pt,P) 3720 Hz, 1 P, P(1)), 40.95 (m with ^{195}Pt satellites ^{1}J(Pt,P) 2251 Hz, 1 P, P(2)). From one preparation, colourless single crystals of *cis*−[PtCl(C_6F_5)(dppe)] · 0.5 py (1) were grown, but single crystals of the unsolvated species could not be obtained.

***cis*−[PtCl(C_6F_5)(dppp)] (2):** $C_{33}H_{26}ClF_5P_2Pt$ (810.0 g/mol); M.p.: 312−314 °C (dec.); C 48.6 (calc. 48.9); H 3.4 (3.2); Cl 4.4 (4.4); F 11.7 (11.7) %.

IR cm^{-1}: 1499 vs, 1485 m, 1456 vs, 1437 vs, 1414 m, 1358 m, 1153 m, 1103 s, 1068 m, 1055 s, 972 m, 955 vs, 837 m, 789 s, 744 s, 714 m(sh), 698 vs, 669 s, 532 m, 513 vs, 503 s, 482 m. **MS** (*m/z*) (%): **ESMS**(−): 1655 (40) [2M+Cl]$^-$, 845 (100) [M+Cl]$^-$; **MS**(EI): 810 (<1 %) [M$^+$], 774 (8) [Pt(C_6F_5)dppp$^+$], 643 (10) [PtCldppp$^+$], 607 (100) [Ptdppp$^+$], 565 (10) [Pt(Ph_2P)$_2^+$], 380 (10) [Pt(Ph_2P)$^+$], 303 (40) [Pt(PhP)$^+$]. **^1H NMR**: δ = 1.85−2.16 (m, 2 H, CH_2), 2.24−2.56 (m, 2 H, CH_2), 2.59−2.95 (m, 2 H, CH_2), 7.10−7.22 (m, 4 H, Ph), 7.27−7.54 (m, 12 H, Ph), 7.68−7.84 (m, 4 H, Ph). **^{19}F NMR**: δ = −119.4 (m with ^{195}Pt satellites ^{3}J(Pt,F) 274 Hz, 2 F, F(2,6)), −163.2 (m, 1 F, F(4)), −164.4 (m, 2 F, F(3,5)). ^{31}P NMR: δ = −3.82 (d, J(P,P) 28 Hz, with ^{195}Pt satellites ^{1}J(Pt,P) 3603 Hz, 1 P, P(1)), −4.09 (m with ^{195}Pt satellites ^{1}J(Pt,P) 2072 Hz, 1 P, P(2)).

***cis*−[PtCl(C_6F_5)(dppb)] (3):** Isolated as acetone solvate (see X-ray structure, Table 2 and 3) $C_{34}H_{28}ClF_5P_2Pt \cdot C_3H_6O$ (882.1 g/mol); M.p.: 267−269 °C; C 50.36 (calc. 50.38); H 3.84 (3.88) %.

Table 3 Crystal data and structure refinement for **1**−**3**, **7** and **8**

	1[a]	**2**	**3**	**7**	**8**
Crystal data					
Empirical formula	$C_{34.5}H_{24}ClF_5N_{0.5}P_2Pt$	$C_{33}H_{26}ClF_5P_2Pt$	$C_{37}H_{34}ClF_5OP_2Pt$	$C_{28}H_{28}Cl_4P_2Pt$	$C_{28}H_{28}Cl_2P_2Pt$
Colour, habit	Colourless, block	Colourless, block	Colourless, block	Colourless, needles	Colourless, block
Crystal size mm	0.25 x 0.17 x 0.15	0.21 x 0.17 x 0.16	0.20 x 0.14 x 0.13	0.72 x 0.09 x 0.08	0.10 x 0.10 x 0.08
Crystal system, Space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$	orthorhombic, Pnma	triclinic, $P\bar{1}$
a /pm	842.3(2)	1351.5(2)	1236.4(2)	1215.11(8)	870.5(1)
b /pm	1426.1(3)	1541.6(2)	2272.9(4)	1535.8(1)	1080.6(2)
c /pm	1432.5(3)	1541.1(2)	1383.8(2)	1588.9(2)	1454.3(2)
α /°	101.53(2)	90.00	90.00	90.00	87.01(2)
β /°	94.36(2)	106.57(2)	113.17(1)	90.00	78.85(2)
γ /°	103.43(2)	90.00	90.00	90.00	72.65(2)
Volume /10^6 pm^3, Z	1626.3(6), 2	3077.5(7), 4	3575.0(9), 4	2965.2(4), 4	1281.1(3), 2
FW, g/mol	833.02	810.02	882.12	763.33	692.43
ρ (calc.), g/cm^3	1.701	1.748	1.639	1.710	1.795
μ_{Mo} /mm^{-1}	4.548	4.803	4.144	5.217	5.826
F(000)	809	1576	1736	1488	676
Data Collection					
$2\theta_{max}$°	50	50	50	50	48.08
N_t	23804	21654	25319	32676	10189
N	5717	5389	6031	2718	3767
R_{int}, R_σ	0.1514, 0.1887	0.0620, 0.0640	0.0771, 0.0724	0.1257, 0.0470	0.0318, 0.0308
N_o	3281	3667	4075	2261	3414
Absorption correction	numerical	numerical	numerical	numerical	numerical
$T'_{min,max}$	0.411, 0.506	0.390, 0.464	0.503, 0.583	0.575, 0.659	0.564, 0.627
Solution and Refinement					
Number of parameters refined	397	379	436	158	298
Final R indices (obs. data)	R = 0.0477, wR = 0.0632	R = 0.0332 wR = 0.0583	R = 0.0354 wR = 0.0724	R = 0.0476 wR = 0.1116	R = 0.0263 wR = 0.0.635
Final R indices (all data)	R = 0.1042, wR = 0.0773	R = 0.0596 wR = 0.0629	R = 0.0655 wR = 0.0786	R = 0.0564 wR = 0.1152	R = 0.0305 wR = 0.0650
Goodness−of−fit	0.712	0.867	0.928	1.019	1.062
CCDC No.	253563	253565	253560	253566	253561

[a] Hydrogen atoms of pyridine solvent have not been calculated owing to disorder.

IR cm^{-1}: 1678 vs(br), 1499 vs, 1485 m, 1456 vs, 1437 vs, 1387 m, 1358 m, 1101 s, 1055 s, 955 vs, 908 m, 820 m, 785 m, 741 s, 714 m, 692 vs, 658 m, 530 m, 563 s, 484 m, 436 m. **MS** (*m/z*) (%): **ESMS**(−): 937 (20) $[M+O_2CCF_3]^-$, 883 (50) $[M+O_2CCH_3]^-$, 869 (50) $[M+O_2CH]^-$, 859 (100) $[M+Cl]^-$. **^{1}H NMR**: δ = 1.50−1.65 (m, 2 H, CH_2) (observed in d_6−acetone, obscured by H_2O In $CDCl_3$), 2.05−2.29 (m, 8 H, CH_2 and C_3H_6O), 2.31−2.58 (m, 2 H, CH_2), 2.66−2.91 (m, 2 H, CH_2), 7.15−7.25 (m, 4 H, Ph), 7.30−7.53 (m, 12 H, Ph), 7.68−7.79 (m, 4 H, Ph). **^{19}F NMR**: δ = −119.5 (m with ^{195}Pt satellites ^{3}J(Pt,F) 286 Hz, 2 F, F(2,6)), −163.4 (m, 1 F, F(4)), −164.4 (m, 2 F, F(3,5)). **^{31}P NMR**: δ = 20.72 (d, J(P,P) 21 Hz, with ^{195}Pt satellites ^{1}J(Pt,P) 3861 Hz, 1 P, P(1)), −0.44 (m with ^{195}Pt satellites ^{1}J(Pt,P) 2083 Hz, 1 P, P(2)).

***cis*−[Pt(C$_6$F$_5$)$_2$(dppe)] (4):** $C_{38}H_{24}F_{10}P_2Pt$ (927.6 g/mol); M.p.: 270−272 °C (lit.: 269−270 °C [16]); C 49.0 (calc. 49.2); H 2.5 (2.6); F 20.4 (20.5) %.

IR cm^{-1}: 1500 vs, 1456 vs, 1437 s, 1357 m, 1105 s, 1057 vs, 955 vs, 881 m, 835 m, 824 m, 789 m, 781 m, 746 m, 715 m(sh), 706 s, 690 s, 536 vs, 486 s values overlap with the limited reported frequencies [30]. **MS** (*m/z*) (%): **ESMS**(+): 1877 (20) $[2M+Na]^+$, 1008 (20) $[M+Na+C_3H_6O]^+$, 950 (100) $[M+Na]^+$; **MS**(EI): 760 (2) $[Pt(C_6F_5)dppe^+]$, 593 (100) $[Ptdppe^+]$, 579 (<1) $[Pt(Ph_2P)_2CH_2^+]$, 565 (20) $[Pt(Ph_2P)_2^+]$ and 303 (40) $[Pt(PhP)^+]$. **^{1}H NMR**: δ = 2.18−2.47 (m, 4 H, CH_2), 7.34−7.44 (m, 8 H, Ph), 7.45−7.57 (m, 12 H, Ph). **^{19}F NMR**: δ = −118.3 (m with ^{195}Pt satellites ^{3}J(Pt,F) 309 Hz, 4 F, F(2,6)), −162.9 (m, 2 F, F(4)), −164.7 (m, 4 F, F(3,5)). **^{31}P NMR**: δ = 43.15 (m with ^{195}Pt satellites ^{1}J(Pt,P) 2303 Hz, P(1,2)).

***cis*−[Pt(C$_6$F$_5$)$_2$(dppp)] (5):** $C_{39}H_{26}F_{10}P_2Pt$ (941.6 g/mol); M.p.: >325 °C; C 49.4 (calc. 49.7); H 2.6 (2.8); F 20.1 (20,2.9) %.

IR cm^{-1}: 1500 vs, 1456 vs, 1437 s, 1358 m, 1153 m, 1103 s, 1057 vs, 974 m, 957 vs, 835 m, 792 s, 781 m, 754 m, 741 s, 704 s, 690 s, 665 s, 519 vs, 497 s. **MS** (*m/z*) (%): **ESMS**(+): 1905 (30) $[2M+Na]^+$, 1022 (25) $[M+Na+C_3H_6O]^+$, 964 (100) $[M+Na]^+$; **ESMS**(−):1995 (20) $[2M+O_2CCF_3]^-$, 1945 (15) $[2M+OMe+MeOH]^-$, 1927 (15) $[2M+O_2CH]^-$, 1918 (40) $[2M+Cl]^-$, 1054 (100) $[M+O_2CCF_3]^-$, 1004 (20) $[M+OMe+MeOH]^-$, 986 (40) $[M+O_2CH]^-$, 977 (65) $[M+Cl]^-$, 972 (40) $[M+OCH_3]^-$; MS(EI): 774 (<1 %) $[Pt(C_6F_5)dppp^+]$, 607 (100) $[Ptdppp^+]$, 565 (10) $[Pt(Ph_2P)_2^+]$ and 303 (50) $[Pt(PhP)^+]$. **^{1}H NMR**: δ = 1.91−2.19 (m, 2 H, CH_2), 2.69−2.92 (m, 4 H, CH_2), 7.19−7.36 (m, 12 H, Ph), 7.37−7.49 (m, 8 H, Ph). **^{19}F NMR**: δ = −117.4 (m with ^{195}Pt satellites ^{3}J(Pt,F) 329 Hz, 4 F, F(2,6)), −163.7 (m, 2 F, F(4)), −164.6 (m, 4 F, F(3,5)). **^{31}P NMR**: δ = −4.23 (m with ^{195}Pt satellites ^{1}J(Pt,P) 2190 Hz, P(1,2)).

Additional to the X−ray structure of **5** a solvated species was also crystallized: **3** · 2 C_3H_6O(P 2_1/a (No. 14), a = 1211.90(2) pm, b = 3032.29(2) pm, c = 1287.07(3) pm, β = 117.979(2)°, V = 4177.0(1) 10^6 pm^3, Z = 4). Because of less satisfactory refinement parameters, this structure has not been deposited with CCDC.

***cis*−[Pt(C$_6$F$_5$)$_2$(dppb)] (6):** $C_{40}H_{28}F_{10}P_2Pt$ (955.7 g/mol); M.p.: 307−309 °C; C 50.60 (calc. 50.27); H 3.16 (2.95) %.

IR cm^{-1}: 1499 vs, 1458 vs, 1437 vs, 1414 m, 1358 m, 1101 s, 1057 vs, 1047 s(sh), 1000 m, 958 vs, 901 m, 819 s, 791 s, 777 s, 750 vs, 739 vs, 698 vs, 690 vs, 658 s, 511 vs, 496 vs, 434 m. **ESMS**(−): 1946 (20) $[2M+Cl]^-$, 1100 (15) $[M+O_2CCF_3+MeOH]^-$, 1068 (20) $[M+O_2CCF_3]^-$, 1017 (25), 1000 (40) $[M+O_2CH]^-$, 991 (100) $[M+Cl]^-$; **ESMS**(−)(sample diluted x5): 1946 (3) $[2M+Cl]^-$, 1100 (40) $[M+O_2CCF_3+MeOH]^-$, 1068 (65) $[M+O_2CCF_3]^-$, 1017 (45), 1000 (100) $[M+O_2CH]^-$, 990 (85) $[M+Cl]^-$. **^{1}H NMR**: δ = 1.68−1.89 (m, 4 H, CH_2), 2.61−2.86 (m, 4 H, CH_2), 7.28−7.38 (m, 8 H, Ph), 7.39−7.52 (m, 12 H, Ph). **^{19}F NMR**: δ = −117.8 (m with ^{195}Pt satellites, ^{3}J(Pt,F) 310 Hz, 4 F, F(2,6)), −163.5 (m, 2 F, F(4)), −164.6 (m, 4 F, F(3,5)). **^{31}P NMR**: δ = 10.00 (m with ^{195}Pt satellites ^{1}J(Pt,P) 2307 Hz, P(1,2)).

X−ray crystal structure analyses

Colourless single crystals of good X−ray quality were grown by slow evaporation of a solution of the crude product in acetone (**1**−**6**, **8**) or dichloromethane (**7**).

Table 4 Crystal data and structure refinement for bis pentafluorophenyl complexes **4**−**6**

	4	**5**	**6**
Crystal data			
Empirical formula	$C_{38}H_{24}F_{10}P_2Pt$	$C_{39}H_{26}F_{10}P_2Pt$	$C_{40}H_{28}F_{10}P_2Pt$
Colour, habit	Colourless, block	Colourless, block	Colourless, needle
Crystal size /mm	0.20 x 0.16 x 0.15	0.38 x 0.19 x 0.15	0.27 x 0.17 x 0.13
Crystal system, Space group	monoclinic, $P2_1/c$	tetragonal, $P4_3$	monoclinic, C2
a /pm	1858.1(3)	1492.0(2)	1680.8(2)
b /pm	1878.2(2)	1492.0(2)	1011.5(2)
c /pm	2131.1(3)	1628.4(2)	1108.6(1)
α /°	90.00	90.00	90.00
β /°	109.48(2)	90.00	109.02(1)
γ /°	90.00	90.00	90.00
Volume /10^6 pm^3, *Z*	7012(2), 8	3625.1(7), 4	1781.8(4), 2
FW g/mol	927.60	941.63	955.65
ρ (calc.) g/cm^3	1.757	1.725	1.781
μ_{Mo} /mm^{-1}	4.174	4.039	4.110
F(000)	3600	1832	932
Data Collection			
$2\theta_{max}$°	50	50	50
N_t	58657	21793	6320
N	11753	6157	3127
R_{int}, R_σ	0.1583, 0.1841	0.0595, 0.0586	0.0342, 0.0301
N_o	5402	5043	3123
Absorption correction	numerical	numerical	numerical
$T'_{min,max}$	0.453, 0.535	0.414, 0.546	0.437, 0.586
Solution and Refinement			
Number of parameters refined	919	469	240
Final *R* indices (obs. data)	$R = 0.0433$	$R = 0.0279$	$R = 0.0214$
	w$R = 0.0552$	w$R = 0.0531$	w$R = 0.0516$
Final *R* indices (all data)	$R = 0.1204$	$R = 0.0408$	$R = 0.0217$
	w$R = 0.0689$	w$R = 0.0558$	w$R = 0.0517$
Goodness−of−fit	0.714	0.915	1.040
Flack−x		−0.021(6)	
CCDC No.	253562	253564	253559

Diffraction intensities from small single crystals (in sealed glass capillaries) were measured with image plate diffractometers (IPDS I or II, Stoe) at room temperature. Data acquisition: Mo−Kα−radiation (graphite monochromator, λ = 71.07 pm); Δφ = 2°; detector distance: 60 mm (**1**−**6**) and 80 mm (**7** and **8**); φ = 0−200° (**2**, **3**, **5** and **6**), 0−250° (**4** and **8**), 0° ≤ ω ≤ 180° (φ = 0°, Δω = 2°) and 0° ≤ ω ≤ 180° (φ = 90°, Δω = 2°) (**1** and **7**); irradiation time: 5 min (**4**), 4 min (**1**), 3 min (**2**, **3**, **5**, **6** and **8**) and 2.6 min (**7**). Numerical absorption corrections were applied to the data by the programs X−RED and X−SHAPE [31, 32]. The structures were solved by conventional methods and refined with anisotropic thermal parameter for the non−hydrogen atoms (except of the disordered pyridine solvent in *cis*−[PtCl(C_6F_5)(dppe)] which was refined with isotropic thermal parameters) using the SHELX 97 software package [33, 34]. All hydrogen atoms were located in difference maps; not all would refine meaningfully in (x, y, z, U_{iso}) so all were constrained in these parameters in the final refinement cycles.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, for CCDC numbers see Tables 3 and 4. Copies of the data can be obtained free of charge on application to The Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 (1223)336−033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; email for deposition: deposit@ccdc.cam.ac.uk).

Crystal and refinement parameters for mono- (**1**−**3**) and bis-pentafluorophenyl (**4**−**6**) substituted and dichloro (**7**, **8**) complexes are listed in Table 3 and 4, with selected bond distances and angles in Table 2. Figs. 1−5 pictures were made with the aid of the program DIAMOND [35].

Hydrogen atoms of the pyridine solvent in **1** have not been calculated due to high thermal parameters. In **3** the atom C2 of the ligand's carbon chain is disordered with occupation 50.5 % for C2A and 49.5 % for C2B owing to a disorder of the hydrogen atoms of C1A/B and C3A/B (Fig. 5).

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