Binuclear Pentafluorophenyl Complexes containing Halide and/or Bis(diphenylphosphino)methane (dppm) as Bridging Ligands. Molecular Structure of $[N(PPh_3)_2][Pt_2(\mu\text{-}I)(\mu\text{-}dppm)(C_6F_5)_4]\cdot 2CHCl_3$†

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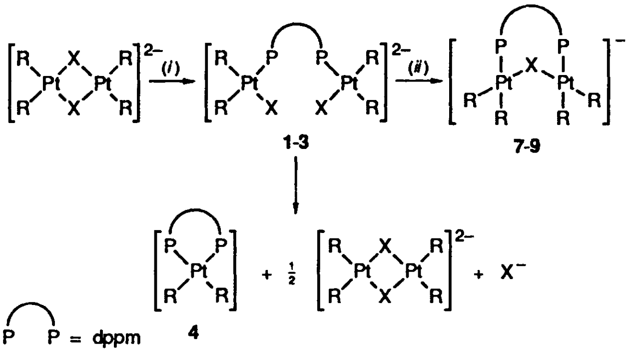
The reaction of $[N(PPh_3)_2]_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ (X = Cl, Br or I) with bis(diphenylphosphino)methane (dppm) at room temperature in CH_2Cl_2 affords $[N(PPh_3)_2]_2[(C_6F_5)_2XPt(\mu\text{-}dppm)PtX(C_6F_5)_2]$ (X = Cl **1**, Br **2** or I **3**) in good yield as the kinetic products. Further reactions between **1**–**3** and $AgClO_4$ (molar ratio 1 : 1) in acetone–tetrahydrofuran render the corresponding derivatives $[N(PPh_3)_2][(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ [X = Cl, Br or I) and AgX. These complexes are very stable, and the bridging system is not cleaved by anionic (X^-) or neutral ligands (NCMe, tetrahydrothiophene, $SPPh_3$, PPh_3). The structure of $[N(PPh_3)_2][Pt_2(\mu\text{-}I)(\mu\text{-}dppm)(C_6F_5)_4]\cdot 2CHCl_3$ has been determined by a single-crystal X-ray diffraction study, showing strain in the bridging (μ-X)(μ-dppm) system. Crystals are triclinic, space group $P\bar{1}$, with $a = 11.609(2)$, $b = 19.113(2)$, $c = 19.997(2)$ Å, $\alpha = 101.83(1)$, $\beta = 93.32(1)$, $\gamma = 92.61(1)°$, $Z = 2$; 8052 data with $I > 3\sigma(I)$ refined to $R = 0.051$, $R' = 0.068$.

Bis(diphenylphosphino)methane (dppm = $Ph_2PCH_2PPh_2$) is a versatile ligand which unusually bridges two metal centres forming homo- or hetero-binuclear complexes, although there are some cases in which it acts as a chelate or a monodentate ligand.[1] Most complexes containing dppm acting as an exobidentate ligand are formed by two metal centres which are joined by two dppm groups, and in many cases metal–metal bonds and/or other bridging ligands are present as well.[1] As far as palladium or platinum derivatives are concerned, two well represented types of complexes are those of Pd^I or Pt^I of stoichiometry $[MM'X_2(\mu\text{-}dppm)_2]$ (M, M′ = Pd or Pt; X = halide or organic groups[1,2]), in which the two metals are singly bonded, and their derivatives resulting from the insertion of small molecules into the metal–metal bond (A-frame compounds), with the latter containing two dppm and one other bridging ligand. In addition, some face-to-face dimers of Pd^{II} or Pt^{II} with two dppm bridging ligands and without metal–metal bonds[3] as well as some heterobinuclear complexes containing the $M(\mu\text{-}dppm)_2M'$ (M = Pd or Pt; M′ = other metal) core[4] have been prepared, and their reactivity or rearrangement reactions studied.

This paper deals with the synthesis of the anionic binuclear pentafluorophenyl platinate(II) complexes $Q_2[cis,cis\text{-}(C_6F_5)_2PtX(\mu\text{-}dppm)PtX(C_6F_5)_2]$ **1**–**3** [Q = $N(PPh_3)_2{}^+$ or $NBu_4{}^+$] which are the kinetic products resulting from the reaction between $Q_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ and dppm and which contain only one dppm ligand bridging the two metal centres. Moreover, binuclear derivatives of the type $Q[cis,cis\text{-}(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-}dppm)Pt(C_6F_5)_2]$ containing two very different bridging ligands are prepared by treatment of **1**–**3** with a halide abstractor.

Results and Discussion

(*a*) *Reactions of* $Q_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ *with dppm* (1 : 1).—The salts $[N(PPh_3)_2]_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ (X = Cl, Br or I) react with dppm in CH_2Cl_2 (molar ratio 1 : 1), the products formed depending on the reaction time. If the reactions are carried out at room temperature and after 10 min of stirring the solvent is evaporated to dryness and the oily residue treated with Pr^iOH, the anionic binuclear platinum complexes $[N(PPh_3)_2]_2[(C_6F_5)_2XPt(\mu\text{-}dppm)PtX(C_6F_5)_2]$ (X = Cl **1**, Br **2** or I **3**) are obtained in high yields (≈90%). In these complexes the dppm acts as an exobidentate bridging ligand (see Scheme 1). However if the reactions are carried out for a longer time (12 h) a mixture of *cis*-$[Pt(C_6F_5)_2(dppm)]$‡ **4**[3d] and the respective starting material $[N(PPh_3)_2]_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ (identified by ^{19}F and ^{31}P NMR spectra) is obtained. Such behaviour indicates that **1**–**3** are the kinetic products of cleavage of the bridges, which takes place in a symmetric way, and that the formation, after longer times, of neutral **4** and the anionic starting material is a consequence of posterior rearrangement of **1**–**3** and not of an asymmetric cleavage of the bridges in the binuclear starting material.



Scheme 1 R = C_6F_5. (*i*) dppm; (*ii*) +$AgClO_4$, −AgX

As expected, a similar behaviour, rendering $[NBu_4]_2[(C_6F_5)_2XPt(\mu\text{-}dppm)PtX(C_6F_5)_2]$ **1a**–**3a** respectively, has been observed when the corresponding $[NBu_4]_2[Pt_2(\mu\text{-}X)_2$-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ Identified by C, H and N analyses, IR and ^{31}P NMR spectroscopy.

Table 1 NMR data

	^{19}F NMR^a				^{31}P NMR^a		
Complex	δ(F$_o$)	δ(F$_m$)	δ(F$_p$)	^3J(Pt–F$_o$)/Hz	δ[N(PPh$_3$)$_2$$^+$]	δ(dppm)	^1J(Pt–P)/Hz
1 $[N(PPh_3)_2]_2[(C_6F_5)_2ClPt(\mu\text{-dppm})PtCl(C_6F_5)_2]$	−117.03	≈ −166^b		355.0	21.72	13.41	2529
	−117.50	−167.40	−168.71	473.4			
2 $[N(PPh_3)_2]_2[(C_6F_5)_2BrPt(\mu\text{-dppm})PtBr(C_6F_5)_2]$	−117.36	−166.01	−164.67	348.6	21.75	11.39	2578
	−117.77	−166.77	−166.35	481.1			
3 $[N(PPh_3)_2]_2[(C_6F_5)_2IPt(\mu\text{-dppm})PtI(C_6F_5)_2]$	−114.57	*c*	−164.50	348.6	21.69	11.82	2593
	−116.12	*c*	*c*	459.8			
7 $[N(PPh_3)_2]_2[(C_6F_5)_2Pt(\mu\text{-Cl})(\mu\text{-dppm})Pt(C_6F_5)_2]$	−117.65	−166.14	−164.18	364.1	21.70	12.96	2540
	d	−166.90	−166.68	455.2			
8 $[N(PPh_3)_2]_2[(C_6F_5)_2Pt(\mu\text{-Br})(\mu\text{-dppm})Pt(C_6F_5)_2]$	−117.33	−166.00	−164.68	312.6	21.73	13.39	2516
	−117.79	−166.76	−166.32	484.4			
9 $[N(PPh_3)_2]_2[(C_6F_5)_2Pt(\mu\text{-I})(\mu\text{-dppm})Pt(C_6F_5)_2]$	−116.30	−166.51	−164.63	343.1	21.71	11.73	2503
	−118.03	≈ −166^b		450.0			

[a] Solvent $CDCl_3$; δ_F values are referred to $CFCl_3$, δ_P to 85% H_3PO_4. [b] Both signals are overlapped. [c] Overlapping of the three signals giving a complex signal at ≈δ −166. [d] The F_o signals for the two pentafluorophenyl groups are coincident, although their corresponding coupling constants with ^{195}Pt are different.

$(C_6F_5)_4]$ are treated with dppm. The choice of **1**–**3** or **1a**–**3a** in the following is inconsequential. The $N(PPh_3)_2^+$ complexes **1**–**3** are generally easier to crystallize and their ^{31}P NMR spectra are more informative. However, the IR spectra of **1a**–**3a** (the NBu_4^+ derivatives) give some more information concerning their anions since the $N(PPh_3)_2^+$ salts display many more internal absorptions than do the NBu_4^+ salts. The same applies for the complexes derived from them.

The ^{19}F and ^{31}P NMR data for complexes **1**–**3** are collected in Table 1, and as expected for the proposed structure clearly show that in each case the pentafluorophenyl groups are inequivalent while both phosphorus atoms of the dppm are equivalent and show platinum satellites. No signals due to the presence of **4**, as an impurity, are observed if the reaction time is limited to 10 min. In addition the ratio dppm:$N(PPh_3)_2^+$ for complexes **1**–**3** is 1:2 which indicates that these complexes are not contaminated with the corresponding starting material $[N(PPh_3)_2]_2[Pt_2(\mu\text{-X})_2(C_6F_5)_4]$.

The IR spectra of complexes **1a**–**3a** show typical absorptions for the C_6F_5 groups at around 1500, 1050, 950 and 810 cm^{-1}, although the latter (X-sensitive mode of the C_6F_5 group), which usually gives structural information,[5] is in this case obscured by internal absorptions of the dppm. On the other hand, the absorptions in the range 520–410 cm^{-1} are due to the dppm ligand; the absence of an extra absorption in the range 550–530 cm^{-1} indicates that the dppm is not acting as a chelate.[3d]

In contrast, $[NBu_4]_2[Pt_2(\mu\text{-SCN})_2(C_6F_5)_4]$ reacts with dppm in CH_2Cl_2 and after 15 min of stirring at room temperature compound **4** and $[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2(SCN)_2]$ **5** are obtained. Furthermore, when dppe [1,2-bis(diphenylphosphino)ethane] is used for such reactions, no binuclear derivatives analogous to **1**–**3** are obtained, since even in short time periods *cis*-$[Pt(C_6F_5)_2(dppe)]$ **6** is obtained. It should be mentioned that the formation of **6** is very rapid since the ^{31}P NMR spectrum of a mixture of $[NBu_4]_2[Pt_2(\mu\text{-Cl})_2(C_6F_5)_4]$ and dppe (1:1) at room temperature shows the signal corresponding to the neutral compound **6** [^{31}P NMR (solvent $CDCl_3$): δ 42.843, *J*(Pt–P) = 2309 Hz] and a very weak signal at δ 10–15 which could be due to $[cis,cis\text{-}(C_6F_5)_2ClPt(\mu\text{-dppm})PtCl(C_6F_5)_2]^{2-}$. The ^{31}P NMR spectrum after 3 d shows only the signal due to **6**.

(*b*) *Reactions of* $[N(PPh_3)_2]_2[(C_6F_5)_2XPt(\mu\text{-dppm})PtX(C_6F_5)_2]$ *with* $AgClO_4$.—The reaction of complexes **1**–**3** with $AgClO_4$ (1:1) in tetrahydrofuran (thf)–acetone results in the precipitation of AgCl. From the supernatant, after elimination of the donor solvents (thf, acetone) by evaporation to dryness and treatment several times with $CHCl_3$, the binuclear complexes $[N(PPh_3)_2][cis,cis\text{-}(C_6F_5)_2Pt(\mu\text{-X})(\mu\text{-dppm})Pt(C_6F_5)_2]$ (X = Cl **7**, Br **8** or I **9**) are obtained in high yield (> 70%) (Scheme 1). The complexes $[NBu_4][cis,cis\text{-}(C_6F_5)_2Pt(\mu\text{-X})(\mu\text{-dppm})Pt(C_6F_5)_2]$ **7a**–**9a** can be obtained similarly, and their preparation is described in the Experimental section.

The formation of complexes **7**–**9** can be easily understood, since the elimination of a terminal halide ligand from one of the platinum centres obliges the other terminal halide to act as a bridging ligand in order to complete the co-ordination sphere of both metal centres. Nevertheless, their formation is noteworthy since, as we have commented before, complexes **1**–**3** decompose spontaneously in solution, although not rapidly (Scheme 1) with elimination of halide and formation of **4** and the binuclear $[N(PPh_3)_2]_2[Pt_2(\mu\text{-X})_2(C_6F_5)_4]$. Also, complexes **7**–**9** are stable in solution and no sign of decomposition or reorganization to **4** and $[N(PPh_3)_2]_2[Pt_2(\mu\text{-X})_2(C_6F_5)_4]$ has been observed.

Surprisingly, when a dichloromethane solution of complex **7** or **8a** is treated with QX (molar ratio 1:1), in order to regenerate the binuclear complexes with two terminal halides, **1** or **2a**, the binuclear species with μ-X and μ-dppm (**7** or **8a**) are the only products isolated. Moreover, these complexes seem to be the only species in such solutions since the ^{31}P NMR spectrum of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-Br})(\mu\text{-dppm})Pt(C_6F_5)_2]$ **8a** in $CDCl_3$ does not show any difference after adding NBu_4Br. Also, when a dichloromethane solution of $[NBu_4][(C_6F_5)_2Pt(\mu\text{-Cl})(\mu\text{-dppm})Pt(C_6F_5)_2]$ **7a** is treated either with MeCN (molar ratio 1:2), tht (tetrahydrothiophene) (1:1), $SPPh_3$ (1:1) or PPh_3 (1:1) the starting material **7a** is recovered in all cases. This behaviour of complexes **7**–**9** must be attributed to kinetic effects.

The structural characterization of complexes **7**–**9** has been carried out on the basis of their ^{19}F and ^{31}P NMR spectra. The most relevant data are collected in Table 1, and these indicate that the two C_6F_5 groups of each platinum environment are inequivalent, while both phosphorus atoms of the dppm are equivalent. The abundance ratio between the phosphorus signals of the dppm and $N(PPh_3)_2^+$, as expected, is 1:1. The IR spectra of complexes **7a**–**9a** show, as for **1a**–**3a**, typical absorptions of the C_6F_5 groups and of dppm, although they do not supply structural information.

Structure of $[N(PPh_3)_2][Pt_2(\mu\text{-I})(\mu\text{-dppm})(C_6F_5)_4]\cdot 2CHCl_3$.—The structure of the anion $[Pt_2(\mu\text{-I})(\mu\text{-dppm})(C_6F_5)_4]^-$ is shown in Fig. 1 and the core is given in Fig. 2; selected bond distances and angles are listed in Table 2, fractional atomic coordinates and their estimated standard deviations in Table 3. The $N(PPh_3)_2^+$ cation shows quite typical geometry, with N–P distances of 1.570(12) and 1.584(12)

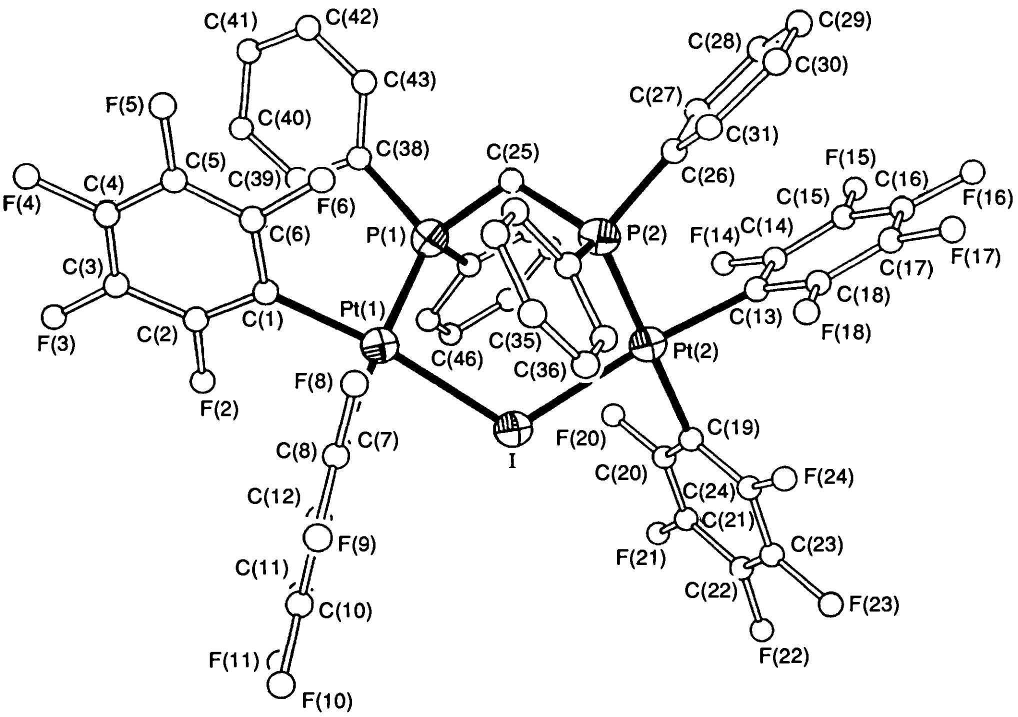

Fig. 1 Crystal structure of $[Pt_2(\mu\text{-}I)(\mu\text{-dppm})(C_6F_5)_4]^-$

Table 2 Selected bond distances (Å) and angles (°) for the complex $[N(PPh_3)_2][(C_6F_5)_2Pt(\mu\text{-}I)(\mu\text{-dppm})Pt(C_6F_5)_2]\cdot 2CHCl_3$

Pt(1)–I	2.645(1)	Pt(2)–I	2.643(1)
Pt(1)–P(1)	2.271(3)	Pt(2)–P(2)	2.290(3)
Pt(1)–C(1)	2.027(13)	Pt(2)–C(13)	2.036(13)
Pt(1)–C(7)	2.074(12)	Pt(2)–C(19)	2.064(12)
P(1)–C(25)	1.846(12)	P(2)–C(25)	1.827(14)
P(1)–C(38)	1.849(16)	P(2)–C(26)	1.818(13)
P(1)–C(44)	1.827(12)	P(2)–C(32)	1.808(12)
Pt(1)–I–Pt(2)	114.4(1)	P(1)–C(25)–P(2)	120.0(7)
Pt(1)–P(1)–C(25)	112.6(4)	Pt(2)–P(2)–C(25)	117.8(4)
I–Pt(1)–P(1)	91.6(1)	I–Pt(2)–P(2)	93.3(1)
I–Pt(1)–C(7)	85.5(4)	I–Pt(2)–C(19)	85.8(3)
C(1)–Pt(1)–C(7)	89.6(5)	C(13)–Pt(2)–C(19)	88.8(5)
C(1)–Pt(1)–P(1)	93.4(3)	C(13)–Pt(2)–P(2)	91.9(4)
C(7)–Pt(1)–P(1)	176.4(4)	C(19)–Pt(2)–P(2)	175.6(3)
C(1)–Pt(1)–I	172.8(4)	C(13)–Pt(2)–I	174.3(4)

Dihedral angles

Square-planar environment of Pt(1)–square-planar environment of Pt(2)	44.9(1)
Plane Pt(1)–I–Pt(2)–plane P(1)–C(25)–P(2)	40.2(5)

Å. The P–C distances lie in the range 1.753(14)–1.818(14) Å, average 1.792 Å. The angle at nitrogen is 142.1(7)° and the angles around the phosphorus atoms all lie near the tetrahedral value, range 105.7(7)–115.5(7).

As can be seen, the anion is formed by two *cis*-$Pt(C_6F_5)_2$ fragments joined by an exobidentate dppm and an iodide acting as bridging ligands. Both platinum atoms are in distorted square-planar environments showing similar Pt–C, Pt–I and Pt–P distances with angles between the *cis*-ligands around 90°. The Pt–C distances are in the range found for such distances in other pentafluorophenylplatinum(II) complexes.[6] The Pt–P and Pt–I distances are similar to the corresponding platinum(II) distances in $[Me_3Pt(\mu\text{-}I)(\mu\text{-}Me_2PCH_2PMe_2)_2PtMe]^+$,[7] a binuclear compound containing platinum-(II) and -(IV) centres.

The large space requirements of the phenyl rings of the dppm ligand and those of the pentafluorophenyl rings could be responsible for steric overcrowding and the long distance between the platinum atoms (4.45 Å), thus enforcing a large Pt(1)–I–Pt(2) angle 114.4(1)° and a high value for the bite angle between the phosphorus atoms of the dppm. The P(1) • • • P(2) distance is 3.18 Å and the P(1)–C(25)–P(2) angle is 120.0(7)°, closer to the value for a sp^2-hybridized C atom [C(25)] than to those for sp^3 hybrid orbitals. A similar structural situation concerning the Pt–I–Pt angle and the C angle of the $Me_2PCH_2PMe_2$ (dmpm) ligand has been found in $[Me_3Pt^{IV}(\mu\text{-}I)(\mu\text{-}Me_2PCH_2PMe_2)_2Pt^{IV}Me_3]I$ [Pt–I–Pt 118.0(1), P–C–P 125.8(5)°] for which severe steric overcrowding has been suggested,[8] although in that case smaller substituents (methyl groups) are present at the metal centre and at the phosphorus atoms.

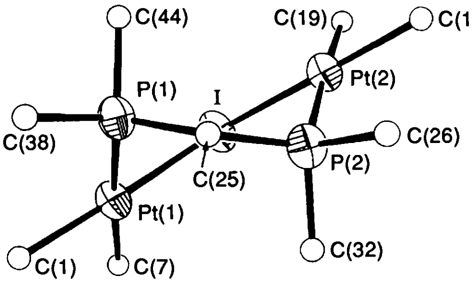

Fig. 2 Core of the $[Pt_2(\mu\text{-}I)(\mu\text{-dppm})(C_6F_5)_4]^-$ anion

Assuming that complexes **7** and **8** display similar structures, the steric overcrowding could be responsible for their lack of reactivity, because of the steric difficulties of the reactants (X^-, NCMe, tht, PPh_3) in reaching the Pt(μ-I)(μ-dppm)Pt bridging system.

It is worth noting (Fig. 2) that one of the 'PtC_2PI' planar units is twisted with respect to the other, so that the Pt • • • Pt and P • • • P vectors make an angle of 40.4°.

Experimental

The C, H and N analyses and conductance measurements were performed as described elsewhere.[3d] Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin Elmer 833 or 1710 FTIR spectrophotometer from Nujol mulls between polyethylene

Table 3 Atomic coordinates (× 10^4) for $[N(PPh_3)_2][Pt_2(\mu\text{-}I)(\mu\text{-dppm})(C_6F_5)_4]\cdot 2CHCl_3$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	3 007(1)	7 749(1)	1 705(1)	C(37)	330(15)	6 475(8)	2 457(8)
Pt(2)	1 795(1)	7 768(1)	3 777(1)	C(38)	2 040(12)	9 476(7)	1 710(7)
I	3 365(1)	7 362(1)	2 893(1)	C(39)	3 010(18)	9 756(10)	1 486(10)
P(1)	2 239(3)	8 779(2)	2 217(2)	C(40)	2 993(23)	10 284(12)	1 095(10)
P(2)	450(3)	7 922(2)	2 944(2)	C(41)	1 939(23)	10 526(10)	945(10)
C(1)	2 937(11)	8 009(6)	771(6)	C(42)	1 012(20)	10 259(13)	1 170(13)
C(2)	3 855(12)	8 129(8)	439(7)	C(43)	1 053(17)	9 738(12)	1 550(11)
C(3)	3 829(14)	8 292(10)	−209(8)	C(44)	3 088(11)	9 278(7)	2 978(7)
C(4)	2 786(16)	8 343(10)	−521(8)	C(45)	4 278(12)	9 293(8)	2 938(8)
C(5)	1 818(15)	8 230(9)	−227(8)	C(46)	4 985(15)	9 730(8)	3 487(10)
C(6)	1 891(13)	8 058(8)	399(7)	C(47)	4 496(19)	10 102(9)	4 030(9)
F(2)	4 913(7)	8 122(6)	760(5)	C(48)	3 301(17)	10 075(8)	4 079(8)
F(3)	4 849(10)	8 445(8)	−467(6)	C(49)	2 629(13)	9 660(7)	3 542(7)
F(4)	2 761(12)	8 531(7)	−1 149(5)	N	1 078(9)	2 788(6)	2 105(5)
F(5)	800(9)	8 309(7)	−554(6)	P(3)	15(3)	3 070(2)	2 510(2)
F(6)	854(7)	7 952(6)	672(5)	P(4)	2 385(3)	2 996(2)	2 006(2)
C(7)	3 662(11)	6 778(7)	1 281(6)	C(50)	−704(11)	2 352(8)	2 800(6)
C(8)	3 011(14)	6 218(8)	936(7)	C(51)	−608(15)	1 659(8)	2 449(8)
C(9)	3 388(17)	5 534(8)	713(8)	C(52)	−1 174(16)	1 092(10)	2 631(9)
C(10)	4 530(20)	5 434(10)	856(9)	C(53)	−1 857(15)	1 213(11)	3 176(10)
C(11)	5 231(16)	5 986(12)	1 185(9)	C(54)	−1 979(16)	1 910(13)	3 538(9)
C(12)	4 791(13)	6 636(7)	1 383(7)	C(55)	−1 371(13)	2 448(10)	3 342(9)
F(8)	1 845(8)	6 287(5)	784(6)	C(56)	344(14)	3 744(8)	3 243(7)
F(9)	2 635(12)	4 985(6)	380(6)	C(57)	950(20)	3 613(10)	3 812(8)
F(10)	4 903(12)	4 754(5)	645(6)	C(58)	1 331(23)	4 153(12)	4 357(11)
F(11)	6 364(10)	5 858(7)	1 286(6)	C(59)	1 037(22)	4 850(10)	4 376(10)
F(12)	5 582(8)	7 151(6)	1 723(5)	C(60)	484(19)	4 998(10)	3 822(11)
C(13)	671(11)	8 027(7)	4 521(6)	C(61)	116(15)	4 486(9)	3 259(9)
C(14)	789(12)	8 666(7)	4 990(7)	C(62)	−1 025(13)	3 386(8)	1 948(8)
C(15)	2(13)	8 884(8)	5 481(7)	C(63)	−713(17)	3 490(8)	1 319(8)
C(16)	−907(14)	8 400(10)	5 517(8)	C(64)	−1 501(24)	3 716(12)	878(11)
C(17)	−1 044(13)	7 745(8)	5 063(8)	C(65)	−2 601(24)	3 872(14)	1 110(17)
C(18)	−245(12)	7 557(7)	4 591(7)	C(66)	−2 890(21)	3 777(16)	1 727(18)
F(14)	1 661(8)	9 152(4)	4 971(4)	C(67)	−2 098(15)	3 541(11)	2 152(12
F(15)	116(9)	9 507(5)	5 905(5)	C(68)	3 315(11)	2 389(7)	2 319(7)
F(16)	−1 653(9)	8 577(6)	6 009(5)	C(69)	4 487(14)	2 414(9)	2 200(9)
F(17)	−1 949(8)	7 299(5)	5 098(5)	C(70)	5 195(16)	1 942(12)	2 441(11)
F(18)	−441(7)	6 925(4)	4 152(4)	C(71)	4 766(16)	1 483(9)	2 812(8)
C(19)	2 977(9)	7 547(7)	4 506(6)	C(72)	3 647(16)	1 442(9)	2 922(8)
C(20)	3 996(11)	7 972(7)	4 739(6)	C(73)	2 903(13)	1 922(8)	2 676(7)
C(21)	4 856(12)	7 810(8)	5 188(7)	C(74)	2 878(12)	3 906(8)	2 418(7)
C(22)	4 628(17)	7 162(10)	5 423(8)	C(75)	2 590(14)	4 466(8)	2 107(8)
C(23)	3 679(16)	6 768(9)	5 235(9)	C(76)	2 861(16)	5 148(9)	2 451(10)
C(24)	2 830(14)	6 963(8)	4 795(8)	C(77)	3 426(19)	5 293(9)	3 085(12)
F(20)	4 222(7)	8 561(4)	4 511(4)	C(78)	3 702(22)	4 724(11)	3 369(12)
F(21)	5 806(8)	8 190(5)	5 358(5)	C(79)	3 474(16)	4 044(9)	3 066(9)
F(22)	5 477(10)	6 990(6)	5 859(6)	C(80)	2 561(12)	2 892(7)	1 109(7)
F(23)	3 464(13)	6 166(7)	5 490(7)	C(81)	1 809(13)	2 456(8)	648(8)
F(24)	1 905(9)	6 507(5)	4 621(6)	C(82)	1 981(14)	2 320(9)	−62(8)
C(25)	762(10)	8 627(7)	2 474(6)	C(83)	2 886(15)	2 662(10)	−299(9)
C(26)	−953(10)	8 167(7)	3 245(7)	C(84)	3 634(17)	3 117(10)	174(9)
C(27)	−1 020(11)	8 836(8)	3 679(7)	C(85)	3 522(14)	3 247(8)	876(8)
C(28)	−2 057(14)	9 027(9)	3 977(8)	Cl(1)	7 708(7)	8 979(4)	1 961(4)
C(29)	−3 023(15)	8 563(9)	3 813(9)	Cl(2)	6 115(6)	10 026(5)	1 619(6)
C(30)	−2 969(13)	7 923(10)	3 371(10)	Cl(3)	8 030(9)	9 614(6)	854(4)
C(31)	−1 921(11)	7 719(8)	3 062(8)	C(86)	6 925(19)	9 345(13)	1 302(17)
C(32)	117(11)	7 118(7)	2 294(7)	Cl(4)	7 179(10)	5 079(6)	3 835(5)
C(33)	−462(12)	7 109(8)	1 665(7)	Cl(5)	5 945(8)	6 297(5)	4 066(5)
C(34)	−775(13)	6 469(9)	1 208(8)	Cl(6)	6 846(13)	5 800(5)	2 789(5)
C(35)	−551(15)	5 818(9)	1 374(8)	C(87)	6 990(22)	5 901(13)	3 615(12)
C(36)	9(18)	5 823(9)	1 981(10)				

sheets, NMR spectra on either a Varian XL200 or a Unity 300 instrument. The salts $[NBu_4]_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ were prepared as described elsewhere;[9,10] $[N(PPh_3)_2]_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ were prepared similarly, but using $[N(PPh_3)_2]_2[Pt(C_6F_5)_4]$ as starting material. This compound was prepared as for $[NBu_4]_2[Pt(C_6F_5)_4]$[9] but using $[N(PPh_3)_2]Cl$ instead of NBu_4Br. All the reactions in which a silver reagent was used were carried out under exclusion of light.

Preparation of Q_2[*cis,cis*-$(C_6F_5)_2XPt(\mu\text{-dppm})PtX(C_6F_5)_2$] [Q = $N(PPh_3)_2{}^+$, X = Cl **1**, Br **2** *or* I **3**; Q = $NBu_4{}^+$, X = Cl **1a**, Br **2a** *or* I **3a**].—To a solution of $[N(PPh_3)_2]_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ (X = Cl, 1.000 g, 0.453 mmol; Br, 2.000 g, 0.871 mmol; I, 1.000 g, 0.419 mmol) in CH_2Cl_2 (25 cm^3) [for X = I, CH_2Cl_2–Me_2CO (1 : 1) was used] was added an equimolar amount of dppm, and the mixture was stirred at room temperature for 10 min. The solution was evaporated to dryness and the oily residue was washed with Pr^{i}OH (15 cm^3) giving a white solid. Complexes **1**–**3** were isolated as white solids in 95, 91 and 84% yield respectively [Found(Calc.): **1**, C, 55.70 (56.10); H, 3.15 (3.20); N, 0.90 (1.10). **2**, C, 53.60 (54.25); H, 2.95 (3.10); N, 0.95 (1.05). **3**, C, 51.85 (52.40); H, 2.70 (2.95); N, 1.00 (1.00)%].

Complexes **1a**–**3a** (Q = NBu_4^+) were prepared similarly but using $[NBu_4]_2[Pt_2(\mu\text{-}X)_2(C_6F_5)_4]$ as starting materials. Since **3a** is rather soluble in Pr^{i}OH the oily residue obtained after evaporating the initial solution to dryness was dissolved in MeOH (10 cm^3) and precipitated by adding water (50 cm^3). Yields: **1a**, 96; **2a**, 86; **3a**, 96% [Found(Calc.): **1a**, C, 48.25 (48.70); H, 4.65 (4.75); N, 1.30 (1.40). **2a**, C, 46.75 (46.60); H, 4.60 (4.55); N, 1.15 (1.35). **3a**, C, 44.35 (44.60); H, 4.30 (4.35); N, 1.35 (1.30)%].

Reaction of $[NBu_4]_2[Pt_2(\mu\text{-}SCN)_2(C_6F_5)_4]$ *with dppm*.—To a solution of $[NBu_4]_2[Pt_2(\mu\text{-}SCN)_2(C_6F_5)_4]$ (0.750 g, 0.452 mmol) in CH_2Cl_2 (25 cm^3) was added dppm (0.174 g, 0.452 mmol), and the mixture was stirred at room temperature for 15 min. The solution was evaporated to dryness and the oily residue was treated with Pr^{i}OH (15 cm^3) giving a white solid, partially soluble in MeOH. The insoluble fraction was identified, after filtration, as *cis*-$[Pt(C_6F_5)_2(dppm)]$.[3d] The MeOH solution was evaporated to dryness, and the residue was treated with Pr^{i}OH giving a white solid which was identified as $[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2(SCN)_2]$ **5**, 0.375 g, 36.7% yield [Found(Calc.): C, 49.75 (48.90); H, 6.75 (6.40); N, 4.85 (4.95)%].

Preparation of Q[*cis,cis*-$(C_6F_5)_2Pt(\mu\text{-}X)(\mu\text{-dppm})Pt(C_6F_5)_2$] [Q = $N(PPh_3)_2^+$, X = Cl **7**, Br **8** *or* I **9**; Q = NBu_4^+, X = Cl **7a**, Br **8a** *or* I **9a**].—To a solution of $[N(PPh_3)_2]_2$-$[(C_6F_5)_2XPt(\mu\text{-dppm})PtX(C_6F_5)_2]$ (X = Cl, 0.500 g, 0.193 mmol; Br, 1.000 g, 0.373 mmol; I, 0.600 g, 0.216 mmol) in thf–Me_2CO (1:1, 25 cm^3) was added an equimolar amount of $AgClO_4$, and the mixture was stirred at room temperature for 15 min. The AgX precipitate was filtered off and the resulting solution was evaporated to dryness. The residue was treated with $CHCl_3$ (10 cm^3) and then evaporated to dryness; by treating the resulting residue twice in a similar way a white solid was obtained. Complexes **7**–**9** were isolated in 82, 76 and 88% yields respectively [Found(Calc.): **7**, C, 50.70 (50.60); H, 2.40 (2.60); N, 0.80 (0.70). **8**, C, 50.20 (49.55); H, 2.55 (2.55); N, 0.50 (0.70). **9**, C, 48.25 (48.40); H, 2.30 (2.50); N, 0.55 (0.65)%].

Complexes **7a**–**9a** were obtained in a similar way using **1a**–**3a** as starting materials. After a similar treatment with $CHCl_3$, **7a** and **8a** were obtained by washing the residues with Pr^{i}OH, and **9a** was precipitated by addition of water (50 cm^3) to a methanolic solution of the compound. Yields: **7a**, 84; **8a**, 74; **9a**, 78% [Found(Calc.): **7a**, C, 45.60 (45.35); H, 3.45 (3.40); N, 0.90 (0.80). **8a**, C, 44.25 (44.25); H, 3.20 (3.30); N, 0.75 (0.80). **9a**, C, 43.65 (43.10); H, 3.20 (3.20); N, 0.80 (0.75)%].

Crystal Structure Determination of Compound **9**.—*Crystal data*. $C_{85}H_{52}F_{20}INP_4Pt_2\cdot 2CHCl_3$, *M* 2347.03, triclinic, space group $P\bar{1}$, $a = 11.609(2)$, $b = 19.113(2)$, $c = 19.997(2)$ Å, $\alpha = 101.83(1)$, $\beta = 93.32(1)$, $\gamma = 92.61(1)°$, $U = 4328(1)$ Å^3, $Z = 2$, $D_c = 1.801$ g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, $\mu = 41.1$ cm^{-1}, $F(000) = 2268$, $T = 20$ °C, crystal dimensions 0.68 × 0.3 × 0.15 mm.

Crystallographic data were collected on a Siemens/Stoe AED2 four-circle diffractometer, $4 < 2\theta < 46°$ (ω–θ scan); 12 047 independent reflections, 8052 with $I > 3\sigma(I)$ were used for all calculations (program system SHELXTL-PLUS[11]). Cell constants were refined from 2θ values of 60 reflections including Friedel pairs ($20 < 2\theta < 30°$). An absorption correction based on ψ scans was applied (transmission factors: 0.910–0.641).

Three standard reflections were measured every 45 min but showed no decay; however, they oscillated (−13%, +4%), most likely as a result of instability of the diffractometer. The structure was solved by Patterson methods and refined on $|F_o|$ to $R = 0.051$ and $R' = 0.068$ for 1090 variables [weighting scheme $w^{-1} = \sigma^2(F_o) + 0.003\,57F_o^2$]; highest shift/error 0.005. All of the non-hydrogen atoms, including those of the two solvent molecules, were refined anisotropically. Owing to the number of variables involved in the model the final refinement was conducted in blocks. The platinum, iodine and phosphorus atoms of the anion were refined in all cycles, and the remaining atoms were refined in two groups: first, the remainder of the anion, and secondly, the atoms of the $N(PPh_3)_2^+$ cation and the interstitial $CHCl_3$ molecules. All hydrogen atoms were included in calculated positions (C–H 0.96 Å, $U = 0.0916$ Å^2). A difference map following convergence showed nine peaks higher than 1 e Å^{-3} (2.27–1.2). The seven most dense peaks lay within 1.1 Å of platinum atoms, and the remaining two peaks fell near (< 1.1 Å) the iodine atom. These are most likely due to the quality of the data (maximum and minimum difference densities 2.27 and −2.33 e Å^{-3}), in terms of the presence of residual uncorrected absorption.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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