Molecular and Crystal Structures of Pentafluorophenyl-platinum(II) Complexes with Bis(diphenylphosphino)methane, Bis(diphenylarsino)methane and 1,2-Bis(diphenylarsino)ethane

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Abstract. The X-ray crystal structures of $[PtCl_2(dppm)]$, $[Pt(C_6F_5)_2L]$ (L = dppm (bis(diphenylphosphino)methane), dpam (bis(diphenylarsino)methane), dpae (bis(diphenylarsino)ethane)) and $[PtCl(C_6F_5)(dpae)]$ show the complexes to be monomeric with chelating dipnictido ligands, and not alternatives with bridging ligands. In $[Pt(C_6F_5)_2(dpam)_2]$, there are two unidentate diarsine ligands in a cis-arrangement.

Keywords: Crystal structure; Platinum; Arsenic ligands; Phosphorus ligands; Organometallic compounds

Introduction

We have recently prepared a range of $[Pt(C_6F_5)Cl(Ph_2P-(CH_2)_nPPh_2)]$ and $[Pt(C_6F_5)_2(Ph_2P(CH_2)_nPPh_2)]$ (n = 2–4) complexes by decarboxylation reactions between the corresponding dichloroplatinum(II) complexes and thallium(I) pentafluorobenzoate in pyridine. All products were shown to have chelating diphosphines by X-ray crystallography regardless of chain length [1]. Even a seven membered chelate ring was preferred over a bridging structure.

With the corresponding bis(diphenylphosphino)methane (dppm) and bis(diphenylarsino)methane (dpam) complexes. there are additional structural and composition possibilities as shown by the isolation and spectroscopic characterization of $[Pt(C_6F_5)_2(dppm)]$ and *cis*- and *trans*- $[Pt(C_6F_5)_2(\eta'$ dppm)₂] [2]. Further, we have recently obtained three structural isomers, chelating, trans, trans-dimeric, and cis, transdinuclear of [PtCl₂(dpam)] [3]. We have now extended our X-ray crystal structural investigation to the complexes $[Pt(C_6F_5)_2L]$ (L = dppm, dpam, dpae (1,2-bis(diphenylarsino)ethane)), cis-[Pt(C₆F₅)₂(dpam)₂], [PtCl(C₆F₅)(dpae)], and $[PtCl_2(dppm)]$. Attempted syntheses of L = dppm and dpam complexes by decarboxylation have revealed the method generally unsuitable for these ligand systems, though sufficient $[Pt(C_6F_5)_2(dppm)]$ for crystallography was obtained, and diene displacement has also been used.

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Results and Discussion

Synthesis

Initial exploration of reactions of cis-[PtCl₂(dppm)] (1) and cis-[PtCl₂(dpam)] with thallium(I) pentafluorobenzoate in hot pyridine did not yield [Pt(C₆F₅)L] (L = dppm or dpam) complexes. From the reaction of the arsine complex, *trans*-[Pt(C₆F₅)₂(py)₂] [4] was the sole organometallic product identified.

$[PtCl_2(dpam)] + 2 py + 2 TlCO_2$	$C(C_6F_5) \xrightarrow{py}$	• $trans$ -[Pt(C ₆ F ₅)]	$_{2}(py)_{2}]$
	$+ 2 CO_2 +$	- 2 TlCl + dpan	n (1)

The large excess of the donor solvent and the elevated reaction temperature promote ligand displacement as observed in the synthesis of platinum(II) organoamides [5]. On the other hand, the corresponding reaction using $[PtCl_2(dpae)]$ proceeded effectively and the target $[Pt(C_6F_5)_2(dpae)]$ (2) was obtained in good yield.

$$[PtCl_2(dpae)] + 2 TlO_2C(C_6F_5) \xrightarrow{py} [Pt(C_6F_5)_2(dpae)] + 2 TlCl + 2 CO_2 \quad (2)$$

The monosubstituted product $[Pt(Cl)(C_6F_5)(dpae)]$ (3) was only obtained in low yield but single crystals were grown for X-ray crystal structure analysis.

 $[PtCl_2(dpae)] + TlO_2C(C_6F_5) \xrightarrow{py} [Pt(C_6F_5)(Cl)(dpae)]$

+ TlCl + CO₂ (3)

To try and avoid ligand displacement, decarboxylation between [PtCl₂(dppm)] and thallium(I) pentafluorobenzoate was attempted in N-methylpyrrolidinone (NMP), a



	[Pt(dppm)Cl ₂]	$[Pt(dpae)(C_6F_5)_2]$	$[Pt(dpae)(Cl)(C_6F_5)]$	$[Pt(dpam)(C_6F_5)_2](H_2O)$	$[Pt(dpam)_2(C_6F_5)_2]$
Empirical formula Formula weight	C ₂₅ H ₂₂ Cl ₂ P ₂ Pt 650.36	C ₃₈ H ₂₄ As ₂ F ₁₀ Pt 1015.50	C ₃₂ H ₂₄ As ₂ Cl F ₅ Pt 883.88	C ₃₇ H ₂₂ As ₂ F ₁₀ O Pt 1017.48	C ₆₂ H ₄₄ As ₄ F ₁₀ Pt 1473.74
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	C2/c	$P2_1/c$	$P\bar{1}$	$P2_{1}/c$	C2/c
Unit cell dimensions	a = 16.322(1) Å	a = 18.3667(1) Å	a = 10.046(2) Å	a = 18.242(4) Å	a = 23.540(5) Å
	b = 7.854(1) Å	b = 10.2925(1) Å	b = 10.048(2) Å	b = 9.973(2)Å	b = 10.292(2) Å
	c = 19.414(3) Å	c = 19.8662(2) Å	c = 15.230(3) Å $\alpha = 83.39(3)^{\circ}$	c = 19.549(4) Å	c = 45.646(9) Å
	$\beta = 98.54(3)^{\circ}$	$\beta=\!115.048(1)^\circ$	$\beta = 74.16(3)^{\circ}$ $\gamma = 85.31(3)^{\circ}$	$\beta = 103.36(3)^{\circ}$	$\beta = 100.87(3)^{\circ}$
Volume	2461.06(6) Å ³	3402.3(5) Å ³	1467.1(5) Å ³	3460.24(12) Å ³	10864(4) Å ³
Z	4	4	2	4	8
Density (calculated)	1.755 g cm^{-3}	1.983 g cm^{-3}	2.001 g cm^{-3}	1.953 g cm^{-3}	1.802 g cm^{-3}
Absorption coefficient	6.059 mm^{-1}	6.138 mm^{-1}	7.165 mm^{-1}	6.037 mm^{-1}	5.076 mm^{-1}
Reflections collected	10616	38973	20509	37101	51581
Independent refl. / R_{int} Absorption correction	2166 / 0.0590 numerical	7997 / 0.0517 numerical	6875 / 0.0681 numerical	8174 / 0.0663 numerical	12567 / 0.0912 numerical
$T_{\rm max}$ / $T_{\rm min}$	0.406 / 0.549	0.4807 / 0.3530	0.9461 / 0.7428	0.4347 / 0.2461	0.5610 / 0.3599
Parameters	460	460	370	457	694
GooF on F^2	0.947	1.080	0.993	1.057	0.991
Final <i>R</i> indices $[I>2\sigma(I)]$	$R_1 = 0.0243$ wR ₂ = 0.0421	$R_1 = 0.0262$ wR ₂ = 0.0663	$R_1 = 0.0388$ wR ₂ = 0.0823	$R_1 = 0.0373$ wR ₂ = 0.0937	$R_1 = 0.0430$ wR ₂ = 0.0773
R indices (all data)	$R_1 = 0.0321$ wR ₂ = 0.0432	$R_1 = 0.0442$ wR ₂ = 0.0798	$R_1 = 0.0636$ wR ₂ = 0.0913	$R_1 = 0.0465$ wR ₂ = 0.0997	$R_1 = 0.0856$ wR ₂ = 0.0884

Table 1 Crystallographic data and refinement details of 1-3, 5 and 6.

Table 2 Selectet bond lenghts/Å and angles/° of 1-3, 5, 6.

$[PtCl_2(dppm)] \qquad [Pt(C_6F_5)_2(dpae)]$		[PtCl(C ₆ F ₅)(dpae)]		$[Pt(C_6F_5)_2(dpam)](H_2O)$		$[Pt(C_6F_5)_2(dpam)_2]$			
Pt-Cl Pt-P1	2.358(1) 2.212(1)	Pt(1)-C(50) Pt(1)-C(60) Pt(1)-As(2)	2.058(3) 2.066(3) 2.3892(3)	Pt(1)-C(50) Pt(1)-As(1) Pt(1)-Cl(1)	2.088(5) 2.336(1) 2.351(2)	Pt(1)-C(60) Pt(1)-C(50) Pt(1)-As(2)	2.031(4) 2.048(4) 2.3934(6)	Pt(1)-C(90) Pt(1)-C(100) Pt(1)-As(3)	2.059(5) 2.059(5) 2.4089(7)
Cl(1)-Pt-Cl(1)* P(1)-Pt-Cl(1) P(1)-Pt-P(1)*	90.67(6) 97,62(2) 74.17(7)	Pt(1)-As(1) C(50)-Pt(1)-C(60) C(50)-Pt(1)-As(2) C(60)-Pt(1)-As(2) C(50)-Pt(1)-As(1) C(60)-Pt(1)-As(1) As(2)-Pt(1)-As(1)	2.4096(3) 89.35(11) 88.28(8) 177.19(8) 172.53(8) 98.11(7) 84.25(1)	Pt(1)-As(2) C(50)-Pt(1)-As(1) C(50)-Pt(1)-Cl(1) As(1)-Pt(1)-Cl(1) C(50)-Pt(1)-As(2) As(1)-Pt(1)-As(2) Cl(1)-Pt(1)-As(2)	2.3998(8) 92.25(15) 90.53(15) 174.98(4) 176.37(2) 85.21(3) 92.20(4)	Pt(1)-As(1) C(60)-Pt(1)-C(50) C(60)-Pt(1)-As(2) C(50)-Pt(1)-As(2) C(60)-Pt(1)-As(1) C(50)-Pt(1)-As(1) As(2)-Pt(1)-As(1)	2.4144(7) 88.47(17) 93.92(12) 177.09(13) 167.89(11) 103.33(12) 74.372(19)	Pt(1)-As(1) C(90)-Pt(1)-C(100) C(90)-Pt(1)-As(3) C(100)-Pt(1)-As(3) C(90)-Pt(1)-As(1) C(100)-Pt(1)-As(1) As(3)-Pt(1)-As(1)	2.4279(10) 86.10(19) 90.67(14) 175.16(14) 172.95(14) 87.80(14) 95.19(3)

much poorer ligand for platinum than pyridine. After chromatography and crystallisation, a modest yield of impure $[Pt(C_6F_5)_2(dppm)]$ (4) was obtained including single crystals of the target compound.

$$[PtCl_2(dppm)] + 2 TlO_2C(C_6F_5) \xrightarrow{NMP} [Pt(C_6F_5)_2(dppm)] + 2 TlCl + 2 CO_2 \quad (4)$$

However, $[Pt(C_6F_5)_2(dpam)]$ (5) could not be obtained by this modification and use of acetonitrile was also ineffective. Accordingly (5) and *cis*- $[Pt(C_6F_5)_2(dpam)_2]$ (6) were obtained by ligand exchange reactions of $[Pt(C_6F_5)_2(hex)]$ (hex = hexa-1,5-diene), a method we have extensively used for bis(polyfluorophenyl)platinum complexes [6].

$$[Pt(C_6F_5)_2(hex)] + n \text{ dpam} \xrightarrow{CH_2Cl_2} [Pt(C_6F_5)_2(dpam)_n] + hex n = 1 \text{ or } 2 \quad (5)$$

X-ray crystal structures

X-ray crystal structures have been determined for 1–6. As $[Pt(C_6F_5)_2(dppm)]$ (4) and $[Pt(C_6F_5)_2(dpam)]$ (5) are isostructural compounds and 4 has the poorer data set [7], only the structure of 5 is discussed. The structures of 2, 3 and 6 are not isotypic but homeotypic with the analogous phosphorus complexes [1] and nor is compound 1 isotypic with the analogous arsenic complex [3]. Structures of 1–3, 5 and 6 are shown in Fig. 1–5, with selected bond lenghts and angles listed in Table 2.

In compound 1 the ligand forms a four-membered ring around the platinum atom, with a bridge-head-angle P-Pt-P of 74.27(7)° which is smaller than the one observed in the analogous arsenic compound, As-Pt-As (75.98(3)°) [3], and in the structure of *cis*-[PtCl₂(dipm)] (75.96(3)°) (dipm = bis(di(*o*-*iso*-propylphenyl)phosphino)methane) [8]. The Pt-P distances of 1 (2.2117(11) Å) are in good agreement with the Pt-P distances reported for [PtCl₂(dppe)]



Fig. 1a Molecular structure of [PtCl₂(dppm)] (1).



Fig. 1b Crystal structure of [PtCl₂(dppm)] (1).

(2.208(26)-2.230(2) Å) (dppe = bis(diphenylphosphino)ethane) [9] and shorter than the Pt-As distances in [Pt(Cl₂(dpam)] (2.3334(9), 2.3261(6) Å) by near the difference between the ionic radii of the donor atoms [10]. The Pt-Cl distances (2.3575(11) Å) are slightly elongated by comparison with the distances observed in [PtCl₂(dpam)] (2.3420(11) Å, 2.3480(11) Å), consistent with the stronger trans-influence of phosphorus than arsenic [11]. The molecules of 1 are packed in the [001] direction, such that strands of coplanar oriented molecules are formed, the layers of which point alternately in opposite directions (Fig. 1b). The driving force for such an arrangement is to minimize steric interactions between the phenyl groups. However, besides the steric effect, there are close intermolecular contacts between hydrogen atoms and of the phenyl group



Fig. 2 Molecular structure of $[Pt(C_6F_5)_2(dpae)]$ (2).

and the chlorine atoms (2.80 Å), which is smaller than the sum of the van der Waals radii (3.20 Å [12]) and indicative of H-bonding interactions. These also play a role in the strandwise orientation of the molecules.

The X-ray crystal structures of 2-6 show that the molecules are monomers with *cis* geometry in the solid state, despite the number of possible alternatives. In 2 the Pt-As distances (2.3892(3), 2.4096(3) Å) are in good agreement with the ones observed in **5** and **6** (2.3934(6) - 2.4279(19) Å, Table 2). The Pt-C distances (2.058(3), 2.066(3) Å) of 2 with a five-membered ring are in the range of the observed distances in the non-chelating 6 (2.059(5) Å), but are significantly larger than in 5 (2.031(4), 2.048(4) Å) which has a four-membered chelate ring involving the same ligand as 6. Evidently the *trans* influence of the constrained dpam-ring is weaker than that of either the unstrained five-membered ring or the pair of unidentate dpam ligands. In contrast, the Pt-C bond in 3 (2.088(5) Å) is the longest observed in the present compounds, but is comparable with those of *cis*- $[PtCl(C_6F_5)(Ph_2P(CH_2)_nPPh_2)]$ (n = 2-4) [1] while the Pt-As distance (2.336(1) Å) trans to Cl(1) is the shortest, and is in the range of the corresponding distances of [PtCl₂(dpam)] (2.3334(9), 2.3261(6) Å). This is illustrative of the weak *trans* influence of the chloride ligand [11]. In 3, there is a little displacement of the chlorine atom from the best fit plane around platinum. This chlorine atom is involved in hydrogen-bonding to one of the phenylhydrogen atoms H(45) viz Cl(1)-H(45) 2.755(32) A; Cl(1)-C(45) 3.619(29) Å; Cl(1)-H(45)-C(45) 151.61(4)° (Fig 3). Another noteworthy feature of **3** is that one atom of the carbon bridge, C(2), is coplanar with platinum and the donor atoms. This contrasts 2, $[Pt(C_6F_5)_2(dppe)]$,and $[PtCl(C_6F_5)(dppe)]$ [1] where the carbon atoms are located above and below the plane. The square planar stereochemistry is distorted in all compounds, most notably seen in the decrease of the As1-Pt-As2 bite angle with decreasing ring size, $74.37(2)^{\circ}$ in 5 compared with $84.26(2)^{\circ}$ in 2.



Fig. 3 Molecular structure of $[PtCl(C_6F_5)(dpae)]$ (3).



Fig. 4 Molecular structure of $[Pt(C_6F_5)_2(dpam)]$ (5).

Although ligand dppm chelating the is in $[Pt(C_6F_5)_2(dppm)]$ as in the previously reported $[PtCl(C_6F_5)(dppm)]$ [13], the arsenic ligand dpam forms both chelating 5 and *cis*-[Pt(C_6F_5)₂(η^1 -dpam)₂] 6, the latter with unidentate dpam. The structure of 6 provides support for the spectroscopically proposed structure of cis- $[Pt(C_6F_5)_2(\eta^1-dppm)_2]$, this complex being derived by ligand displacement from cis-[Pt(C₆F₅)₂(THF)₂]. In **6**, one can observe intramolecular π -stacking between the C₆F₅group (C(90)-C(95)) and one phenyl group of the arsenic ligand (C(80)-C(85)) (Fig 5a, b). The distance of C(93) to



Fig. 5a Molecular structure of $[Pt(C_6F_5)_2(dpam)_2]$ (6).

the nearest aromatic plane is 3.416 Å, cf. 3.46 Å for the sum of the van der Waals radii of two aromatic rings [12], but the distance between the centroids of the planes is 3.879 Å indicating some lateral displacement of the rings.

Experimental Part

The decarboxylation reactions were carried out under nitrogen atmosphere using Schlenk techniques and dried solvents. However the products are air-stable. NMR spectra were recorded on a 300 MHz Bruker Avance spectrometer at 30 °C. IR data (4000-650 cm⁻¹) were obtained from Nujol mulls between NaCl plates with a Perkin Elmer 1600 FT-IR spectrometer. Elemental analyses (C, H) were determined by the Campbell Microanalytical Service, University of Otago, New Zealand. Suitable single crystals for X-ray studies for 2-4 were obtained by slow evaporation of the solvent (acetone), whilst 5 and 6 were recrystallised from $CH_2Cl_2/$ hexane. Bis(diphenylarsino)methane and bis(diphenylarsino)ethane were obtained from Strem, bis(pentafluorophenyl)-1,5-hexadieneplatinum(II) was synthesized by the reaction of LiC_6F_5 with dichloro-1,5-hexadieneplatinum(II) [14].

Bis(diphenylphosphino)methane(P,P')dichloroplatinum(II), (1)

After a preparation by the method of *Sanger* [15] the crude product was refluxed in a mixture of 15 ml concentrated hydrochloric acid and 15 ml ethanol for 4 h [16]. The white precipitate was filtered off and crystallized from dichloromethane giving block like crystals with an edge length of 2 to 3 mm (85 %).

 $\rm IR/cm^{-1}:~3051~m,~1585~w,~1572~w,~1485~m,~1437~vs,~1383~w,~1344~w,~1325~w,~1211~w,~1188~w,~1163~w,~1103~vs,~1026~w,~997~w,~881~w,~845~w,~773~w,~742~sh,~731~vs,~714~s,~690~vs,~617~w,~559~m,~511~vs,~480~w,~463~m$ and 426 w.

Bis(diphenylarsino)ethane(As,As')bis(pentafluorophenyl)platinum(II), (2)

Bis(diphenylarsino)ethanedichloroplatinum(II) (0.30 mg, 0.39 mmol) and thallium(I) pentafluorobenzoate (0.56 g, 1.34 mmol) were



Fig. 5b Crystal structure of $[Pt(C_6F_5)_2(dpam)_2]$, view along *b*-axis.

dried for 1 h in high vacuum and anhydrous pyridine (8 ml) was added under a nitrogen stream. The reaction mixture was heated to 80 °C and stirred for 2 h. The liberated CO₂ was passed through a saturated Ba(OH)₂ solution and determined as BaCO₃. After the reaction, pyridine was removed under vacuum and the residue washed with hexane (30 ml). The product was extracted with hot acetone (150 ml) and evaporated to 10 ml, giving white, transparent crystals (0.29 g, 75 %; CO₂ 77 %). [C₃₈H₂₄As₂F₁₀Pt (1015.5 g/mol)]: C 45.30 (calc. 44.94); H 2.18 (2.38) %.

¹**H** NMR (CDCl₃) δ = 2.20 (s with ¹⁹⁵Pt satellites, J(Pt, H) = 9.8 Hz, 4H, CH₂), 7.42 (m, 20H (Ph)) ¹⁹F NMR (CDCl₃) δ = -117.41 (m with ¹⁹⁵Pt satellites, J³(Pt, F) = 370 Hz, 4F, *o*-F), -162.6 (m, 2F, *p*-F), -164.8 (m, 4F, *m*-F).

 ${\rm IR/cm^{-1}:}~1705$ m, 1500 vs, 1360 s, 1306 w, 1275 w, 1221 m, 1183 m, 1081 m, 1058 vs, 1025 m, 999 m, 956 vs, 852 m, 792 s, 774 m, 741 vs, 693 vs.

The monosubstituted product (3) was obtained following the procedure of **2** but using a 1:1 stochiometric ratio of thallium(I) pentafluorobenzoate to bis(diphenylarsino)ethane dichloroplatinum(II). The compound was obtained in very low yield and was solely characterized by X-ray crystallography.

Bis(diphenylphosphino)methane(P,P')bis(pentafluorophenyl)platinum(II), (4):

To bis(diphenylphosphino)methanedichloroplatinum(II) (0.384 g, 0.59 mmol) and thallium(I) pentafluorobenzoate (0.739 g, 1.78 mmol) was added NMP (10 ml) and the mixture was heated to 120 °C. After 2 h the reaction mixture was cooled and water (100 ml) was added to precipitate the product. The solids were separated from the solvents by centrifugation (3400 rpm, 99 min) and were extracted with hot acetone (100 ml). The solution was clarified by centrifugation and evaporated slowly giving white, transparent crystals. TLC on neutral Al₂O₃ with acetone/hexane (1:3.5) showed Pt(C₆F₅)₂(dppm) (R_f = 0.31) contaminated by a side product (R_f = 0.12). Despite the big difference in the R_f values, the compounds could not be separated by column chromatography. From acetone solution crystals of [Pt(C₆F₅)₂(dppm)] were formed

which were identified by Xray crystallography but were contaminated by the side product ($\sim 0.20 \text{ g} \sim 38 \%$, CO₂ 90 %).

Bis(diphenylarsino)methane(As,As')bis(pentafluorophenyl)platinum(II), (5):

Hexa-1,5-dienebis(pentafluorophenyl)platinum(II) (0.27 g, 0.50 mmol) and bis(diphenylarsino)methane (0.24 g, 0.50 mmol) were dissolved in CH₂Cl₂ (15 ml) and stirred for 17 h at room temperature. After removing the solvent and washing with ethanol (30 ml) the product was recrystallised from CH₂Cl₂/hexane to give colorless crystals (0.30 g, 60 %).

¹**H** NMR (CDCl₃) δ = 4.72 (s with ¹⁹⁵Pt satellites, J(Pt, H) = 22 Hz, 2H, CH₂), 6.90-7.20 (m, 20H (Ph)). ¹⁹**F** NMR (CDCl₃) δ = -116.8 (m with ¹⁹⁵Pt satellites, ³J(Pt, F) = 341 Hz, 4F, *o*-F); -162.3 (m, 2F, *p*-F), -164.5 (m, 4F, *m*-F). [C₃₇H₂₂As₂F₁₀Pt (1001.50 g/mol)]: C 44.07 (calc. 44.37); H 1.98 (2.21) %.

 $\rm IR\ cm^{-1}:$ 1634 w, 1606 w, 1582 w, 1498 vs, 1363 m, 1308 w, 1270 w, 1184 m, 1160 w, 1080 m, 1057 vs, 1024 m, 998 s, 958 vs, 917 w, 844 w, 798 s, 785 s, 743 s, 737 vs, 695 s, 690 vs, 655 m, 626 m.

Di(bis(diphenylarsino)methane(As,As')bis(pentafluorophenyl)platinum(II), (6):

Hexa-1,5-dienebis(pentafluorophenyl)platinum(II) (0.64 g, 1.0 mmol) and bis(diphenylarsino)methane (0.96 g, 2.0 mmol) were dissolved in CH₂Cl₂ (20 ml) and stirred overnight at room temperature. After removing the solvent and washing with ethanol (50 ml) the product was recrystallised from CH₂Cl₂/hexane to give colorless crystals (0.96 g, 71 %). [C₆₂H₄₄As₄F₁₀Pt (1473.79 g/mol)]: C 50.58 (calc. 50.53); H 2.77 (3.01) %.

¹**H NMR** (CDCl₃) δ = 2.39 (s with ¹⁹⁵Pt satellites, J(Pt, H) = 15 Hz, 4H, CH₂), 6.94-7.20 (m, 40H (Ph)). ¹⁹**F NMR** (CDCl₃) δ = -116.8 (m with ¹⁹⁵Pt satellites, ³J(Pt, F) = 342 Hz, 4F, *o*-F), -162.3 (m, 2F, *p*-F), -164.5 (m, 4F, *m*-F). **IR**/cm⁻¹: 1633 w, 1580 w, 1503 vs, 1306 w, 1184 w, 1160 w, 1080 m, 1060 s, 1023 m, 998 s, 958 vs, 794 m, 784 m, 736 vs, 693 vs, 668 m.

X-ray-crystal structure determinations

For all compounds, a hemisphere of data (1° frames in phi and omega) were collected at 123(1) K using an Enraf-Nonius CCD area-detector diffractometer (monochromatic Mo-K α radiation, $\lambda = 0.71073$ Å), yielding N_{total} collected reflections after integration and scaling using the DENZO SMN software package [17]. Each data set was merged to N unique reflections (N₀ (*I*>2 σ (*I*)) 'observed').

The structures were solved using Direct Methods and refinedwith anisotropic thermal parameters for the non-hydrogen atoms by full matrix least-squares on all F^2 data using the SHELX97 [18] and XSEED [19] software packages. For all compounds hydrogen atoms were placed geometrically and refined isotropically using the riding model. A numerical absorption correction was applied to the data by the programs X–RED and X–SHAPE [20, 21]. Crystallographic data and refinement details are given in Table 1.

Although the *cis*-[Pt(dppm)Cl₂] (1) crystals had a regular shape and showed no signs for twinning under polarized light and in the first patterns, several crystals had to be measured to obtain a solvable diffraction data set. Because of weak packing forces, 10 % of the molecules are disordered, which may explain why a crystal structure of the well known *cis*-[Pt(dppm)Cl₂] has not been reported previously. In the Table 2 and Figure 1a, 1b only one of the molecule-orientations is reported.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 291797-291802. 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 details for each compound are listed in Table 1, with selected bond distances and angles in Table 2.

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