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## PLATINUM DERIVATIVES OF DECAFLUOROPHOSPHOROBENZENE AND DECAFLUOROARSENOBENZENE. THE CRYSTAL STRUCTURE OF $\text{Pt}(\text{PPh}_3)_2(\text{PC}_6\text{F}_5)_2$

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### Summary

The platinum complexes  $\text{Pt}(\text{PPh}_3)_2(\text{PC}_6\text{F}_5)_2$  and  $\text{Pt}(\text{PPh}_3)_2(\text{AsC}_6\text{F}_5)_2$  have been isolated from reactions of  $\text{Pt}(\text{PPh}_3)_3$  with  $(\text{PC}_6\text{F}_5)_4$  and  $(\text{AsC}_6\text{F}_5)_4$  respectively. A single-crystal X-ray analysis of  $\text{Pt}(\text{PPh}_3)_2(\text{PC}_6\text{F}_5)_2$  has shown that the compound crystallizes in space group  $P2_1$  with  $a = 9.286(5)$ ,  $b = 20.95(1)$ ,  $c = 11.226(5)$  Å,  $\beta = 90.7(1)^\circ$ ,  $Z = 2$ . The structure has been solved by Patterson and Fourier methods and refined to  $R = 0.043$  from three-dimensional diffractometer data. The complex contains the decafluorophosphorobenzene unit  $\text{C}_6\text{F}_5\text{P}-\text{PC}_6\text{F}_5$  bound through each P atom to the platinum. Coordination around the platinum is distorted square planar; the dihedral angle between the two  $\text{PtP}_2$  planes is  $20.4^\circ$ .

### Introduction

The phosphorus and arsenic analogues of azo derivatives have not been detected in the free state. The inability of these elements to form multiple bonds with other atoms of the same type has resulted instead in the formation of ring compounds, the "cyclic" phosphines or arsines [1].

These molecules usually having five or six atoms in the ring are known to react with a variety of metal carbonyls to yield compounds which either contain the intact ring, bonded through one [2] or two P(As) atoms [2,3] to the metal or where a bridge between metal atoms results from the ring having been fissioned. Each of the atoms at the ends of the chain of P(As) atoms so formed can bridge two metal atoms [4,5].

The four membered homocycle tetrakis(pentafluorophenyl)cyclotetraarsine however has been shown to react with  $\text{Fe}(\text{CO})_5$  to form a complex  $\text{Fe}(\text{CO})_4(\text{C}_6\text{F}_5\text{As})_2$  in which the unit  $\text{C}_6\text{F}_5\text{As}-\text{AsC}_6\text{F}_5$  is bound through each As atom

to the metal [6]. This species can thus be regarded as an azobenzene analogue, viz. "decafluoroarsenobenzene" which has been stabilized by coordination.

Further platinum complexes have been isolated containing both the arsenic and phosphorus species  $C_6F_5-M-M-C_6F_5$  ( $M = P, As$ ) and the structure of the phosphorus derivative has been determined.

## Results and discussion

Tris(triphenylphosphine)platinum reacts with either  $(C_6F_5P)_4$  or  $(C_6F_5As)_4$  in boiling benzene to yield the compounds  $Pt(PPh_3)_2(PC_6F_5)_2$  and  $Pt(PPh_3)_2(AsC_6F_5)_2$ .

Both complexes give molecular ions in their mass spectral patterns ( $m/e = 1115$  (P) and 1203 (As) based on  $^{195}Pt$ ) while the As derivative alone shows a peak indicating the loss of two As atoms to form the (apparent) pentafluorophenyl-platinum derivative  $Pt(PPh_3)_2(C_6F_5)_2^+$  ( $m/e = 1053$ ).

Neither phosphorus nor arsenic derivatives showed mass spectral peaks for the cyclic compounds  $(C_6F_5P(As))_4$  or the azo-analogues  $(C_6F_5P(As))_2$ .

### *The crystal structure of $Pt(PPh_3)_2(PC_6F_5)_2$*

A complete X-ray crystallographic study of the above compound has shown that the  $(C_6F_5P)_2$  unit exists in the molecule with the P atoms bonded together. Each P atom is in turn directly bonded to platinum.

A stereoscopic view [21] of the molecule showing the atom labelling system used in the analysis is presented in Fig. 1; selected bond lengths and interbond angles are listed in Table 1. The two phosphorus atoms, P(3) and P(4), of the  $(PC_6F_5)_2$  moiety and the two  $PPh_3$  phosphorus atoms, P(1) and P(2), form a distorted square planar array around the platinum atom (Fig. 2). The four phosphorus atoms lie up to 0.28 Å from their plane of best fit, with the Pt atom 0.08 Å from that plane (Table 2, plane 1). The dihedral angle between the Pt, P(1), P(2) and Pt, P(3), P(4) planes is  $20.4^\circ$ , much larger than those usually found in olefin complexes of  $Pt(0)$ . These angles are usually less than  $10^\circ$  while

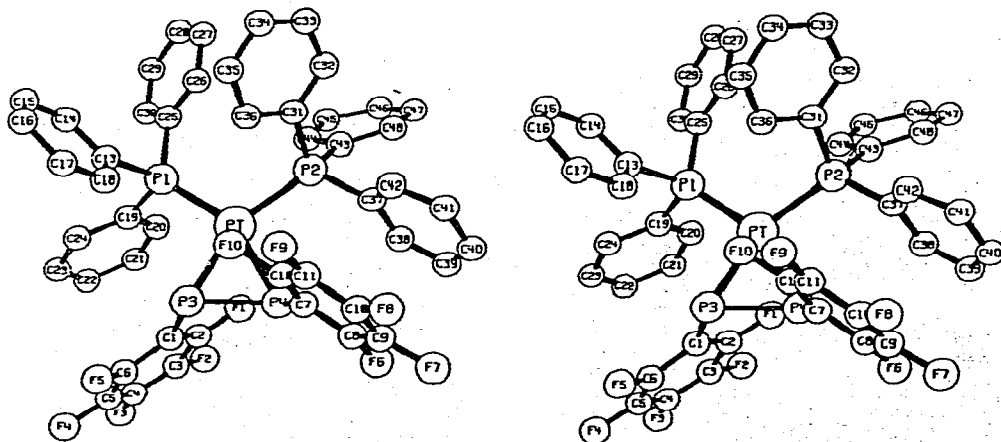


Fig. 1. A stereoscopic view of the molecule.

TABLE 1

SELECTED BOND LENGTHS (Å) AND INTERBOND ANGLES (°) FOR Pt(PPh<sub>3</sub>)<sub>2</sub>(PC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>*Distances from Platinum atom*

Pt—P(1)	2.349(5) <sup>a</sup>	Pt—P(2)	2.329(4)
Pt—P(3)	2.364(5)	Pt—P(4)	2.319(5)

*Distances within (PC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> ligand*

P(3)—P(4)	2.156(7)	P(4)—C(7)	1.87(2)
P(3)—C(1)	1.83(2)	C(7)—C(8)	1.36(2)
C(1)—C(2)	1.47(2)	C(8)—C(9)	1.35(3)
C(2)—C(3)	1.40(3)	C(9)—C(10)	1.35(3)
C(3)—C(4)	1.34(3)	C(10)—C(11)	1.39(3)
C(4)—C(5)	1.35(4)	C(11)—C(12)	1.33(3)
C(5)—C(6)	1.30(3)	C(12)—C(7)	1.41(2)
C(6)—C(1)	1.42(2)	C(8)—F(6)	1.36(2)
C(2)—F(1)	1.32(2)	C(9)—F(7)	1.33(2)
C(3)—F(2)	1.41(3)	C(10)—F(8)	1.35(2)
C(4)—F(3)	1.34(3)	C(11)—F(9)	1.32(2)
C(5)—F(4)	1.31(2)	C(12)—F(10)	1.38(2)
C(6)—F(5)	1.36(2)		

*Distances within PPh<sub>3</sub> ligands*

P(1)—C(13)	1.88(2)	P(2)—C(31)	1.84(2)
P(1)—C(19)	1.83(2)	P(2)—C(37)	1.84(1)
P(1)—C(25)	1.86(2)	P(2)—C(43)	1.81(2)
Average C—C distance 1.403(6)			

*Angles around Pt atom*

P(1)—Pt—P(2)	107.0(2)	P(2)—Pt—P(3)	149.2(2)
P(1)—Pt—P(3)	100.5(2)	P(2)—Pt—P(4)	99.9(2)
P(1)—Pt—P(4)	152.8(2)	P(3)—Pt—P(4)	54.8(2)

*Angles within the (PC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> ligand*

Pt—P(3)—P(4)	61.5(2)	Pt—P(4)—P(3)	63.6(2)
Pt—P(3)—C(1)	111.3(6)	Pt—P(4)—C(7)	111.3(6)
P(4)—P(3)—C(1)	102.0(6)	P(3)—P(4)—C(7)	104.1(6)
P(3)—C(1)—C(2)	127(1)	P(4)—C(7)—C(8)	119(1)
P(3)—C(1)—C(6)	121(1)	P(4)—C(7)—C(12)	128(1)
C(6)—C(1)—C(2)	112(1)	C(12)—C(7)—C(8)	113(2)
C(1)—C(2)—C(3)	116(2)	C(7)—C(8)—C(9)	125(2)
C(2)—C(3)—C(4)	126(2)	C(8)—C(9)—C(10)	118(2)
C(3)—C(4)—C(5)	118(2)	C(9)—C(10)—C(11)	122(2)
C(4)—C(5)—C(6)	120(2)	C(10)—C(11)—C(12)	116(2)
C(5)—C(6)—C(1)	128(2)	C(11)—C(12)—C(7)	126(2)
F(1)—C(2)—C(1)	120(1)	F(6)—C(8)—C(7)	118(2)
F(1)—C(2)—C(3)	124(2)	F(6)—C(8)—C(9)	117(2)
F(2)—C(3)—C(2)	110(2)	F(7)—C(9)—C(8)	122(2)
F(2)—C(3)—C(4)	124(2)	F(7)—C(9)—C(10)	120(2)
F(3)—C(4)—C(3)	115(2)	F(8)—C(10)—C(9)	120(2)
F(3)—C(4)—C(5)	127(2)	F(8)—C(10)—C(11)	118(2)
F(4)—C(5)—C(4)	116(2)	F(9)—C(11)—C(10)	120(2)
F(4)—C(5)—C(6)	124(2)	F(9)—C(11)—C(12)	123(2)
F(5)—C(6)—C(1)	114(2)	F(10)—C(12)—C(11)	115(2)
F(5)—C(6)—C(5)	118(2)	F(10)—C(12)—C(7)	120(1)

*Selected angles within PPh<sub>3</sub> ligands*

Pt—P(1)—C(13)	114.3(6)	Pt—P(2)—C(31)	112.0(6)
Pt—P(1)—C(19)	107.4(5)	Pt—P(2)—C(37)	112.6(5)
Pt—P(1)—C(25)	124.5(6)	Pt—P(2)—C(43)	120.7(6)
C(13)—P(1)—C(19)	106.3(7)	C(31)—P(2)—C(37)	103.1(7)
C(13)—P(1)—C(25)	98.2(8)	C(31)—P(2)—C(43)	105.4(8)
C(19)—P(1)—C(25)	104.5(8)	C(37)—P(2)—C(43)	101.2(7)
P(1)—C(19)—C(20)	117(1)	P(2)—C(37)—C(38)	117(1)
P(1)—C(19)—C(24)	121(1)	P(2)—C(37)—C(42)	121(1)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the units of the least significant digit of the preceding number.

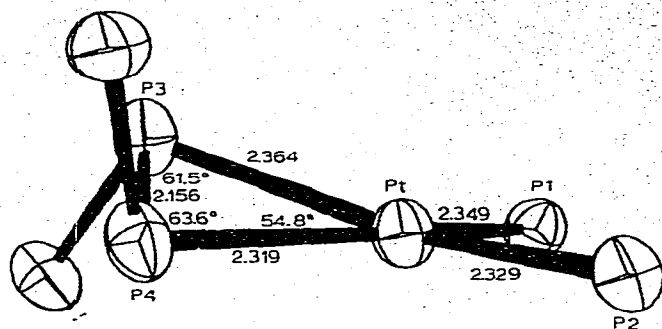


Fig. 2. A view of the Platinum environment.

in the case of  $\text{Pt}(\text{PPh}_3)_2(\text{CCl}_2)_2$  [7], it is increased to  $12.5^\circ$ . The distortions from planarity are presumably the results of steric effects. Potential interactions between the bulky triphenylphosphine and pentafluorophenyl rings are overcome to some extent by the fact that the two  $\text{C}_6\text{F}_5$  rings lie on opposite sides of the "square plane" and almost perpendicular to it.

TABLE 2

LEAST SQUARES PLANES IN  $\text{Pt}(\text{PPh}_3)_2(\text{PC}_6\text{F}_5)_2$ (a) Equations of planes  $pX + qY + rZ + s = 0$  where  $X$ ,  $Y$  and  $Z$  are in orthogonal coordinates

Plane	$p$	$q$	$r$	$s$
1	0.9450	0.3043	-0.1196	-3.5427
2	0.9452	0.2520	-0.2074	-3.2940
3	-0.9401	-0.3099	-0.1423	3.8100
4	-0.2712	0.8050	-0.5276	-4.3620
5	0.3047	-0.7006	-0.6452	4.6731
6	-0.2382	-0.6082	-0.7572	4.9143
7	-0.4375	0.8115	-0.3873	-0.6968
8	0.5015	0.4195	-0.7567	-1.3456
9	-0.7015	0.4187	-0.5767	-0.9908
10	0.4439	-0.6128	-0.6538	0.6764
11	0.2975	0.9435	-0.1456	-4.5807

(b) Deviations from planes (Å). (e.s.d.'s are Pt 0.0004; P 0.005; C 0.02; F 0.01 Å)

Plane	Deviation
1	P(1) 0.153; P(2) -0.157; P(3) -0.276; P(4) 0.280 [Pt 0.0809]
2	Pt P(1) P(2)
3	Pt P(3) P(4)
4	C(1) -0.04; C(2) -0.01; C(3) 0.04; C(4) 0.00; C(5) 0.03; C(6) -0.02; F(1) 0.00; F(2) 0.02; F(3) -0.04; F(4) -0.01; F(5) 0.03 [Pt -0.1898]
5	C(7) 0.02; C(8) -0.03; C(9) -0.02; C(10) 0.00; C(11) 0.00; C(12) 0.02; F(6) -0.01; F(7) 0.02; F(8) 0.01; F(9) -0.03; F(10) 0.00 [P(1) 0.167]
6	C(13) 0.01; C(14) -0.01; C(15) -0.01; C(16) 0.03; C(17) -0.03; C(18) 0.01 [Pt 1.2697]
7	C(19) 0.02; C(20) -0.02; C(21) 0.00; C(22) 0.01; C(23) -0.01; C(24) -0.01 [P(4) 0.155]
8	C(25) -0.02; C(26) 0.00; C(27) 0.00; C(28) 0.01; C(29) -0.02; C(30) 0.02 [P(1) 0.140]
9	C(31) 0.01; C(32) -0.01; C(33) 0.00; C(34) 0.00; C(35) 0.00; C(36) -0.01 [P(1) 0.167]
10	C(37) 0.02; C(38) 0.02; C(39) -0.03; C(40) 0.01; C(41) 0.03; C(42) -0.05 [P(1) -0.021]
11	C(43) 0.01; C(44) 0.00; C(45) -0.01; C(46) 0.01; C(47) 0.01; C(48) -0.02 [P(2) -0.042]
	[P(2) 0.038]
	[P(2) 0.020]

TABLE 3

ATOMIC POSITIONAL PARAMETERS <sup>a</sup> IN FRACTIONAL COORDINATES FOR Pt(PPh<sub>3</sub>)<sub>2</sub>(PC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> WITH ISOTROPIC OR ANISOTROPIC TEMPERATURE FACTORS <sup>b</sup>

Atom	10 <sup>4</sup> x	10 <sup>4</sup> y	10 <sup>4</sup> z	10 <sup>4</sup> β <sub>11</sub>	10 <sup>4</sup> β <sub>22</sub>	10 <sup>4</sup> β <sub>33</sub>	10 <sup>4</sup> β <sub>12</sub>	10 <sup>4</sup> β <sub>13</sub>	10 <sup>4</sup> β <sub>23</sub>
Pt	2409(1)	2500	572(1)	82(1)	11(0)	44(0)	0(1)	-3(0)	1(1)
P(1)	3246(5)	1807(2)	2072(4)	81(6)	13(1)	50(4)	4(2)	1(4)	2(2)
P(2)	2273(5)	1910(2)	-1184(4)	84(6)	12(1)	46(4)	-2(2)	-5(4)	1(2)
P(3)	1573(6)	3360(2)	1738(4)	115(7)	12(1)	63(4)	1(2)	-1(5)	-2(2)
P(4)	1788(5)	3500(2)	-155(4)	91(7)	11(1)	63(4)	0(2)	-13(4)	4(2)
Atom	10 <sup>3</sup> x	10 <sup>3</sup> y	10 <sup>3</sup> z	10 <sup>3</sup> β <sub>11</sub>	10 <sup>3</sup> β <sub>22</sub>	10 <sup>3</sup> β <sub>33</sub>	10 <sup>3</sup> β <sub>12</sub>	10 <sup>3</sup> β <sub>13</sub>	10 <sup>3</sup> β <sub>23</sub>
C(1)	307(2)	383(1)	233(1)	7(2)	2(0)	8(2)	-1(1)	-4(2)	1(1)
C(2)	452(2)	390(1)	184(1)	13(3)	0(0)	8(2)	-1(1)	-2(2)	0(1)
C(3)	549(2)	429(1)	247(2)	12(3)	2(1)	21(3)	-3(1)	-5(3)	3(1)
C(4)	521(3)	459(1)	350(2)	30(5)	2(1)	14(3)	-1(2)	-7(3)	-4(1)
C(5)	387(3)	456(1)	393(2)	27(5)	2(1)	8(2)	1(1)	-6(3)	-1(1)
C(6)	291(2)	420(1)	340(2)	18(3)	1(0)	6(2)	-1(1)	0(2)	0(1)
C(7)	-11(2)	351(1)	-73(1)	6(2)	1(0)	7(2)	0(1)	1(2)	1(1)
C(8)	-48(2)	392(1)	-163(2)	10(3)	2(1)	7(2)	2(1)	-4(2)	-1(1)
C(9)	-177(2)	394(1)	-219(2)	15(3)	3(1)	8(2)	2(1)	-2(2)	0(1)
C(10)	-281(2)	354(1)	-181(2)	11(3)	2(1)	13(2)	2(1)	1(2)	-2(1)
C(11)	-258(2)	312(1)	-88(2)	8(3)	2(1)	10(2)	1(1)	-1(2)	-1(1)
C(12)	-127(2)	312(1)	-39(1)	15(3)	2(1)	7(2)	2(1)	1(2)	-1(1)
F(1)	484(1)	360(1)	84(1)	11(2)	3(0)	9(1)	-1(1)	-1(1)	-1(1)
F(2)	684(1)	429(1)	192(1)	17(2)	3(0)	20(2)	-2(1)	-3(2)	1(1)
F(3)	633(2)	490(1)	399(1)	31(3)	4(0)	20(2)	-3(1)	-13(2)	-2(1)
F(4)	365(2)	485(1)	494(1)	44(4)	3(0)	10(1)	0(1)	-4(2)	-3(1)
F(5)	156(2)	418(1)	385(1)	27(3)	3(0)	8(1)	0(1)	0(1)	0(1)
F(6)	57(1)	431(1)	-204(1)	18(2)	3(0)	10(1)	0(1)	-1(1)	1(1)
F(7)	-201(2)	433(1)	-311(1)	22(2)	5(1)	15(2)	2(1)	-6(2)	3(1)
F(8)	-413(1)	355(1)	-234(1)	11(2)	5(1)	21(2)	2(1)	-5(1)	-1(1)
F(9)	-364(1)	275(1)	-50(1)	11(2)	4(0)	16(1)	-2(1)	3(1)	-1(1)
F(10)	-108(1)	270(0)	55(1)	13(2)	2(0)	12(1)	-1(1)	3(1)	1(0)
Atom	10 <sup>3</sup> x	10 <sup>3</sup> y	10 <sup>3</sup> z	B					
C(13)	180(2)	149(1)	307(1)	3.1(4)					
C(14)	209(2)	96(1)	382(2)	3.8(4)					
C(15)	99(2)	71(1)	450(2)	5.7(5)					
C(16)	-43(2)	98(1)	441(2)	4.8(5)					
C(17)	-65(2)	153(1)	371(2)	5.4(5)					
C(18)	47(2)	176(1)	302(2)	3.5(4)					
C(19)	449(2)	226(1)	302(1)	3.1(4)					
C(20)	580(2)	242(1)	254(1)	3.5(3)					
C(21)	677(2)	284(1)	321(2)	4.0(4)					
C(22)	641(2)	305(1)	435(2)	4.9(5)					
C(23)	512(2)	285(1)	484(2)	4.7(4)					
C(24)	410(2)	244(1)	417(1)	3.2(3)					
C(25)	420(2)	104(1)	179(2)	3.8(4)					
C(26)	362(2)	61(1)	102(2)	4.2(4)					
C(27)	431(2)	2(1)	79(2)	4.8(5)					
C(28)	560(2)	-10(1)	136(2)	5.0(5)					
C(29)	622(2)	32(1)	216(2)	4.6(4)					
C(30)	555(2)	92(1)	237(1)	2.8(3)					
C(31)	110(2)	120(1)	-104(1)	2.7(3)					
C(32)	117(2)	68(1)	-180(2)	4.6(5)					
C(33)	22(2)	16(1)	-156(2)	5.8(5)					
C(34)	-67(3)	16(1)	-65(2)	6.6(6)					
C(35)	-74(2)	66(1)	11(2)	5.5(5)					
C(36)	20(2)	121(1)	-8(2)	4.3(4)					

TABLE 3 (continued)

Atom	$10^3x$	$10^3y$	$10^3z$	B
C(37)	142(2)	236(1)	-241(1)	2.5(3)
C(38)	219(2)	288(1)	-289(1)	3.0(3)
C(39)	159(2)	324(1)	-378(2)	4.8(5)
C(40)	24(2)	306(1)	-428(2)	5.8(5)
C(41)	-53(2)	254(2)	-382(1)	5.1(4)
C(42)	6(2)	221(1)	-282(2)	4.6(4)
C(43)	389(2)	162(1)	-189(1)	3.0(3)
C(44)	515(2)	150(1)	-117(2)	4.7(5)
C(45)	647(3)	127(1)	-166(2)	7.0(6)
C(46)	642(2)	118(1)	-292(2)	5.2(5)
C(47)	523(2)	128(1)	-365(2)	4.8(5)
C(48)	392(2)	150(1)	-310(2)	4.7(5)

<sup>a</sup> Numbers in parentheses are estimated standard deviations in the units of the least significant digit of the preceding number. <sup>b</sup> The form of the anisotropic temperature factor is:  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

The angles Pt—P—C are both 111.3° and the P—P—C angles are 102.0 and 104.1°. P(3) and P(4) have the same chirality.

The two Pt—PC<sub>6</sub>F<sub>5</sub> distances are significantly different (2.364(5) and 2.319(5) Å). There is no apparent explanation for this difference except to attribute it, once again, to steric effects. The mean Pt—PC<sub>6</sub>F<sub>5</sub> distance is 2.34 Å which is the same as the mean Pt—PPh<sub>3</sub> distance and lies within the expected range for Pt—P bond lengths. It is interesting to note that the longer Pt—PC<sub>5</sub>F<sub>5</sub> bond is *trans* to the shorter Pt—PPh<sub>3</sub> bond. Other average bond lengths in the structure are: P—C 1.845(8); C—C(C<sub>6</sub>F<sub>5</sub>) 1.37(1); C—F 1.35(1); C—C(Ph) 1.403(6) Å. The P—P distance of 2.156(7) Å is shorter than those found in cyclic phosphorus systems e.g. [8] (PCF<sub>3</sub>)<sub>4</sub> 2.213(5); [9] (PCF<sub>3</sub>)<sub>5</sub> 2.22(2); [10,11] (PPh)<sub>6</sub> 2.234(2) and 2.233(5); [2] (PCH<sub>3</sub>)<sub>6</sub>W(CO)<sub>4</sub> 2.24(1) Å. This reduction in the bond length in going from a cyclic to a dimeric unit is consistent with that observed in Fe(CO)<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>As)<sub>2</sub> [6] where the As—As distance is 2.388(7) Å compared with those in (AsMe)<sub>5</sub> [12] 2.428(8) and (AsPh)<sub>6</sub> [13] 2.456(5) Å.

The only other compound so far described in which a P<sub>2</sub>M triangle has been postulated is Cy<sub>2</sub>MoP<sub>2</sub>H<sub>2</sub> [14] in which the structure has been suggested on the basis of <sup>1</sup>H and <sup>31</sup>P NMR spectra allied to other chemical evidence.

## Experimental

### Preparation of Pt(PPh<sub>3</sub>)<sub>2</sub>(PC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and Pt(PPh<sub>3</sub>)<sub>2</sub>(AsC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>

Tetrakis(pentafluorophenyl)-cyclotetraphosphine [15] and -cyclotetraarsine [16], and tris(triphenylphosphine) platinum(0) [17] were prepared by established procedures.

A mixture of the appropriate cyclic compound (1 mM) and tris(triphenylphosphine)platinum(0) (2 mM) was refluxed in benzene (40 ml) under nitrogen for 4 h. The solvent was then removed and the oil remaining redissolved in acetone from which pale yellow crystals of the product were obtained by slow evaporation. Each complex was further recrystallized twice from acetone. Phosphorobenzene derivative analysis: Found: C, 51.6; H, 2.82; F, 17.1; P, 10.9.

$C_{48}H_{30}F_{10}P_4Pt$  calcd.: C, 51.7; H, 2.71; F, 17.0; P, 11.1%. Arsenobenzene derivative analysis: Found: C, 47.5; H, 2.59; F, 15.6; As, 12.0.  $C_{48}H_{30}F_{10}As_2P_2Pt$  calcd.: C, 47.9; H, 2.51; F, 15.8; As, 12.4%.

### $^{19}F$ NMR spectra

The  $^{19}F$  shift parameters measured in ppm relative to  $CCl_3F$  as external standard and increasing to high field are:  $Pt(PPh_3)_2(PC_6F_5)_2$ : 125.8 (*ortho*); 157.6 (*para*); 164.4 (*meta*).  $Pt(PPh_3)_2(AsC_6F_5)_2$ : 122.5 (*ortho*); 157.3 (*para*); 163.9 (*meta*).

### Crystal and molecular structure of $Pt(PPh_3)_2(PC_6F_5)_2$

Crystal data:  $C_{48}H_{30}F_{10}P_4Pt$ ,  $M = 1115.7$ , Monoclinic,  $a = 9.286(5)$ ,  $b = 20.95(1)$ ,  $c = 11.226(5)$  Å,  $\beta = 90.7(1)^\circ$ ,  $U = 2183(1)$  Å<sup>3</sup>,  $D_m = 1.71$  g cm<sup>-3</sup> (by flotation in a chloroform/1,1,2,2-tetrabromoethane mixture),  $Z = 2$ ,  $D_c = 1.70$  g cm<sup>-3</sup>,  $F(000) = 1092$ . Space group  $P2_1$ , from systematic absences ( $0k0$  absent for  $k = 2n + 1$ ) and structure solution. Mo- $K_\alpha$  radiation monochromated by a graphite crystal,  $\lambda = 0.7107$  Å;  $\mu(Mo-K_\alpha) = 36.4$  cm<sup>-1</sup>. Intensity data recorded from a crystal of dimensions 0.17 mm  $\times$  0.12 mm  $\times$  0.10 mm.

2943 independent reflections within the range  $6^\circ < 2\theta < 45^\circ$  were measured using a Philips PW100 automatic X-ray diffractometer. 466 reflections with  $F^2 < 3\sigma(F^2)$  were not used in the solution or refinement of the structure. The data were corrected for Lorentz and polarization effects but not for absorption or extinction. Standard deviations were given by  $\sigma(I) = [C + B + (0.04 I)^2]^{1/2}$  where  $C$  is the integrated peak count;  $B$  is the background count taken over the same length of time and  $I = C - B$ .

Initially, the space group was assumed to be  $P2_1/m$ . This imposed mirror symmetry on the molecule, which was not inconsistent with its expected geometry. The position of the platinum atom was determined from an unsharpened Patterson map [18]. When likely positions for some of the atoms of the triphenylphosphine were determined, it became apparent that some of the atoms would lie too close to the mirror plane. The symmetry was therefore reduced to that for space group  $P2_1$  and the solution of the structure followed from successive Fourier syntheses. The residual,  $[R = \Sigma|F_0 - |F_c||\Sigma F_0]$  with all atoms included was 0.135. Block diagonal least squares refinement [19] with all atoms except those of the phenyl rings having anisotropic thermal parameters converged with  $R = 0.043$  and  $R' = 0.047$  [ $R' = \{\Sigma\omega(F_0 - |F_c|)^2/\Sigma\omega F_0^2\}^{1/2}$ ]. The function minimized was  $\Sigma\omega(F_0 - |F_c|)^2$  and weights,  $\omega$ , were applied as the inverse of the variance of the individual reflections. In the last refinement cycle, no parameter shift was greater than 0.2 of its standard deviation. Atomic scattering factors used were those for Pt, P, C and F [20]. A difference Fourier synthesis based on the final parameters contained no peaks or troughs greater than  $0.4e$  Å<sup>-3</sup>. The positions of the thirty hydrogen atoms on the phenyl rings were calculated. In most instances positive electron density was to be found in the difference map. However, there were other areas of equally high electron density and so the hydrogen atoms were not included in the structure factor calculations. The final atomic parameters with their estimated standard deviations are given in Table 3. Observed and calculated structure factors may be obtained from the authors.

All calculations were carried out using the Monash University CDC3200 computer.

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