International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JAYADEVAN, N. C. & CHACKRABURTTY, D. M. (1972). *Acta Cryst.* B**28**, 3178–3182.
LEGROS, J. P. & JEANNIN, Y. (1976). *Acta Cryst.* B**32**, 2497–2503.
MENTZEN, B. F. (1977). *Acta Cryst.* B**33**, 2546–2549.
MENTZEN, B. F., PUAUX, J. P. & LOISELEUR, H. (1977). *Acta Cryst.* B**33**, 1848–1851.
STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination, a Practical Guide*, pp. 454–458. New York: Macmillan.

Acta Cryst. (1978). B**34**, 1849–1853

The Crystal Structure of Bis(triphenylphosphine)(perfluoro-1,2-3,4-5,6-triethanobenzene)platinum(0)

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Bis(triphenylphosphine)(perfluoro-1,2-3,4-5,6-triethanobenzene)platinum(0).$\frac{1}{2}C_5H_{12}$ (?) is triclinic, space group $P\bar{1}$, with $a = 17{\cdot}435$ (9), $b = 12{\cdot}795$ (6), $c = 11{\cdot}248$ (5) Å, $\alpha = 104{\cdot}39$ (2), $\beta = 108{\cdot}08$ (4), $\gamma = 95{\cdot}37$ (3)°, $Z = 2$. Refinement gave $R = 0{\cdot}061$ for 3316 counter reflexions. The coordination at the Pt atom is essentially trigonal planar and bonding of the $C_{12}F_{12}$ is *via* a double bond of its benzene ring. The C atoms of the bond coordinate symmetrically and are almost coplanar with the Pt and the P atoms of the two coordinating triphenylphosphine ligands. Bond lengths around the $C_{12}F_{12}$ benzene ring alternate, with the exception of the bond coordinated to the Pt atom which is also long [1·52 (2) Å].

Introduction

The structures of the cyclic fluorocarbons perfluoro-1,2-3,4-5,6-triethanobenzene ($C_{12}F_{12}$) (Cobbledick & Einstein, 1976) and perfluorododecahydrotetracyclopentacyclooctene ($C_{20}F_{24}$) (Cobbledick & Einstein, 1977) have been determined. These compounds can coordinate to a transition metal and the structure of the title compound was studied to investigate the bonding of the $C_{12}F_{12}$ moiety to the Pt atom.

Experimental

Weissenberg and precession photographs (Cu $K\alpha$ radiation) showed the yellow crystals to be triclinic. Cell dimensions were obtained by least-squares refinement of the setting angles of ten reflexions with $2\theta > 30°$ centred on a Picker FACS-I automatic four-circle diffractometer [λ(Mo $K\alpha_1$) = 0·70926 Å]. Crystal data are given in Table 1. Intensities were collected (crystal dimensions 0·20 × 0·10 × 0·08 mm) with the diffractometer using a graphite monochromator and a scintillation counter with pulse-height discrimination. A θ–2θ scan was used with a scan speed of 2° min^{-1} in 2θ. The data were collected in two shells; reflexions having $0 < 2\theta \leq 20°$ were measured with a scan base width of 1·3° and reflexions with $20 < 2\theta \leq 40°$ had a width of 1·0° (both widths were increased for dispersion). Background measurements of 4 s duration were made at either side of the reflexions. Intensities were measured for 4265 unique reflexions, of which 3316 were classed as observed ($I > 2{\cdot}3\sigma I$, where σI is the standard deviation). Lorentz and polarization corrections were applied. No absorption correction was made [μ(Mo $K\alpha$) = 34·1 cm^{-1}] and this could give a maximum error of 3% in F.

The space group was assumed to be $P\bar{1}$ and was confirmed by successful refinement. The positions of the Pt and P atoms were obtained from a Patterson synthesis. After least-squares refinement, the remaining non-hydrogen atoms were located from a difference synthesis.

Table 1. *Crystal data*

$C_{48}H_{30}F_{12}P_2Pt.\frac{1}{2}(C_5H_{12})$, $M_r = 1127{\cdot}88$

$a = 17{\cdot}435$ (9) Å	Space group: $P\bar{1}$
$b = 12{\cdot}795$ (6)	$V = 2270{\cdot}3$ Å^3
$c = 11{\cdot}248$ (5)	$Z = 2$
$\alpha = 104{\cdot}39$ (2)°	$D_o = 1{\cdot}65$ g cm^{-3}
$\beta = 108{\cdot}08$ (4)	$D_c = 1{\cdot}650$
$\gamma = 95{\cdot}37$ (3)	μ(Mo $K\alpha$) = 34·1 cm^{-1}

Table 2. *Final fractional coordinates* ($\times 10^4$, $\times 10^5$ *for* Pt) *and isotropic thermal parameters* ($\times 10^3$ Å^2)

	x	*y*	*z*	*U*
Pt	77049 (5)	19600 (6)	2820 (8)	
P(1)	7032 (3)	242 (4)	−1079 (5)	
P(2)	8826 (3)	1720 (4)	1891 (5)	
F(1)	8625 (7)	3671 (9)	−791 (11)	
F(2)	8140 (7)	5125 (9)	−214 (11)	
F(3)	7100 (7)	2707 (9)	−2510 (10)	
F(4)	6667 (7)	4186 (9)	−1756 (11)	
F(5)	4878 (6)	3117 (9)	−1341 (10)	
F(6)	5056 (6)	1785 (8)	−504 (10)	
F(7)	5177 (7)	3093 (8)	1809 (10)	
F(8)	5032 (7)	4467 (9)	1040 (11)	
F(9)	7286 (8)	6322 (9)	3527 (12)	
F(10)	7573 (8)	5108 (10)	4545 (11)	
F(11)	8626 (7)	6223 (8)	2851 (12)	
F(12)	8949 (8)	5028 (10)	3894 (12)	
C(1)	5960 (10)	100 (13)	−1889 (16)	29 (5)
C(2)	5674 (12)	669 (15)	−2808 (19)	51 (6)
C(3)	4817 (13)	522 (16)	−3539 (19)	58 (6)
C(4)	4252 (13)	−176 (17)	−3362 (21)	63 (6)
C(5)	4499 (13)	−717 (17)	−2452 (21)	67 (7)
C(6)	5366 (12)	−564 (15)	−1700 (18)	49 (6)
C(7)	7401 (10)	−108 (13)	−2471 (15)	27 (4)
C(8)	8116 (11)	438 (14)	−2415 (17)	42 (5)
C(9)	8409 (12)	213 (16)	−3470 (20)	55 (6)
C(10)	7945 (13)	−616 (17)	−4566 (20)	63 (6)
C(11)	7223 (13)	−1174 (17)	−4674 (20)	61 (6)
C(12)	6941 (11)	−941 (15)	−3593 (18)	46 (5)
C(13)	7060 (11)	−915 (15)	−432 (17)	39 (5)
C(14)	6957 (12)	−748 (16)	801 (19)	55 (6)
C(15)	6921 (13)	−1635 (19)	1299 (22)	74 (7)
C(16)	6985 (13)	−2639 (18)	641 (22)	67 (7)
C(17)	7101 (13)	−2814 (18)	−532 (22)	74 (7)
C(18)	7138 (11)	−1924 (16)	−1069 (19)	49 (6)
C(19)	9024 (10)	361 (14)	1875 (17)	35 (5)
C(20)	9085 (12)	−67 (17)	2900 (20)	59 (6)
C(21)	9263 (13)	−1126 (18)	2857 (23)	67 (7)
C(22)	9399 (13)	−1723 (17)	1801 (22)	66 (7)
C(23)	9380 (14)	−1316 (18)	771 (22)	72 (7)
C(24)	9198 (12)	−266 (17)	831 (20)	56 (6)
C(25)	9832 (10)	2461 (13)	2150 (15)	25 (4)
C(26)	10540 (12)	2094 (15)	2666 (19)	52 (6)
C(27)	11282 (12)	2708 (16)	2845 (19)	55 (6)
C(28)	11337 (12)	3674 (16)	2512 (19)	51 (6)
C(29)	10631 (13)	4013 (16)	1941 (20)	59 (6)
C(30)	9864 (11)	3429 (14)	1765 (17)	40 (5)
C(31)	8671 (11)	2260 (13)	3442 (16)	33 (5)
C(32)	9326 (12)	2764 (16)	4590 (19)	54 (6)
C(33)	9173 (13)	3127 (16)	5791 (20)	59 (6)
C(34)	8416 (14)	2973 (17)	5780 (21)	69 (7)
C(35)	7735 (13)	2496 (17)	4654 (21)	62 (6)
C(36)	7909 (12)	2140 (16)	3481 (20)	58 (6)
C(37)	7820 (11)	3644 (14)	641 (17)	40 (5)
C(38)	6974 (10)	3031 (13)	−311 (16)	29 (5)
C(39)	6280 (11)	3172 (14)	137 (17)	35 (5)
C(40)	6326 (11)	3851 (14)	1266 (17)	37 (5)
C(41)	7085 (11)	4461 (14)	2174 (17)	40 (5)
C(42)	7791 (11)	4421 (14)	1864 (17)	36 (5)
C(43)	8001 (13)	4022 (17)	−412 (19)	52 (6)
C(44)	7144 (11)	3463 (16)	−1359 (19)	43 (5)
C(45)	5357 (12)	2854 (16)	−317 (19)	42 (5)
C(46)	5449 (12)	3618 (16)	1059 (19)	47 (5)
C(47)	7539 (14)	5340 (20)	3440 (24)	72 (7)
C(48)	8331 (13)	5299 (17)	3077 (20)	53 (6)
C(49)	4940	5110	5000	177
C(50)	4980	6280	4790	177
C(51)	4550	6880	5360	177
C(52)	4239	4572	4408	177

Full-matrix least-squares refinement with anisotropic thermal parameters for Pt gave $R = 0{\cdot}076$ ($R = \sum \| F_o| - |F_c\| / \sum |F_o|$). A difference map indicated anisotropic motion of the F atoms and the positions of some of the phenyl H atoms. Peaks around $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ showed that the crystals contained solvent of crystallization. Crystals were grown from a 50:50 mixture of CH_2Cl_2 and petroleum ether. Although a mass spectrum indicated traces of CH_2Cl_2, an analysis for Cl (0·00%) ruled out CH_2Cl_2 as the solvent of crystallization. Petroleum ether contains a variety of fractions (mainly pentane and hexane isomers) making it difficult to fit a satisfactory model for the solvent of crystallization. Analyses for C (53·61%) and H (3·21%) are consistent with hydrocarbon solvent of crystallization.

In the hope of obtaining better resolution of solvent peaks, the phenyl H atoms were included in calculated positions (C–H = 0·96 Å) and the F atoms were refined anisotropically. R improved to 0·066 but did not clean up the difference map around the special position. Four atoms of a chemically reasonable linear fragment were assigned from the difference map and included in fixed positions with site occupancy factors of 0·5 and isotropic temperature factors of 14 Å^2. Further least-squares refinement reduced R to 0·061. No chemically reasonable positions of other solvent atoms were indicated from a difference map. The largest features of the difference map (−5·5 to 7·3 σ) occurred in the region surrounding the Pt atom. No chemically reasonable positions of other solvent atoms were indicated, despite the fact that the density and C and H analysis best fitted the formula $C_{48}H_{30}F_{12}P_2$-$Pt.\frac{1}{2}(C_5H_{12})$, leaving our model with a chemically incomplete C_4-based fragment in the large, otherwise vacant, space. The maximum coordinate shift was 0·03σ and the refinement was terminated.

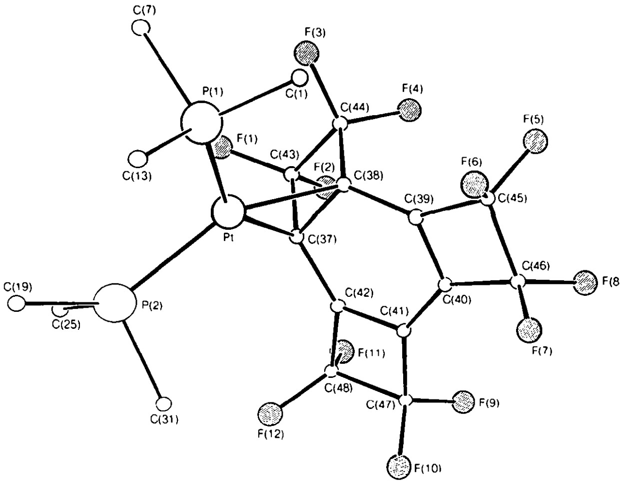

Fig. 1. Perspective view of a molecule of $[Pt(C_{12}F_{12})(PPh_3)_2]$, drawn by *ORTEP* (Johnson, 1965). For clarity the phenyl groups are omitted.

Table 3. *Interatomic distances* (Å) *and angles* (°)

Pt–P(1)	2·298 (5)	Pt–P(2)	2·320 (5)
Pt–C(37)	2·07 (2)	Pt–C(38)	2·05 (2)
P(1)–C(1)	1·78 (2)	P(1)–C(7)	1·84 (2)
P(1)–C(13)	1·80 (2)	P(2)–C(19)	1·80 (2)
P(2)–C(25)	1·82 (2)	P(2)–C(31)	1·82 (2)
C(1)–C(2)	1·40 (2)	C(1)–C(6)	1·38 (2)
C(2)–C(3)	1·43 (3)	C(3)–C(4)	1·36 (2)
C(4)–C(5)	1·36 (3)	C(5)–C(6)	1·45 (3)
C(7)–C(8)	1·35 (2)	C(7)–C(12)	1·38 (2)
C(8)–C(9)	1·41 (2)	C(9)–C(10)	1·37 (2)
C(10)–C(11)	1·34 (2)	C(11)–C(12)	1·42 (2)
C(13)–C(14)	1·42 (2)	C(13)–C(18)	1·35 (2)
C(14)–C(15)	1·39 (3)	C(15)–C(16)	1·35 (3)
C(16)–C(17)	1·36 (3)	C(17)–C(18)	1·42 (3)
C(19)–C(20)	1·37 (2)	C(19)–C(24)	1·38 (2)
C(20)–C(21)	1·41 (3)	C(21)–C(22)	1·35 (3)
C(22)–C(23)	1·38 (3)	C(23)–C(24)	1·40 (3)
C(25)–C(26)	1·37 (2)	C(25)–C(30)	1·41 (2)
C(26)–C(27)	1·38 (2)	C(27)–C(28)	1·38 (2)
C(28)–C(29)	1·37 (2)	C(29)–C(30)	1·40 (2)
C(31)–C(32)	1·39 (2)	C(31)–C(36)	1·34 (2)
C(32)–C(33)	1·43 (2)	C(33)–C(34)	1·31 (3)
C(34)–C(35)	1·39 (3)	C(35)–C(36)	1·42 (2)
C(37)–C(38)	1·52 (2)	C(37)–C(43)	1·49 (2)
C(37)–C(42)	1·50 (2)	C(38)–C(39)	1·46 (2)
C(38)–C(44)	1·51 (2)	C(39)–C(40)	1·32 (2)
C(39)–C(45)	1·51 (2)	C(40)–C(41)	1·41 (2)
C(40)–C(46)	1·46 (2)	C(41)–C(42)	1·38 (2)
C(41)–C(47)	1·50 (3)	C(42)–C(48)	1·50 (2)
C(43)–C(44)	1·52 (3)	C(43)–F(1)	1·36 (2)
C(43)–F(2)	1·36 (2)	C(44)–F(3)	1·39 (2)
C(44)–F(4)	1·37 (2)	C(45)–C(46)	1·56 (2)
C(45)–F(5)	1·34 (2)	C(45)–F(6)	1·36 (2)
C(46)–F(7)	1·36 (2)	C(46)–F(8)	1·36 (2)
C(47)–C(48)	1·56 (3)	C(47)–F(9)	1·36 (2)
C(47)–F(10)	1·33 (3)	C(48)–F(11)	1·36 (2)
C(48)–F(12)	1·32 (2)		

P(1)–Pt–P(2)	107·0 (2)	P(1)–Pt–C(37)	147·9 (5)
P(1)–Pt–C(38)	106·0 (5)	P(2)–Pt–C(37)	104·8 (5)
P(2)–Pt–C(38)	146·2 (5)	C(37)–Pt–C(38)	43·4 (6)
Pt–P(1)–C(1)	116·1 (6)	Pt–P(1)–C(7)	109·6 (5)
Pt–P(1)–C(13)	119·7 (6)	C(1)–P(1)–C(7)	101·7 (7)
C(1)–P(1)–C(13)	101·0 (8)	C(7)–P(1)–C(13)	107·0 (8)
Pt–P(2)–C(19)	120·2 (6)	Pt–P(2)–C(25)	118·0 (5)
Pt–P(2)–C(31)	106·5 (6)	C(19)–P(2)–C(25)	102·1 (8)
C(19)–P(2)–C(31)	104·5 (8)	C(25)–P(2)–C(31)	103·7 (8)
P(1)–C(1)–C(2)	120 (1)	P(1)–C(1)–C(6)	124 (1)
C(2)–C(1)–C(6)	116 (2)	C(1)–C(2)–C(3)	121 (2)
C(2)–C(3)–C(4)	121 (2)	C(3)–C(4)–C(5)	120 (2)
C(4)–C(5)–C(6)	120 (2)	C(1)–C(6)–C(5)	122 (2)
P(1)–C(7)–C(8)	121 (1)	P(1)–C(7)–C(12)	120 (1)
C(8)–C(7)–C(12)	119 (2)	C(7)–C(8)–C(9)	123 (2)
C(8)–C(9)–C(10)	117 (2)	C(9)–C(10)–C(11)	122 (2)
C(10)–C(11)–C(12)	120 (2)	C(7)–C(12)–C(11)	119 (2)
P(1)–C(13)–C(14)	117 (1)	P(1)–C(13)–C(18)	124 (1)
C(14)–C(13)–C(18)	119 (2)	C(13)–C(14)–C(15)	119 (2)
C(14)–C(15)–C(16)	121 (2)	C(15)–C(16)–C(17)	121 (2)
C(16)–C(17)–C(18)	119 (2)	C(13)–C(18)–C(17)	121 (2)
P(2)–C(19)–C(20)	124 (1)	P(2)–C(19)–C(24)	119 (1)
C(20)–C(19)–C(24)	117 (2)	C(19)–C(20)–C(21)	122 (2)
C(20)–C(21)–C(22)	119 (2)	C(21)–C(22)–C(23)	121 (2)
C(22)–C(23)–C(24)	118 (2)	C(19)–C(24)–C(23)	122 (2)
P(2)–C(25)–C(26)	122 (1)	P(2)–C(25)–C(30)	117 (1)
C(26)–C(25)–C(30)	120 (2)	C(25)–C(26)–C(27)	119 (2)
C(26)–C(27)–C(28)	122 (2)	C(27)–C(28)–C(29)	119 (2)
C(28)–C(29)–C(30)	121 (2)	C(25)–C(30)–C(29)	119 (2)
P(2)–C(31)–C(32)	122 (1)	P(2)–C(31)–C(36)	119 (1)

Table 3 (*cont.*)

C(32)–C(31)–C(36)	119 (2)	C(31)–C(32)–C(33)	119 (2)
C(32)–C(33)–C(34)	119 (2)	C(33)–C(34)–C(35)	124 (2)
C(34)–C(35)–C(36)	115 (2)	C(31)–C(36)–C(35)	123 (2)
Pt–C(37)–C(38)	68 (1)	Pt–C(37)–C(42)	125 (1)
Pt–C(37)–C(43)	112 (1)	C(38)–C(37)–C(42)	113 (1)
C(38)–C(37)–C(43)	91 (1)	C(42)–C(37)–C(43)	123 (2)
Pt–C(38)–C(37)	69 (1)	Pt–C(38)–C(39)	119 (1)
Pt–C(38)–C(44)	114 (1)	C(37)–C(38)–C(39)	117 (2)
C(37)–C(38)–C(44)	89 (1)	C(39)–C(38)–C(44)	126 (2)
C(38)–C(39)–C(40)	125 (2)	C(38)–C(39)–C(45)	142 (2)
C(40)–C(39)–C(45)	93 (1)	C(39)–C(40)–C(41)	121 (2)
C(39)–C(40)–C(46)	96 (2)	C(41)–C(40)–C(46)	143 (2)
C(40)–C(41)–C(42)	120 (2)	C(40)–C(41)–C(47)	148 (2)
C(42)–C(41)–C(47)	91 (2)	C(37)–C(42)–C(41)	123 (2)
C(37)–C(42)–C(48)	141 (2)	C(41)–C(42)–C(48)	95 (2)
C(37)–C(43)–C(44)	90 (2)	C(37)–C(43)–F(1)	118 (2)
C(37)–C(43)–F(2)	116 (2)	C(44)–C(43)–F(1)	115 (2)
C(44)–C(43)–F(2)	113 (2)	F(1)–C(43)–F(2)	105 (2)
C(38)–C(44)–C(43)	90 (1)	C(38)–C(44)–F (3)	118 (2)
C(38)–C(44)–F(4)	115 (2)	C(43)–C(44)–F(3)	116 (2)
C(43)–C(44)–F(4)	113 (2)	F(3)–C(44)–F(4)	105 (2)
C(39)–C(45)–C(46)	85 (1)	C(39)–C(45)–F(5)	121 (2)
C(39)–C(45)–F(6)	116 (2)	C(46)–C(45)–F(5)	116 (2)
C(46)–C(45)–F(6)	113 (2)	F(5)–C(45)–F(6)	105 (1)
C(40)–C(46)–C(45)	86 (1)	C(40)–C(46)–F(7)	120 (2)
C(40)–C(46)–F(8)	118 (2)	C(45)–C(46)–F(7)	114 (2)
C(45)–C(46)–F(8)	115 (2)	F(7)–C(46)–F(8)	104 (2)
C(41)–C(47)–C(48)	88 (2)	C(41)–C(47)–F(9)	115 (2)
C(41)–C(47)–F(10)	118 (2)	C(48)–C(47)–F(9)	114 (2)
C(48)–C(47)–F(10)	116 (2)	F(9)–C(47)–F(10)	106 (2)
C(42)–C(48)–C(47)	85 (2)	C(42)–C(48)–F(11)	114 (2)
C(42)–C(48)–F(12)	118 (2)	C(47)–C(48)–F(11)	115 (2)
C(47)–C(48)–F(12)	116 (2)	F(11)–C(48)–F(12)	108 (2)

Weights were assigned to the F_o's on the basis of the standard deviations ($w = 1/\sigma F_o^2$). Scattering factors, including anomalous dispersion factors for the Pt and P atoms, were taken from *International Tables for X-ray Crystallography* (1974). The computer programs have been cited elsewhere (Einstein & Jones, 1972). Final atomic parameters are given in Table 2. Fig. 1 shows the stereochemistry and atom labelling.* Bond distances and angles are given in Table 3.

Discussion

The coordination at the Pt atom is essentially trigonal planar, two of the sites being occupied by the P atoms and the remaining site by a near symmetrically coordinated double bond of the perfluoro-1,2-3,4-5,6-triethanobenzene ($C_{12}F_{12}$) moiety. Thus this structure is another example of a 1,2-di-*hapto*-arene complex, the first being bis(triethylphosphine)[hexakis(trifluoro-

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33353 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Deviations of atoms* (Å) *from least-squares planes*

The equations of the planes are referred to orthogonal axes with *x* along **a**, *z* along **c*** and *y* in the *ab* plane.

(*a*) Plane through C(1), C(2), C(3), C(4), C(5) and C(6)

$$0{\cdot}4101x - 0{\cdot}5791y - 0{\cdot}7046z - 5{\cdot}4551 = 0$$

C(1)	0·015	C(5)	−0·002
C(2)	−0·010	C(6)	−0·016
C(3)	−0·009	P(1)	0·119
C(4)	0·016		

$\chi^2 = 2{\cdot}40$

(*b*) Plane through C(7), C(8), C(9), C(10), C(11) and C(12)

$$-0{\cdot}4616x + 0{\cdot}8090y - 0{\cdot}3639z + 4{\cdot}9299 = 0$$

C(7)	0·004	C(11)	0·014
C(8)	−0·003	C(12)	−0·009
C(9)	0·006	P(1)	0·034
C(10)	−0·012		

$\chi^2 = 1{\cdot}02$

(*c*) Plane through C(13), C(14), C(15), C(16), C(17) and C(18)

$$-0{\cdot}8800x - 0{\cdot}0976y - 0{\cdot}4648z + 10{\cdot}7638 = 0$$

C(13)	0·008	C(17)	−0·005
C(14)	−0·006	C(18)	−0·004
C(15)	−0·003	P(1)	0·118
C(16)	0·009		

$\chi^2 = 0{\cdot}50$

(*d*) Plane through C(19), C(20), C(21), C(22), C(23) and C(24)

$$-0{\cdot}8528x - 0{\cdot}2873y - 0{\cdot}4362z + 13{\cdot}6395 = 0$$

C(19)	0·019	C(23)	−0·005
C(20)	−0·019	C(24)	−0·015
C(21)	−0·001	P(2)	−0·047
C(22)	0·015		

$\chi^2 = 2{\cdot}73$

(*e*) Plane through C(25), C(26), C(27), C(28), C(29) and C(30)

$$0{\cdot}3055x - 0{\cdot}2727y - 0{\cdot}9123z - 2{\cdot}2531 = 0$$

C(25)	−0·011	C(29)	0·018
C(26)	0·015	C(30)	0·001
C(27)	0·004	P(2)	−0·016
C(28)	−0·020		

$\chi^2 = 3{\cdot}00$

(*f*) Plane through C(31), C(32), C(33), C(34), C(35) and C(36)

$$-0{\cdot}1324x + 0{\cdot}9799y - 0{\cdot}1492z + 0{\cdot}5627 = 0$$

C(31)	−0·006	C(35)	0·007
C(32)	0·006	C(36)	0·002
C(33)	0·003	P(2)	−0·083
C(34)	−0·012		

$\chi^2 = 0{\cdot}62$

(*g*) Plane through C(37), C(38), C(39), C(40), C(41) and C(42)

$$-0{\cdot}0879x + 0{\cdot}9046y - 0{\cdot}4172z - 2{\cdot}6443 = 0$$

C(37)	−0·040	C(43)	1·087
C(38)	0·023	C(44)	1·212
C(39)	−0·011	C(45)	0·069
C(40)	0·005	C(46)	0·009
C(41)	−0·020	C(47)	0·072
C(42)	0·036	C(48)	0·151

$\chi^2 = 12{\cdot}06$

Table 4 (*cont.*)

(*h*) Plane through C(37), C(38), C(43) and C(44)

$$0{\cdot}5733x - 0{\cdot}7712y - 0{\cdot}2768z - 3{\cdot}8468 = 0$$

C(37)	−0·016	C(43)	0·022
C(38)	0·013	C(44)	−0·019

$\chi^2 - 3{\cdot}04$

(*i*) Plane through C(39), C(40), C(45), C(46)

$$-0{\cdot}0642x + 0{\cdot}9154y - 0{\cdot}3972z - 2{\cdot}9462 = 0$$

C(39)	−0·017	C(45)	0·018
C(40)	0·018	C(46)	−0·019

$\chi^2 = 3{\cdot}32$

(*j*) Plane through C(41), C(42), C(47) and C(48)

$$-0{\cdot}1447x + 0{\cdot}8726y - 0{\cdot}4665z - 1{\cdot}7235 = 0$$

C(41)	0·003	C(47)	−0·005
C(42)	−0·003	C(48)	0·004

$\chi^2 = 0{\cdot}12$

(*k*) Plane through P(1), P(2) and Pt

$$0{\cdot}7896x + 0{\cdot}2293y - 0{\cdot}5692z - 10{\cdot}7320 = 0$$

P(1)	0·000	C(37)	0·157
P(2)	0·000	C(38)	−0·243
Pt	0·000		

methyl)benzene]platinum (Browning, Green, Penfold, Spencer & Stone, 1973; Browning & Penfold, 1974). The C atoms of the coordinating double bond are almost coplanar with the Pt and P atoms and the bond is considerably lengthened [1·52 (2) Å]. The geometry around the Pt atom: Pt—P(1) = 2·298 (5), Pt—P(2) = 2·320 (5), Pt—C(37) = 2·07 (2), Pt—C(38) = 2·05 Å and angle between planes defined by Pt, P(1), P(2) and Pt, C(37), C(38) = 15·3°, can be compared with the geometries of bis(triphenylphosphine)platinum(0) complexes with olefins and related compounds (Muir, 1973) where the Pt—C distances range from 2·02 to 2·12 Å and the dihedral angle ranges from 1 to 13°. The larger dihedral angle in this structure can be attributed to non-bonded interactions between the triphenylphosphine groups and the bulkier substituents of $C_{12}F_{12}$. A larger dihedral angle (24°) is observed in bis(triethylphosphine)[hexakis(trifluoromethyl)benzene]platinum and the longer Pt—C bonds of 2·15 (2) and 2·14 (2) Å are attributed to the constraints. Structurally there are many similarities between the present structure and the latter. The present structure has triphenylphosphine groups in place of the triethylphosphine groups and the $C_{12}F_{12}$ ligand could be considered to be derived from hexakis(trifluoromethyl)benzene ($C_{12}F_{18}$) by removal of an F atom from each CF_3 group and bonding of appropriate pairs of adjacent C atoms of these groups. They both have the 1,2-di-*hapto* structure and the C—C distances of the benzene ring are alternately short and long (*i.e.* double and single bonds) with the exception of the double bond coordinated to the Pt atom which is lengthened. The distances around the benzene ring in the $C_{12}F_{12}$ ligand are C(37)—C(38) = 1·52 (2) (coordinated to Pt), C(38)–C(39) = 1·46 (2), C(39)–C(40) = 1·32 (2), C(40)–C(41) = 1·41 (2), C(41)–C(42) = 1·38 (2), C(37)–C(42) = 1·50 (2) Å. For uncoordinated $C_{12}F_{12}$ itself (Cobbledick & Einstein, 1976) the molecule has $\bar{6}$ symmetry with all the C atoms lying in a crystallographic mirror plane and the C–C lengths of the benzene ring are indistinguishable [1·383 (9) and 1·391 (9) Å]. In this structure the C atoms of the coordinated $C_{12}F_{12}$ are far from coplanar, and the plane through the cyclobutene ring whose double bond is coordinated to the Pt atom makes an angle of 51° with the mean plane through the benzene ring. In contrast, the planes through the C atoms of the other two cyclobutene rings make angles of only 2 and 5° with the least-squares plane through the benzene ring. Results of the least-squares-plane calculations for these and other groups are given in Table 4. The C atoms of each of the three cyclobutene rings are not rigorously coplanar but the deviations are small. Similarly, deviation of the benzene ring from planarity is slight. However, this is in contrast to the large departure from planarity (up to 0·22 Å) in the $C_{12}F_{18}$ complex. Harris, Harder & Sausen (1960) suggested that the benzene ring in $C_{12}F_{18}$ was itself non-planar as a result of non-bonded interactions between adjacent CF_3 groups. A recent analysis of the free ligand (Couldwell & Penfold, 1976) indicated that the ring is essentially planar with a mean displacement of 0·024 (3) Å compared with the larger mean displacement of 0·14 Å in the coordinated state.

The difference in planarity of the rings in the two structures appears to result from a difference in contacts with the Pt atom. For the $C_{12}F_{12}$ ligand the closest contacts of each type are Pt···F = 3·27, Pt···C(non-benzene) = 2·98 and Pt···C(benzene) = 3·03 Å, whereas for $C_{12}F_{18}$ the shortest contacts are 3·02, 3·40 and 2·67 Å respectively. The short contact between the Pt atom and the non-bonded ring C atom in $C_{12}F_{18}$ may be a factor in the distortion of the ring from planarity. Although the constraints for coordination of the benzene double bond might be expected to be less for the $C_{12}F_{18}$ ligand because of the less bulky ethyl groups on the P atoms (compared with the phenyl groups in the $C_{12}F_{12}$ structure), it is probable that the CF_3 groups have an influence. In $C_{12}F_{18}$ the C atoms of the CF_3 groups bonded to the ligating C ring atoms are displaced 0·03 and 1·46 Å on opposite sides of the mean plane through the ring atoms, whereas for $C_{12}F_{12}$ the corresponding C atoms are displaced 1·09 and 1·21 Å in the same direction, allowing a better approach of the ligand for coordination. For $C_{12}F_{18}$ the C atoms cannot be displaced a similar magnitude in the same direction because of resulting interactions between the adjacent CF_3 groups. The angle between the mean plane through the benzene ring and the plane through the Pt and P atoms is 101·7° compared with 115·2° in this structure.

There are some short intramolecular contacts between the F atoms and the phenyl atoms of the triphenylphosphine groups. The shortest C···F distance is C(32)···F(12) = 3·26 Å but the next shortest distance of 3·31 Å between C(2) and F(3) also involves a short contact with the assumed (calculated) H atom bonded to C(2). This contact of 2·33 Å is slightly shorter than the sum of the van der Waals radii for F and H and may indicate a weak interaction.

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References

BROWNING, J., GREEN, M., PENFOLD, B. R., SPENCER, J. L. & STONE, F. G. A. (1973). *Chem. Commun.* pp. 31–32.

BROWNING, J. & PENFOLD, B. R. (1974). *J. Cryst. Mol. Struct.* **4**, 335–346.

COBBLEDICK, R. E. & EINSTEIN, F. W. B. (1976). *Acta Cryst.* B**32**, 1908–1909.

COBBLEDICK, R. E. & EINSTEIN, F. W. B. (1977). *Acta Cryst.* B**33**, 2339–2342.

COULDWELL, M. H. & PENFOLD, B. R. (1976). *J. Cryst. Mol. Struct.* **6**, 59–64.

EINSTEIN, F. W. B. & JONES, R. D. G. (1972). *Inorg. Chem.* **11**, 395–400.

HARRIS, J. F., HARDER, R. J. & SAUSEN, G. N. (1960). *J. Org. Chem.* **25**, 633–634.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MUIR, K. W. (1973). *Molecular Structure by Diffraction Methods*, Vol. 1, p. 623. *Specialist Periodical Report*. Senior Reporters G. A. SIM & L. E. SUTTON. London: The Chemical Society.