Molecular Structures of Tetrafluoroethylene Complexes of Platinum(0). Part I. Crystal Structure of Tetrafluoroethylenebis(triphenylarsine)-platinum(0)

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Crystals of the title compound are monoclinic, space group $P2_1/n$ with $a = 11.291 \pm 0.010$, $b = 21.018 \pm 0.015$, $c = 14.380 \pm 0.010$ Å, $\beta = 95.54 \pm 0.05°$. The structure was determined from counter intensity data by heavy-atom techniques and refined by block-diagonal least-squares to R 0.053 for 5 110 reflections. Important mean bond lengths are: Pt–As 2.435, Pt–C 2.015, and C–C 1.45 Å. The extent of rehybridisation of the olefinic carbon atoms is discussed and the geometry of the complex compared with that in related molecules.

THE preparation of a series of tetrafluoroethylene complexes of platinum(0) with different amine, arsine, and phosphine ligands has recently been reported.[1] The ^{19}F n.m.r. spectra of the series suggest a possible relationship between the σ-donor ability of amine, arsine, or phosphine and the platinum–fluorine coupling constant. We wished to discover if this relationship was also reflected in the geometry of the bonded olefin. We now report the structure of (1) which has an intermediate coupling constant [$J_{(Pt-F)}$ 343 Hz].[1] In subsequent parts

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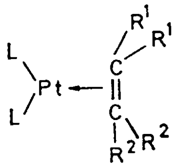
[1] R. D. W. Kemmitt and R. D. Moore, *J. Chem. Soc.* (*A*), 1971, 2472.

of this series the structures of complexes with coupling constants at either end of the range will be reported.[2]



	L	R^1	R^2
(1)	$AsPh_3$	F	F
(2)	PPh_3	Cl	Cl
(3)	PPh_3	CN	CN
(4)	PPh_3	H	H
(5)	PPh_3	CN	Cl
(6)	PPh_3	F	F

EXPERIMENTAL

Crystal Data.—$C_{38}H_{30}As_2F_4Pt$, $M = 907.6$, Monoclinic, $a = 11.291 \pm 0.010$, $b = 21.018 \pm 0.015$, $c = 14.380 \pm 0.010$ Å, $\beta = 95.54 \pm 0.05°$, $U = 3396.6$ Å^3, $D_m = 1.79$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.78$ g cm^{-3}, $F(000) = 1\,752$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 64.5 cm^{-1}. Space group $P2_1/n$ from systematic absences: $h0l$ for $h + l = 2n + 1$, $0k0$ for $k = 2n + 1$.

Crystals from benzene–light petroleum are plates on {010} with the forms {100}, {10$\bar{1}$}, and {101} commonly developed. Unit-cell dimensions were obtained from Weissenberg and precession photographs using, respectively, Cu-K_α ($\lambda = 1.5418$ Å) and Mo-K_α radiation.

Intensity data for reflections with $\sin\theta/\lambda < 0.7$ Å^{-1} were collected in 15 layers, $hk0$—14, from a crystal of dimensions *ca.* 0.05 × 0.02 × 0.02 cm. Intensities were measured on a Stoe automatic Weissenberg diffractometer by use of monochromatic Mo-K_α radiation and an ω-scan technique. Corrections for Lorentz, polarisation, and absorption[3] effects were made to the 5 110 reflections with $I > 3\sigma(I)$ and with $\sin\theta/\lambda > 0.1$ Å^{-1}.

Structure Determination.—Scattering factors for the atoms were taken from ref. 4 for platinum, fluorine, carbon, and hydrogen, and from ref. 5 for arsenic. During the least-squares refinement corrections for anomalous dispersion[6] were applied for the platinum and arsenic atoms.

The atomic co-ordinates of the platinum and arsenic atoms were determined from a three-dimensional Patterson synthesis and the positions of the remaining non-hydrogen atoms were found from successive Fourier syntheses phased on the atomic co-ordinates already determined.

Six cycles of block-diagonal least-squares refinement using a limited data set of 2 437 reflections ($\sin\theta/\lambda < 0.5$ Å^{-1}) and refining isotropic temperature factors reduced R to 0.059. Subsequently phenyl hydrogen atoms, with positions calculated from the molecular geometry (assuming C–H 1.0 Å), and B (5.0 Å^{-2}), were included in the structure factor calculations. After three cycles of refinement on the complete data set, including the refinement of anisotropic temperature factors for all non-hydrogen atoms, a weighting scheme was introduced to make $|w(F_o - F_c)^2|$ approximately constant over the whole range of $|F_o|$. The weight was given by $w = (10.0 + |F_o| + 0.03|F_o|^2)^{-1}$. The refinement converged after a further four cycles with a maximum shift in the final cycle of 0.5σ. The final R is 0.053 and R' 0.062 [$R' = \Sigma w(|F_o| - |F_c|)/\Sigma w|F_o|$] for 5 110 reflections.

RESULTS AND DISCUSSION

The atomic co-ordinates and thermal parameters are in Tables 1 and 2, and bond lengths and angles in Tables 3 and 4. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21332 (25 pp., 1 microfiche).* The molecular geometry and the atom numbering are shown in Figure 1. Each hydrogen atom has the same number as the carbon atom to which it is bonded.

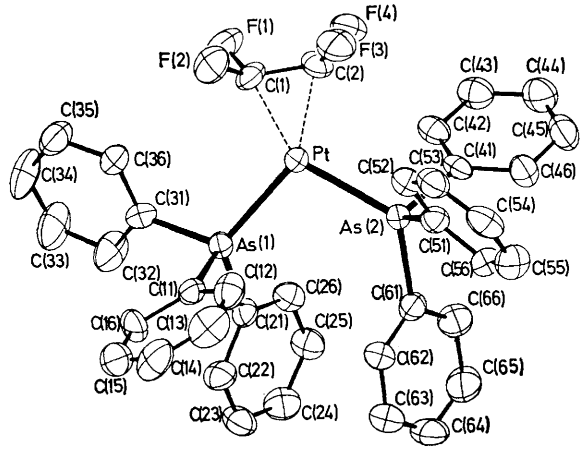


FIGURE 1 The molecular shape and atom numbering; thermal ellipsoids scaled to 50% probability

The mean Pt–C distance (2.015 Å) compares with the mean (2.03 Å)[7] in (2), being significantly shorter than the means (2.11) in (3)[8] and (2.11 Å) in (4).[9] The longer bond to platinum from the dicyano-substituted carbon of the olefin in (5)[10] has led to the suggestion that there is a limit to the effectiveness of back-donation (*i.e.* the loss of σ-bonding is not compensated by an increase in π-bonding). If, as seems reasonable, on the basis of electronegativities, tetrafluoroethylene is as good a π-acceptor as tetracyanoethylene the limit of effectiveness of back-donation should be equally evident in the Pt–C bonds in (6). Assuming that the π-acceptor abilities of

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[2] J. A. Evans and D. R. Russell, unpublished results.

[3] J. DeMeulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014; N. W. Alcock, *ibid.*, 1969, **A25**, 518.

[4] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965, p. 201.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[7] J. N. Francis, A. McAdam, and J. A. Ibers, *J. Organometallic Chem.*, 1971, **29**, 131.

[8] G. Bombieri, E. Forsellini, G. Panattoni, R. Graziani, and G. Bandoli, *J. Chem. Soc.* (*A*), 1970, 1313.

[9] P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Inorg. Chem.*, 1971, **10**, 2210.

[10] A. McAdam, J. N. Francis, and J. A. Ibers, *J. Organometallic Chem.*, 1971, **29**, 149.

triphenyl-phosphine and -arsine ligands are about equal (as spectroscopic evidence[11] suggests), it appears that C_2F_4 is more like C_2Cl_4 than $C_2(CN)_4$ in its bonding properties.

The C(1)-C(2) bond length in (1) is, as expected, greater than in tetrafluoroethylene (1.311 Å[12]) being equal to the C-C bonds in other complexes of the type

TABLE 1

Atomic co-ordinates with standard deviations, in parentheses, calculated from the least-squares refinement; hydrogen atomic co-ordinates were not refined

	x/a	y/b	z/c
Pt	0.21440(3)	0.09039(2)	0.20928(3)
As(1)	0.00296(9)	0.11440(5)	0.18170(8)
As(2)	0.21926(9)	−0.01281(5)	0.28665(8)
C(1)	0.3061(11)	0.1616(5)	0.1595(9)
C(2)	0.3880(10)	0.1140(6)	0.2004(11)
F(1)	0.3067(9)	0.1716(4)	0.0647(7)
F(2)	0.3124(8)	0.2200(4)	0.2016(7)
F(3)	0.4614(7)	0.1297(4)	0.2764(7)
F(4)	0.4528(8)	0.0822(4)	0.1420(8)
C(11)	−0.0604(10)	0.1545(5)	0.2862(8)
C(12)	−0.0009(13)	0.1464(7)	0.3738(11)
C(13)	−0.0500(18)	0.1744(8)	0.4498(12)
C(14)	−0.1495(19)	0.2088(7)	0.4408(13)
C(15)	−0.2077(15)	0.2186(7)	0.3550(15)
C(16)	−0.1652(12)	0.1913(6)	0.2752(12)
C(21)	−0.1056(9)	0.0454(5)	0.1481(8)
C(22)	−0.2238(12)	0.0455(6)	0.1670(10)
C(23)	−0.2973(11)	−0.0060(7)	0.1376(12)
C(24)	−0.2538(12)	−0.0556(7)	0.0905(11)
C(25)	−0.1371(12)	−0.0567(6)	0.0751(9)
C(26)	−0.0624(11)	−0.0061(6)	0.1016(9)
C(31)	−0.0402(10)	0.1752(6)	0.0824(9)
C(32)	−0.1451(15)	0.1669(8)	0.0205(11)
C(33)	−0.1680(18)	0.2136(9)	−0.0481(14)
C(34)	−0.1025(20)	0.2659(8)	−0.0545(12)
C(35)	0.0019(15)	0.2729(7)	0.0038(12)
C(36)	0.0329(12)	0.2268(6)	0.0744(11)
C(41)	0.3269(8)	−0.0672(6)	0.2264(9)
C(42)	0.3413(10)	−0.0561(6)	0.1346(9)
C(43)	0.4178(13)	−0.0954(7)	0.0871(11)
C(44)	0.4766(14)	−0.1446(7)	0.1345(13)
C(45)	0.4612(12)	−0.1567(7)	0.2240(13)
C(46)	0.3844(11)	−0.1190(6)	0.2739(11)
C(51)	0.2873(10)	−0.0073(5)	0.4172(8)
C(52)	0.3404(10)	0.0494(6)	0.4467(10)
C(53)	0.3904(11)	0.0530(7)	0.5387(11)
C(54)	0.3836(12)	0.0026(8)	0.6006(11)
C(55)	0.3249(13)	−0.0544(7)	0.5698(10)
C(56)	0.2742(11)	−0.0584(6)	0.4798(10)
C(61)	0.0810(10)	−0.0680(6)	0.2981(10)
C(62)	−0.0113(12)	−0.0446(7)	0.3427(13)
C(63)	−0.1110(4)	−0.0809(9)	0.3474(17)
C(64)	−0.1154(12)	−0.1422(9)	0.3100(14)
C(65)	−0.0241(13)	−0.1659(8)	0.2693(15)
C(66)	0.0761(13)	−0.1292(7)	0.2607(13)
H(12)	0.0812	0.1188	0.3820
H(13)	−0.0046	0.1681	0.5230
H(14)	−0.1878	0.2315	0.5019
H(15)	−0.2930	0.2463	0.3460
H(16)	−0.2090	0.1990	0.2031
H(22)	−0.2642	0.0847	0.2054
H(23)	−0.3927	−0.0059	0.1501
H(24)	−0.3135	−0.0959	0.0695
H(25)	−0.0965	−0.0958	0.0361
H(26)	0.0330	−0.0074	0.0906
H(32)	−0.2002	0.1245	−0.0276
H(33)	−0.2508	0.2065	−0.0967
H(34)	−0.1243	0.3014	−0.1107
H(35)	0.0607	0.3145	−0.0108
H(36)	0.1140	0.2334	0.1222
H(42)	0.2925	−0.0157	0.0966
H(43)	0.4289	−0.0862	0.0134
H(44)	0.5332	−0.1765	0.0955
H(45)	0.5107	−0.1969	0.2563
H(46)	0.3729	−0.1273	0.3472
H(52)	0.3485	0.0884	0.3995
H(53)	0.4357	0.0963	0.5643
H(54)	0.4209	0.0043	0.6753
H(55)	0.3173	−0.0926	0.6184
H(56)	0.2770	−0.1204	0.4553
H(62)	−0.0030	0.0052	0.3720
H(63)	−0.1853	−0.0616	0.3824
H(64)	−0.1970	−0.1682	0.3189
H(65)	−0.0034	−0.2147	0.2412
H(66)	0.1497	−0.1465	0.2261

TABLE 2

Anisotropic thermal parameters with estimated standard deviations in parentheses

	B_{11} *	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Pt	2.81(2)	2.65(2)	3.85(2)	0.24(1)	0.42(1)	0.00(1)
As(1)	2.93(4)	2.98(4)	3.53(5)	0.20(3)	0.10(3)	0.18(3)
As(2)	2.74(4)	2.82(4)	4.09(6)	0.41(3)	0.38(3)	0.11(3)
C(1)	4.6(5)	3.0(4)	5.0(6)	0.6(4)	0.9(4)	−1.0(4)
C(2)	2.6(4)	3.9(5)	7.0(8)	−0.7(5)	0.3(4)	−0.6(3)
F(1)	7.6(5)	6.1(4)	6.3(5)	2.4(4)	1.3(4)	−1.6(4)
F(2)	6.9(4)	3.2(3)	8.5(6)	−0.9(3)	0.3(4)	−1.2(3)
F(3)	4.0(3)	7.7(5)	7.9(5)	1.1(4)	−0.6(3)	−1.3(3)
F(4)	4.5(4)	5.7(4)	10.1(7)	0.3(4)	3.0(4)	0.0(3)
C(11)	3.9(5)	3.4(4)	3.6(5)	0.5(3)	1.2(4)	−0.1(4)
C(12)	5.6(7)	4.2(6)	5.3(7)	0.1(5)	−0.7(5)	−0.3(5)
C(13)	9.5(12)	5.9(8)	4.4(8)	−1.2(6)	1.1(7)	−1.2(7)
C(14)	11.2(12)	3.4(6)	6.9(10)	−0.6(5)	4.1(9)	0.5(7)
C(15)	6.5(8)	4.1(6)	9.7(13)	0.3(7)	3.8(8)	1.1(6)
C(16)	4.0(5)	3.3(5)	7.7(9)	−0.5(5)	1.1(5)	1.1(4)
C(21)	3.3(4)	2.5(4)	4.3(6)	0.0(3)	−0.2(4)	−0.4(3)
C(22)	4.5(6)	3.4(5)	6.2(8)	−0.7(5)	1.1(5)	−0.9(4)
C(23)	3.0(5)	5.8(7)	6.6(8)	−0.4(6)	0.4(5)	−0.1(4)
C(24)	4.7(6)	5.3(7)	5.4(8)	−0.8(5)	−0.2(5)	−1.4(5)
C(25)	4.5(6)	5.0(6)	4.1(6)	−0.9(5)	0.9(4)	0.0(5)
C(26)	3.9(5)	5.2(6)	3.1(5)	−0.1(4)	0.5(4)	0.0(4)
C(31)	3.9(5)	4.2(5)	4.1(6)	0.6(4)	1.1(4)	−0.5(4)
C(32)	6.9(8)	6.2(8)	4.5(7)	1.5(6)	−2.3(6)	−1.0(6)
C(33)	8.9(11)	6.4(9)	6.3(10)	2.1(7)	−3.1(8)	−0.1(8)
C(34)	11.5(13)	4.6(7)	5.2(9)	1.8(6)	−1.6(8)	0.5(7)
C(35)	7.2(8)	4.6(6)	6.1(8)	1.5(6)	1.8(6)	−0.2(6)
C(36)	4.5(5)	3.7(5)	6.2(8)	1.2(5)	0.6(5)	−0.3(4)
C(41)	2.0(3)	4.2(5)	4.5(6)	−0.6(4)	0.4(3)	−0.1(3)
C(42)	2.9(4)	4.8(6)	4.8(6)	−0.9(4)	0.1(4)	−0.3(4)
C(43)	4.7(6)	5.3(7)	5.5(8)	−1.2(5)	1.2(5)	−0.4(5)
C(44)	5.7(7)	4.7(6)	7.7(10)	−1.2(6)	2.3(6)	0.4(5)
C(45)	3.7(5)	4.7(6)	8.3(10)	−0.3(5)	−0.4(5)	0.7(5)
C(46)	4.1(5)	4.4(6)	5.9(8)	0.0(5)	0.6(5)	0.7(4)
C(51)	3.4(4)	4.1(5)	3.3(5)	0.0(4)	0.8(4)	0.7(4)
C(52)	3.2(4)	4.7(6)	5.3(7)	0.3(5)	0.1(4)	0.0(4)
C(53)	3.3(5)	5.0(6)	6.1(8)	−0.4(5)	0.5(5)	0.0(4)
C(54)	3.7(5)	8.1(9)	4.5(7)	−0.7(6)	1.0(5)	0.8(5)
C(55)	5.4(7)	6.0(7)	4.0(7)	0.4(5)	0.0(5)	−0.2(5)
C(56)	4.2(5)	4.0(5)	5.3(7)	0.7(4)	0.9(4)	−0.4(4)
C(61)	3.0(4)	4.3(5)	5.9(7)	1.8(5)	−0.5(4)	−0.5(5)
C(62)	3.9(6)	5.1(7)	7.9(10)	1.4(6)	2.1(6)	0.5(5)
C(63)	3.8(6)	7.3(10)	11.8(15)	3.0(9)	2.0(7)	0.1(6)
C(64)	3.2(5)	8.4(10)	9.2(11)	2.9(8)	0.4(6)	−1.4(6)
C(65)	4.8(7)	4.8(7)	10.5(12)	0.9(7)	−0.9(7)	−1.4(5)
C(66)	4.4(6)	4.4(6)	8.0(10)	−0.5(6)	−0.1(6)	−1.3(5)

* Temperature factor in the form: $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2lhc^*a^*B_{13} + 2klb^*c^*B_{23})]$.

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[11] W. D. Horrocks and R. Craig Taylor, *Inorg. Chem.*, 1963, 723.

[12] S. H. Bauer, 4th Astin Symposium on Gas-phase Molecular Structure, 1972.

(1)—(6).[7-9] Assuming there is no large torsion angle about the C–C bond, the degree of rehybridisation of the olefin in complexes of this type may be gauged by the angle[13] between the normals to the R^1CR^1 and R^2CR^2 planes: the larger the angle the closer the approach to sp^3 hybridisation for the olefinic carbon atoms. The angle in (1) is 80°, larger than in the complexes (3) and (5) [64 (ref. 8) and 62° (ref. 10)]. It is apparently similar to the value in (2) (81°) but this observation must be regarded with caution because of the unusual $(Cl_2)C-C(Cl_2)$ bond length (1.62 Å) in that complex.* The larger value of this angle in (1) shows that a greater degree of rehybridisation has occurred, indicating a greater degree of back-donation from the metal to the olefin π^*-orbital.

TABLE 3

Bond lengths (Å), with estimated standard deviations in parentheses. Mean phenyl C–C bond length 1.384(5) Å

Pt–As(1)	2.435(1)	Pt–C(1)	1.991(11)
Pt–As(2)	2.436(1)	Pt–C(2)	2.038(11)
		Mean	2.015
C(1)–C(2)	1.447(18)	As(1)–C(11)	1.921(11)
		As(1)–C(21)	1.929(10)
C(1)–F(1)	1.381(16)	As(1)–C(31)	1.944(12)
C(1)–F(2)	1.368(14)	As(2)–C(41)	1.934(11)
C(2)–F(3)	1.347(16)	As(2)–C(51)	1.962(12)
C(2)–F(4)	1.344(16)	As(2)–C(61)	1.965(11)
Mean	1.360(9)	Mean	1.943(7)

TABLE 4

Bond angles (°), with estimated standard deviations in parentheses. Mean phenyl C–C–C ring angle 120.0(3)°

As(1)–Pt–As(2)	103.7(1)	C(2)–C(1)–F(1)	116.2(11)
As(1)–Pt–C(1)	108.7(4)	C(2)–C(1)–F(2)	115.9(11)
As(2)–Pt–C(2)	105.4(4)	F(1)–C(1)–F(2)	107.2(9)
C(1)–Pt–C(2)	42.1(5)	C(1)–C(2)–F(3)	118.6(11)
		C(1)–C(2)–F(4)	117.1(13)
Pt–As(1)–C(11)	113.4(4)	F(3)–C(2)–F(4)	107.4(10)
Pt–As(1)–C(21)	118.3(3)		
Pt–As(1)–C(31)	115.4(3)	As(1)–C(11)–C(16)	121.7(10)
Pt–As(1)–C(41)	108.0(4)	As(1)–C(21)–C(22)	123.4(8)
Pt–As(2)–C(51)	112.0(3)	As(1)–C(31)–C(32)	121.0(9)
Pt–As(2)–C(61)	125.5(3)	As(2)–C(41)–C(46)	121.3(10)
Mean	115.4	As(2)–C(51)–C(56)	120.6(9)
C(11)–As(1)–C(21)	104.5(5)	As(2)–C(61)–C(66)	121.0(10)
C(21)–As(1)–C(31)	101.7(5)	Mean	121.5
C(31)–As(1)–C(11)	101.5(5)	As(1)–C(11)–C(12)	118.3(9)
C(41)–As(2)–C(51)	105.0(5)	As(1)–C(21)–C(26)	117.6(8)
C(51)–As(2)–C(61)	101.3(5)	As(1)–C(31)–C(36)	118.1(10)
C(61)–As(2)–C(41)	103.1(5)	As(2)–C(41)–C(42)	118.1(9)
Mean	102.9	As(2)–C(51)–C(52)	117.5(9)
Pt–C(1)–C(2)	70.7(6)	As(2)–C(61)–C(62)	118.3(11)
Pt–C(2)–C(1)	67.2(6)	Mean	117.9

The co-ordination of platinum is planar (Table 5). This contrasts with some bis(triphenylphosphine)olefin platinum(0) complexes in which there is a significant dihedral angle between the P–Pt–P and C–Pt–C planes.[7,8] Heimbach and Traunmüller[14] have suggested that when the olefin is a good π-acceptor it is possible to stabilise a twist about the C=C bond such that the two pairs of

TABLE 5

Parameters of mean planes through sets of atoms and, in square brackets, distances (Å) of atoms from the planes. The equation of a plane is $lx + my + nz = p$ with co-ordinates (Å) referred to orthogonal axes a', b, and c

	l	m	n	p
Plane (1)				
Pt, As(1), As(2), C(1), C(2)	0.0528	−0.4561	−0.8883	−3.415
[Pt 0.000, As(1) −0.003, As(2) 0.003, C(1) 0.009, C(2) −0.009]				
Plane (2)				
C(1), F(1), F(2)	0.9942	−0.0555	0.0927	3.239
Plane (3)				
C(2), F(3), F(4)	0.2615	0.8618	−0.4347	1.891
Plane (4)				
F(1), C(1), C(2)	0.6891	0.7024	0.1785	5.022
Plane (5)				
F(2), C(1), C(2)	0.7413	0.2894	−0.6056	1.998
Plane (6)				
F(3), C(1), C(2)	0.7480	0.3045	−0.5897	2.107
Plane (7)				
F(4), C(1), C(2)	0.7082	0.6931	0.1343	4.951
Plane (8)				
C(11)—(16)	0.5551	0.8234	−0.1178	1.598
[C(11) −0.01, C(12) 0.01, C(13) 0.00, C(14) −0.01, C(15) 0.01, C(16) 0.00, As(1) −0.05]				
Plane (9)				
C(21)—(26)	0.1626	−0.4566	0.8747	1.198
[C(21) −0.01, C(22) 0.01, C(23) 0.01, C(24) −0.02, C(25) 0.02, C(26) −0.01, As(1) −0.06]				
Plane (10)				
C(31)—(36)	0.5872	−0.5036	−0.6337	−2.925
[C(31) −0.01, C(32) −0.01, C(33) 0.03, C(34) −0.03, C(35) 0.01, C(36) 0.01, As(1) −0.06]				
Plane (11)				
C(41)—(46)	0.7440	0.6032	0.2875	2.574
[C(41) 0.02, C(42) −0.01, C(43) −0.01, C(44) 0.01, C(45) 0.00, C(46) −0.01, As(2) −0.01]				
Plane (12)				
C(51)—(56)	0.8933	−0.3648	−0.2625	0.834
[C(51) 0.03, C(52) −0.02, C(53) 0.00, C(54) 0.01, C(55) 0.01, C(56) −0.02, As(2) 0.04]				
Plane (13)				
C(61)—(66)	0.3206	−0.3648	0.8742	4.418
[C(61) −0.01, C(62) 0.02, C(63) −0.01, C(64) −0.01, C(65) 0.01, C(66) −0.01, As(2) −0.07]				

Dihedral angles (°) between planes

(2)–(3)	80.1	(4)–(5)	2.8
(4)–(6)	51.4	(6)–(7)	1.3
(5)–(7)	49.9	(2)–(6)	10.1

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* A reduction of the C–C bond length to 1.42 Å would reduce the angle to *ca.* 72°.

[13] J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, 1970, **92**, 533.

[14] P. Heimbach and R. Traunmüller, *Annalen*, 1969, **727**, 208.

substituents are no longer eclipsed when viewed along the bond. This twist would lower the energy of the C=C π*-orbital, allowing increased back-donation from the metal to the olefin. In order to retain approximately equal metal–R contacts, the C–Pt–C plane must then twist relative to the L–Pt–L plane. Although tetrafluoroethylene is expected to be an excellent π-acceptor the torsion angle about the C(1)–C(2) bond is very close to zero (see Table 5). Nevertheless we note that the two complexes (2) [7] and (3),[8] with a significant dihedral angle between the P–Pt–P and C–Pt–C planes, have a torsion angle about the C=C bond of roughly 6°.

The mean Pt–As bond is longer than the values reported for platinum(II) complexes with the arsine ligand *trans* to chlorine {*e.g.* 2.308 Å in [$Pt_2Cl_4(AsMe_3)_2$] (ref. 15)} or *trans* to another arsine ligand {*e.g.* 2.375 in [$Pt(As_2Me_4Ph)_2Cl_2$] (ref. 16) and 2.38 Å in [$Pt(As_2Me_4Ph)_2I_2$] (ref. 17)}. It approaches more closely the sum of covalent radii [18] (2.48 Å) for the atoms, and is similar to the length (2.445 Å) reported in the octahedral platinum(IV) complex [$Pt(C_{24}H_{35}As_2)Br_3O$],[19] in which the arsenic atoms are *trans* with respect to the metal.

The triphenylarsine groups have the propellor conformation commonly found for triphenylphosphine ligands. The phenyl groups are planar (Table 5), the appropriate arsenic atom lying no more than 0.07 Å from the mean ring plane. In Figure 2 the two ligands are shown projected along the appropriate As–Pt bonds. The distances of the β-carbon atoms from the arsenic atom show the same pattern as in triphenylphosphine [20] with the smaller As ··· C(β) contacts on the same side of the mean As–C(α)–C(α)–C(α) plane as the platinum atom. This is because the As–C(α)–C(β) angles involving those β-carbon atoms above the As–C–C–C plane are larger than those involving the β-carbon atoms below it, thus minimising non-bonded contacts between the phenyl rings. The propellor shape is governed by the C(α) ··· C(β) contacts shown in Figure 2. In order to minimise non-bonded contacts between the separate triphenylarsine ligands the rings (2) and (6) are nearly parallel (Table 5) with C(21) ··· C(62) and C(26) ··· C(61) distances of 3.46 and 3.38 Å respectively, both close to the van der Waals thickness (3.4 Å [18]) of an aromatic ring. We note that the intramolecular packing requires both ' propellors ' to have the same chirality (Figure 2).

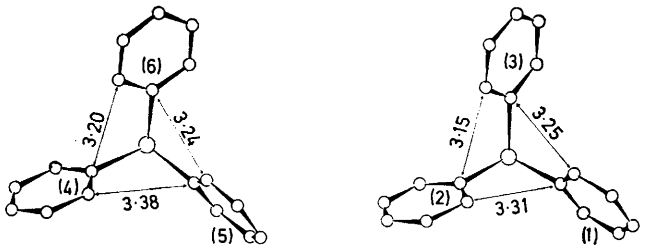

FIGURE 2 Configurations of the triphenylarsine ligands

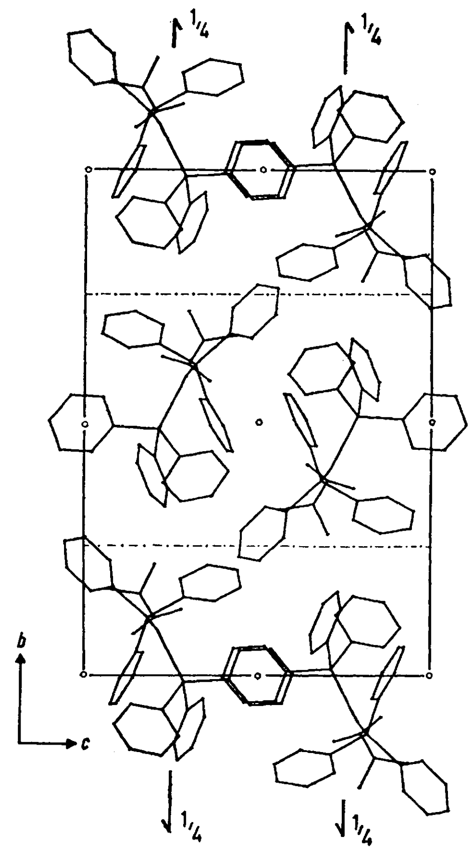

FIGURE 3 Molecular packing projected along [100]

The packing of the molecules, projected along *a*, is shown in Figure 3. The packing is governed largely by the phenyl rings of the triphenylarsine groups. The phenyl rings (5) and (5′) are packed across centres of symmetry at (½,0,½) and (0,½,0) with a perpendicular

TABLE 6

Short intermolecular contacts (Å)

F(1) ··· H(14^{I})	2.23	C(53) ··· H(63^{III})	2.68
C(42) ··· H(32^{II})	2.55	C(54) ··· H(63^{III})	2.59
C(43) ··· H(32^{II})	2.60	H(13) ··· C(64^{III})	2.70

Roman numeral superscripts refer to atoms related to those at *x*, *y*, *z* by the symmetry operations:

I $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$ III $-x, -y, 1 - z$
II $-x, -y, -z$

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[20] J. J. Daly, *J. Chem. Soc.*, 1964, 3799.

distance between rings of 3.39 Å. Similarly the rings (2) and (2″) are packed across centres of symmetry at (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$) with a perpendicular distance between rings of 3.39 Å. Those intermolecular contacts which are >0.1 Å less than the van der Waals distance[18] are listed in Table 6.

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