Crystal Structures of Hydrido-, Fluoro-, and Chloro-tris(triethylphosphine)platinum(II) Salts

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Crystals of [Pt(PEt$_3$)$_3$H][PF$_6$] are triclinic, $P\bar{1}$, with a = 15.969(3), b = 20.600(3), c = 9.081(2) Å, α = 79.87(2), β = 88.91(2), γ = 82.49(2)°, and Z = 4. Crystals of [Pt(PEt$_3$)$_3$F][BF$_4$] are monoclinic, $P2_1/c$ with a = 15.627(13), b = 10.988(8), c = 16.347(16) Å, β = 102.7(3)°, and Z = 4. Crystals of [Pt(PEt$_3$)$_3$Cl][BF$_4$] are monoclinic, $P2_1/n$, with a = 11.507(11), b = 17.452(18), c = 14.199(20) Å, β = 104.6(4)°, and Z = 4. Least-squares refinements for these three complexes converged with R = 0.049 (4 485 reflections), R 0.045 (3 008), and 0.047 (3 634) respectively. Mean bond lengths are Pt–P(*trans* to H) 2.335(4), Pt–P(*cis* to H) 2.300(3), Pt–P (*trans* to F) 2.239(3), Pt–P (*cis* to F) 2.337(4), Pt–P (*trans* to Cl) 2.251(3), Pt–P (*cis* to Cl) 2.353(3), Pt–F 2.043(7), and Pt–Cl 2.366(3) Å. The Pt–P bond lengths *trans* to the anionic ligand (X) in the cations follow the expected *trans*-influence order, whereas those *cis* to X follow the order Pt–P (*cis* to Cl) > Pt–P (*cis* to F) > Pt–P (*cis* to H) which reflects the anionic size of X.

It has been suggested [1,2] that the exploration of *cis* and *trans* influences of a ligand L in a formally square-planar metal (M) complex is least ambiguously tackled by obtaining structural data on complexes of the type [MLL'$_3$] where L' is a second ligand. Some structural determinations of anions of the type [PtCl$_3$L]$^-$ have been reported (ref. 2 and references therein). It appears that the variations in Pt–Cl(*trans* to L) distances are substantial whereas those in Pt–Cl(*cis* to L) are very much smaller.[2,3] However, it is clear, from the large body of structural information on platinum(II) complexes, that bond lengths involving other ligands do vary with changes in the *cis* ligand(s).[3] In order to explore further this *cis* influence we have begun a structural investigation of the cations of [Pt(PEt$_3$)$_3$X]Y (1), initially choosing ligands X which have negligible π-bonding character. We report here results on the complexes (1 : X = H, Y = PF$_6$; X = F, Y = BF$_4$; and X = Cl, Y = BF$_4$).

EXPERIMENTAL

Crystals of (1: X = F, Y = BF$_4$; and X = Cl, Y = BF$_4$) were kindly provided by Dr. K. R. Dixon. The complexes (1: X = H, Y = BF$_4$; and X = H, Y = PF$_6$) were prepared in a similar manner to the previously reported perchlorate salt [4] and were characterised by ^{1}H n.m.r. and i.r. spectra and elemental analyses. We were unable to grow single crystals of (1; X = H, Y = BF$_4$) suitable for *X*-ray structural analysis, but crystals of (1; X = H, Y = PF$_6$) were obtained from ethanol solutions. The colourless crystals are commonly twins [twin plane (100)] but a few single crystals were obtained exhibiting the forms {001}, {010}, {100}, and {110}. Colourless crystals of (1; X = F, Y = BF$_4$) are plates on {100} commonly exhibiting the forms {010}, {001}, and {012} whereas crystals of (1; X = Cl, Y = BF$_4$) are colourless parallelepipeds elongated along [110].

Unit-cell dimensions for (1: X = F, Y = BF$_4$; and X = Cl, Y = BF$_4$) were obtained from precession photographs recorded with Mo-K_α radiation. The unit-cell dimensions for (1; X = H, Y = PF$_6$) were determined by least-squares analysis [5] of the setting angles 2θ, ω, χ, and ϕ for 12 carefully centred high-angle reflections on a Picker FACS-I four-circle diffractometer. The estimated standard deviations (e.s.d.s) given below derive from this least-squares procedure but changes in cell parameters of up to 10σ were observed as crystal degradation occurs.

Crystal Data.—(1; X = H, Y = PF$_6$), [C$_{18}$H$_{46}$P$_3$Pt]-[PF$_6$], M = 695.5, Triclinic, a = 15.969(3), b = 20.600(3), c = 9.081(2) Å, α = 79.87(2), β = 88.91(2), γ = 82.49(2)°, U = 2 915.4 Å^3, D_m = 1.58(1) g cm^{-3}, Z = 4, D_c = 1.59 g cm^{-3}, $F(000)$ = 1 384, λ(Mo-K_α = 0.710 7 Å (for all complexes) μ(Mo-K_α) = 51.2 cm^{-1}, space group $P\bar{1}$.

(1; X = F, Y = BF$_4$), [C$_{18}$H$_{45}$FP$_3$Pt][BF$_4$], M = 655.4, Monoclinic, a = 15.627(13), b = 10.988(8), c = 16.347(16) Å, β = 102.7(3)°, U = 2 738.6 Å^3, Z = 4, D_c = 1.59 g cm^{-3}, $F(000)$ = 1 304, μ(Mo-K_α) = 56.0 cm^{-1}, space group $P2_1/c$ from systematic absences.

(1; X = Cl, Y = BF$_4$), [C$_{18}$H$_{45}$ClP$_3$Pt][BF$_4$], M = 672.0, Monoclinic, a = 11.507(11), b = 17.452(18), c = 14.199(20) Å, β = 104.6(4)°, U = 2 759.2 Å^3, Z = 4, D_c = 1.62 g cm^{-3}, $F(000)$ = 1 336, μ(Mo-K_α) = 54.7 cm^{-1}, space group $P2_1/n$ from systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$.

The intensities for (1: X = F, Y = BF$_4$; and X = Cl, Y = BF$_4$) in the range 0.1 > sinθ > 0.7 Å^{-1} were measured on a Stoe Weissenberg diffractometer using graphite-monochromated Mo-K_α radiation and an ω-scan technique. Corrections for Lorentz, polarisation, and absorption [6] effects were made. Intensity data for (1; X = Cl, Y = BF$_4$) were collected in 18 layers from a crystal of dimensions *ca.* 0.02 × 0.03 × 0.02 cm mounted about [010]. 3 634 Unique reflections with $I > 3\sigma(I)$ were considered observed. Intensity data for (1; X = F, Y = BF$_4$) were collected in 15 layers from a crystal of dimensions *ca.* 0.01 × 0.04 × 0.06 cm mounted about [001]. 3 008 Unique reflections with $I > 3\sigma(I)$ were considered observed. The intensities for (1; X = H, Y = PF$_6$) in the range $3 < \theta < 30°$ were measured on a Picker FACS-I fully automatic four-circle diffractometer using a θ—2θ scan technique with graphite-monochromated Mo-K_α radiation. During data collection severe anisotropic crystal degradation (up to 50% intensity loss), as monitored by the periodic measurement of three 'standard' reflections, was observed. Two crystals of dimensions *ca.* 0.043 × 0.008 × 0.014 and 0.038 × 0.018 × 0.013 cm were used and the data were corrected for decomposition assuming a linearly time-dependent isotropic decay. Intensities from the two crystals were corrected for absorption [6] and placed on the same scale using common reflections. Subsequent data processing followed a procedure described elsewhere.[7] 7 468 Unique reflections with $I > 3\sigma(I)$ were considered observed.

TABLE 1

Fractional atomic co-ordinates for (1; X = H, Y = PF_6)

Atom	x/a	y/b	z/c
Pt	0.404 64(4)	0.244 19(2)	0.181 29(6)
P(1)	0.477 79(28)	0.228 30(14)	0.407 70(40)
P(2)	0.392 91(35)	0.135 41(16)	0.164 64(46)
P(3)	0.387 15(34)	0.358 07(15)	0.116 87(42)
C(11)	0.504 0(11)	0.301 2(5)	0.475 0(16)
C(12)	0.553 7(14)	0.286 5(7)	0.630 1(18)
C(13)	0.580 5(11)	0.174 2(6)	0.410 8(19)
C(14)	0.641 8(11)	0.203 8(8)	0.293 2(22)
C(15)	0.420 9(11)	0.186 0(6)	0.569 5(15)
C(16)	0.336 7(12)	0.229 5(7)	0.597 8(20)
C(21)	0.430 7(14)	0.066 8(5)	0.314 9(18)
C(22)	0.414 4(17)	−0.004 9(6)	0.279 9(22)
C(23)	0.442 3(17)	0.116 7(8)	−0.009 4(22)
C(24)	0.538 5(14)	0.128 5(9)	−0.024 8(26)
C(25)	0.276 7(15)	0.127 4(9)	0.123 6(24)
C(26)	0.222 6(15)	0.147 0(11)	0.237 5(30)
C(31)	0.340 8(14)	0.381 8(7)	−0.075 1(19)
C(32)	0.321 8(15)	0.460 4(7)	−0.129 5(22)
C(33)	0.317 1(16)	0.399 3(7)	0.241 9(25)
C(34)	0.229 3(16)	0.374 7(9)	0.251 6(36)
C(35)	0.483 6(13)	0.402 9(7)	0.115 2(20)
C(36)	0.553 4(13)	0.375 7(9)	0.014 8(27)
Pt	0.881 18(4)	0.253 52(2)	0.651 70(7)
P(1)	1.014 65(41)	0.253 73(24)	0.739 56(81)
P(2)	0.869 10(45)	0.142 44(22)	0.699 82(70)
P(3)	0.834 99(38)	0.364 68(19)	0.568 57(54)
C(11)	1.052 9(14)	0.333 7(9)	0.744 1(31)
C(12)	1.142 1(19)	0.329 6(12)	0.808 8(46)
C(13)	1.092 4(16)	0.212 6(14)	0.629 7(46)
C(14)	1.086 3(26)	0.249 7(20)	0.461 1(44)
C(15)	1.031 2(28)	0.207 2(12)	0.924 3(39)
C(16)	0.987 2(30)	0.238 9(21)	1.034 0(31)
C(21)	0.949 0(16)	0.079 5(7)	0.792 1(25)
C(22)	0.927 1(19)	0.005 3(8)	0.815 9(32)
C(23)	0.842 1(22)	0.112 5(11)	0.542 8(37)
C(24)	0.922 3(24)	0.116 7(13)	0.431 5(32)
C(25)	0.761 5(23)	0.128 9(11)	0.804 1(40)
C(26)	0.770 1(25)	0.164 5(13)	0.944 8(38)
C(31)	0.909 0(17)	0.423 7(9)	0.510 7(30)
C(32)	0.864 0(21)	0.498 9(10)	0.450 1(27)
C(33)	0.766 3(26)	0.398 8(12)	0.709 7(36)
C(34)	0.779 9(24)	0.391 7(16)	0.848 9(31)
C(35)	0.756 7(15)	0.375 3(10)	0.412 2(30)
C(36)	0.802 1(21)	0.348 8(12)	0.274 5(25)
P(7)	0.0	0.5	0.0
P(8)	0.5	0.5	0.5
P(9)	0.255 52(59)	0.018 70(24)	0.740 16(74)
F(71)	−0.087 9(39)	0.490 2(40)	0.051 2(150)
F(72)	0.086 2(49)	0.471 5(39)	−0.041 2(143)
F(73)	0.027 6(21)	0.506 1(13)	0.156 4(22)
F(74)	−0.001 4(32)	0.426 6(9)	0.043 6(38)
F(81)	0.557 2(8)	0.448 1(4)	0.422 3(12)
F(82)	0.538 2(13)	0.468 5(6)	0.654 6(13)
F(83)	0.431 8(9)	0.451 8(5)	0.526 4(17)
F(91)	0.300 8(17)	−0.005 6(9)	0.897 0(19)
F(92)	0.330 6(43)	0.049 5(30)	0.704 7(68)
F(93)	0.274 7(33)	−0.051 7(12)	0.723 3(61)
F(94)	0.254 5(29)	0.091 6(8)	0.754 0(57)
F(95)	0.161 9(26)	0.024 1(25)	0.673 2(104)
F(96)	0.320 4(41)	−0.007 5(31)	0.638 4(58)
F(97)	0.199 3(49)	−0.029 0(37)	0.811 9(64)
F(98)	0.230 8(46)	0.045 4(30)	0.587 2(26)
F(99)	0.198 7(27)	0.049 7(26)	0.837 7(44)

Structure Solution and Refinement.—Scattering factors for neutral atoms including anomalous-dispersion corrections for Pt were taken from ref. 8. Conventional Patterson and difference-Fourier techniques were used. For (1; X = F, Y = BF_4; X = Cl, Y = BF_4) block-diagonal least-squares refinement was carried out using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (C–H 1.0 Å) with a fixed isotropic thermal parameter $B = 5.0$ Å^2. For (1; X = H, Y = PF_6), full-matrix least-squares refinement was used with anisotropic thermal parameters for non-hydrogen atoms; hydrogen atoms were not included. In all cases the function $\Sigma w(|F_o| - |F_c|)^2$ was minimised using weighting schemes which were chosen so that the function was approximately independent of $|F_o|$ and $(\sin\theta)/\lambda$. In the final difference-Fourier syntheses no residual features were greater than 0.5 e Å^{-3} except for positive and negative peaks *ca.* 1 e Å^{-3} close to Pt for (1; X = H).

In the case of (1; X = H, Y = PF_6) 2 983 reflections measured after considerable (>20%) crystal degradation had occurred were omitted from the final refinement cycles. Inclusion of these reflections results only in larger thermal parameters for cation B [Figure 1(*b*)], in particular for the phosphine ligand $P(1)Et_3$, but has no appreciable effect on cation A. A probable consequence of crystal degradation is that some chemically equivalent bond lengths, noticeably Pt–P(1), differ significantly in the two cations. We believe the values for cation A are more reliable.

TABLE 2

Fractional atomic co-ordinates for (1; X = F, Y = BF_4)

Atom	x/a	y/b	z/c
Pt	0.285 25(3)	0.204 76(4)	0.191 60(3)
P(1)	0.157 2(2)	0.106 0(3)	0.174 6(2)
P(2)	0.223 0(2)	0.399 2(3)	0.182 9(2)
P(3)	0.377 1(2)	0.037 0(3)	0.192 2(2)
F(1)	0.399 4(5)	0.301 9(8)	0.220 4(6)
F(2)	0.884 8(10)	0.164 8(13)	0.125 4(9)
F(3)	0.816 8(12)	0.224 9(14)	−0.002 2(9)
F(4)	0.772 5(11)	0.281 6(21)	0.110 4(14)
F(5)	0.893 1(12)	0.353 0(14)	0.088 0(10)
C(11)	0.161 4(11)	−0.057 6(14)	0.195 6(11)
C(12)	0.074 0(12)	−0.117 5(17)	0.195 3(15)
C(13)	0.087 4(9)	0.117 9(17)	0.069 5(9)
C(14)	0.137 4(11)	0.096 0(19)	0.002 0(10)
C(15)	0.091 1(9)	0.164 3(13)	0.246 9(10)
C(16)	0.135 0(11)	0.143 8(17)	0.337 1(11)
C(21)	0.116 0(10)	0.430 5(17)	0.116 2(14)
C(22)	0.083 6(13)	0.558 5(19)	0.114 9(16)
C(23)	0.293 6(11)	0.504 0(15)	0.143 3(12)
C(24)	0.304 8(15)	0.470 6(22)	0.058 5(14)
C(25)	0.214 5(13)	0.461 3(17)	0.284 8(13)
C(26)	0.295 0(14)	0.441 7(28)	0.352 7(14)
C(31)	0.350 3(11)	−0.071 6(17)	0.107 6(12)
C(32)	0.411 7(14)	−0.172 2(18)	0.105 0(14)
C(33)	0.401 1(12)	−0.051 7(18)	0.290 6(12)
C(34)	0.416 8(16)	0.019 5(26)	0.365 5(13)
C(35)	0.485 7(10)	0.088 9(10)	0.181 7(13)
C(36)	0.489 1(14)	0.147 5(21)	0.101 9(15)
B	0.840 7(17)	0.253 5(20)	0.078 3(16)

Final R factors for the three compounds (1) in the order X = H, F, Cl were $R = 0.049$, 0.045, 0.047 and $R' = 0.057$, 0.059, 0.058. Observed and calculated structure factors are listed as part of Supplementary Publication No. SUP 22790 (46 pp.).*

RESULTS AND DISCUSSION

Crystal Structures.—Final atomic co-ordinates for non-hydrogen atoms are given in Tables 1—3 for

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 3

Fractional atomic co-ordinates for (1; X = Cl, Y = BF_4)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Pt	0.202 12(3)	0.155 12(2)	0.227 55(3)
Cl	0.173 3(3)	0.266 5(2)	0.129 4(3)
P(1)	0.240 6(2)	0.048 8(2)	0.320 0(2)
P(2)	0.367 8(3)	0.141 9(2)	0.159 4(3)
P(3)	0.022 3(2)	0.197 8(2)	0.259 8(2)
F(1)	0.664 6(19)	0.370 9(14)	0.111 6(11)
F(2)	0.809 2(15)	0.446 5(12)	0.170 0(10)
F(3)	0.754 6(18)	0.370 7(11)	0.266 7(12)
F(4)	0.645 9(16)	0.461 9(12)	0.210 3(14)
C(11)	0.144 6(11)	0.022 9(7)	0.397 6(9)
C(12)	0.178 7(16)	−0.049 9(9)	0.456 7(11)
C(13)	0.388 7(11)	0.052 1(8)	0.403 9(8)
C(14)	0.401 3(14)	0.117 8(11)	0.474 3(11)
C(15)	0.227 7(9)	−0.038 6(6)	0.242 6(7)
C(16)	0.115 1(16)	−0.055 8(9)	0.183 6(12)
C(21)	0.477 2(14)	0.064 8(9)	0.186 1(13)
C(22)	0.568 1(17)	0.061 1(13)	0.128 9(16)
C(23)	0.463 7(13)	0.227 4(10)	0.185 3(14)
C(24)	0.507 0(15)	0.247 0(12)	0.286 8(19)
C(25)	0.312 9(15)	0.135 9(11)	0.027 5(11)
C(26)	0.226 0(19)	0.070 9(15)	−0.007 2(13)
C(31)	−0.056 4(11)	0.151 78()	0.340 9(11)
C(32)	−0.173 0(16)	0.189 6(12)	0.346 6(15)
C(33)	−0.091 6(10)	0.202 9(9)	0.145 4(10)
C(34)	−0.115 5(16)	0.124 2(13)	0.099 2(13)
C(35)	0.037 6(12)	0.295 8(8)	0.303 5(12)
C(36)	0.126 5(17)	0.305 1(11)	0.399 7(15)
B	0.715 3(20)	0.411 3(14)	0.190 3(16)

compounds (1) in the order X = H, F, and Cl. The atom numbering is the same where possible for all compounds and is shown for the cations in Figure 1. The crystal packing is illustrated in the stereopairs of Figures 2—4. Bond lengths and angles in the cations are compared in Table 4. Anisotropic thermal parameters, hydrogen-atom co-ordinates, bond lengths and

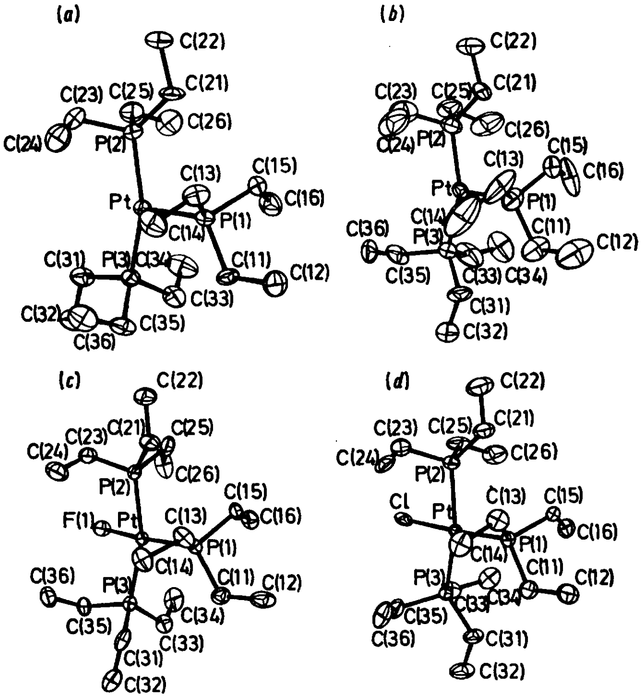

FIGURE 1 Molecular geometry and atom numbering in complexes (1). Hydrogen atoms have been omitted for clarity. (*a*) (1; X = H, Y = PF_6) cation A, (*b*) cation B; (*c*) (1; X = F, Y = BF_4); (*d*) (1; X = Cl, Y = BF_4)

TABLE 4

Bond lengths (Å) and angles (°) in the cations $[Pt(PEt_3)_3X]$

	X = H[a]			
	Cation A	Cation B	X = F[b]	X = Cl[b]
Pt–X			2.043(7)	2.366(3)
Pt–P(1)	2.335(4)[c]	2.291(7)	2.239(3)	2.251(3)
Pt–P(2)	2.304(3)	2.286(5)	2.339(4)	2.357(3)
Pt–P(3)	2.297(3)	2.309(4)	2.335(4)	2.350(3)
P(1)–C(11)	1.816(12)	1.836(19)	1.829(16)	1.804(13)
P(1)–C(13)	1.857(15)	1.797(26)	1.828(13)	1.817(11)
P(1)–C(15)	1.858(13)	1.785(30)	1.847(14)	1.864(10)
P(2)–C(21)	1.832(14)	1.799(20)	1.817(17)	1.816(14)
P(2)–C(23)	1.832(18)	1.732(32)	1.809(17)	1.836(16)
P(2)–C(25)	1.933(22)	1.974(36)	1.832(18)	1.822(17)
P(3)–C(31)	1.866(18)	1.811(19)	1.805(16)	1.823(13)
P(3)–C(33)	1.817(17)	1.844(31)	1.848(19)	1.814(13)
P(3)–C(35)	1.895(19)	1.874(25)	1.834(15)	1.812(14)
mean	1.856(38)	1.828(67)	1.828(15)	1.823(18)
C(11)–C(12)	1.59(2)	1.54(4)	1.52(2)	1.52(2)
C(13)–C(14)	1.53(2)	1.59(5)	1.50(2)	1.50(2)
C(15)–C(16)	1.56(2)	1.41(5)	1.50(2)	1.39(2)
C(21)–C(22)	1.62(2)	1.59(2)	1.49(3)	1.48(2)
C(23)–C(24)	1.58(3)	1.62(4)	1.48(3)	1.44(3)
C(25)–C(26)	1.41(3)	1.60(4)	1.50(3)	1.51(3)
C(31)–C(32)	1.60(2)	1.63(3)	1.47(3)	1.52(2)
C(33)–C(34)	1.55(3)	1.28(4)	1.43(3)	1.52(2)
C(35)–C(36)	1.54(2)	1.58(3)	1.47(3)	1.49(2)
mean	1.55(6)	1.54(11)	1.48(3)	1.49(4)
P(1)–Pt–P(2)	100.1(2)	101.2(2)	95.0(1)	95.6(1)
P(1)–Pt–P(3)	101.5(2)	103.6(2)	98.6(1)	101.6(1)
P(2)–Pt–P(3)	158.4(2)	155.2(2)	165.6	162.5(1)
P(1)–Pt–X			173.2(3)	176.6(1)
P(2)–Pt–X			82.4(3)	81.1(1)
P(3)–Pt–X			84.6(3)	81.7(1)
Pt–P(1)–C(11)	118.2(4)	119.0(7)	117.3(5)	120.1(4)
Pt–P(1)–C(13)	113.9(6)	110.9(12)	114.5(5)	111.7(5)
Pt–P(1)–C(15)	113.8(5)	112.6(15)	111.3(5)	110.9(3)
Pt–P(2)–C(21)	121.4(5)	124.1(8)	121.7(6)	125.2(5)
Pt–P(2)–C(23)	108.9(6)	112.9(8)	109.0(6)	110.2(5)
Pt–P(2)–C(25)	109.4(6)	109.2(7)	113.4(7)	108.7(5)
Pt–P(3)–C(31)	108.7(5)	121.2(7)	118.7(6)	125.8(4)
Pt–P(3)–C(33)	113.3(5)	110.3(8)	115.3(6)	108.3(5)
Pt–P(3)–C(35)	118.3(5)	110.8(7)	109.6(6)	110.6(5)
C(11)–P(1)–C(13)	103.7(8)	103.8(12)	103.7(8)	103.0(6)
C(11)–P(1)–C(15)	102.3(6)	105.4(13)	102.9(7)	109.5(6)
C(13)–P(1)–C(15)	103.1(7)	103.8(18)	105.9(7)	100.7(5)
C(21)–P(2)–C(23)	107.5(9)	104.6(12)	102.6(10)	102.1(8)
C(21)–P(2)–C(25)	107.5(9)	107.3(12)	103.6(10)	102.4(8)
C(23)–P(2)–C(25)	99.9(11)	94.6(16)	105.1(9)	106.7(9)
C(31)–P(3)–C(33)	107.7(10)	106.2(15)	106.7(10)	103.0(6)
C(31)–P(3)–C(35)	106.2(8)	106.7(11)	101.4(8)	102.8(7)
C(33)–P(3)–C(35)	101.9(10)	99.5(15)	103.3(9)	104.2(7)
mean	104.4(29)	103.5(41)	103.9(17)	103.8(27)
P(1)–C(11)–C(12)	115(1)	116(2)	116(1)	116(1)
P(1)–C(13)–C(14)	112(1)	110(3)	112(1)	112(1)
P(1)–C(15)–C(16)	110(1)	113(3)	112(1)	117(1)
P(2)–C(21)–C(22)	113(1)	116(2)	117(1)	118(1)
P(2)–C(23)–C(24)	114(2)	106(2)	113(1)	116(1)
P(2)–C(25)–C(26)	111(2)	101(2)	114(1)	114(1)
P(3)–C(31)–C(32)	113(1)	114(2)	118(1)	115(1)
P(3)–C(33)–C(34)	112(2)	127(3)	115(1)	111(1)
P(3)–C(35)–C(36)	111(1)	109(2)	116(1)	114(1)
mean	112(2)	112(7)	115(2)	115(2)

[a] In the PF_6 anions, two of which lie on inversion centres (one disordered) and the third (disordered) in a general position, the P–F bond length varies from 1.43 to 1.61Å with a mean value of 1.51(5)Å. [b] In the BF_4 anions the mean B–F bond length is 1.32(3)Å and the mean F–B–F angle 109(3)°. [c] Bond lengths corrected for thermal motion, assuming the phosphorus atom to ride on the platinum atom, are: cation A, Pt–P(1) 2.335, Pt–P(2) 2.315, Pt–P(3) 2.305; cation B, Pt–P(1) 2.324, Pt–P(2) 2.315, Pt–P(3) 2.324Å.

angles in the anions, and the shorter intra- and intermolecular contacts are included in the Supplementary Publication. For each compound studied the crystals consist of discrete ions separated by normal van der Waals contacts. In (1; X = H, Y = PF_6) the fluorine atoms attached to P(7) and P(9) are disordered, and in particular the anion P(9) appears to be completely rotationally disordered.

Conformations of the Phosphine Ligands.—In the cations of (1; X = H or Cl) the phosphine ligands exhibit approximate (180, 60, −60) conformations,* as does the $P(1)Et_3$ ligand in (1; X = F). Phosphine ligands $P(2)Et_3$ and $P(3)Et_3$ of (1; X = F) have approximately (180, 60, 60) and (180, −60, −60) conformations respectively. Although the conformation observed[10] in solid PEt_3 (60, 60, 60 with C_3 symmetry) would not be expected in the crowded environment of a square-planar tris complex, all the conformations observed in these complexes are found in liquid PEt_3.[10] The relevant torsion angles are listed in Table 5.

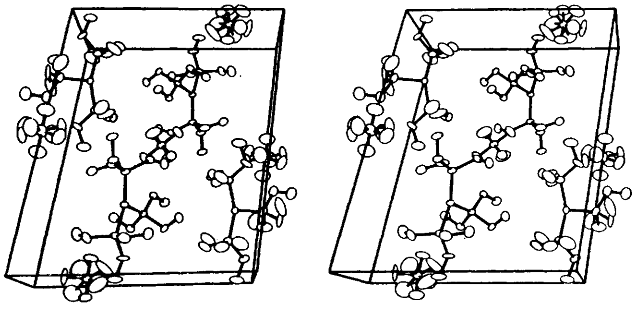

FIGURE 2 Stereoscopic pair view of the crystal structure of (1; X = H, Y = PF_6), approximately along *c*. Hydrogen atoms not determined

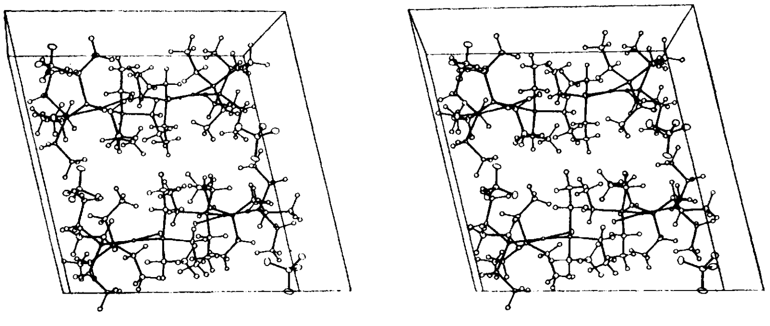

FIGURE 3 Stereoscopic pair view of the crystal structure of (1; X = F, Y = BF_4), approximately along *b*

The Pt–P–C angles vary significantly but fall into two groups such that for any individual triethylphosphine ligand one Pt–P–C angle has a mean value 120.9 ± 2.8° (mean of 12) and the other two average to 112.2 ± 2.5° (mean of 24). In all but one case [$P(3)Et_3$ of cation A of (1; X = H)] the larger angle involves the ethyl group whose Pt–P–C–C torsion angle is *ca.* 180°; this is generally the ethyl group more directly affected by close contact with other phosphine ligands. Repulsions between the ethyl groups of adjacent phosphine ligands are also responsible for deviations of the P(1)–Pt–P(2) and P(1)–Pt–P(3) angles from the ideal of 90°. There are significant differences between these two angles which arise [excepting cation A of (1; X = H)] because, whereas C(21) slots into the gap between C(13) and C(15), C(11) and C(31) approach more closely resulting in P(1)–Pt–P(3) being larger than P(1)–Pt–P(2).

TABLE 5

Bond torsion angles (°) in the cations $[Pt(PEt_3)_3X]^+$

	X = H			
	Cation A	Cation B	X = F	X = Cl
Pt–P(1)–C(11)–C(12)	180	178	172	180
Pt–P(1)–C(13)–C(14)	62	60	46	62
Pt–P(1)–C(15)–C(16)	−64	−71	−63	−64
Pt–P(2)–C(21)–C(22)	179	179	178	174
Pt–P(2)–C(23)–C(24)	57	68	57	56
Pt–P(2)–C(25)–C(26)	−59	−56	50	−58
Pt–P(3)–C(31)–C(32)	177	178	176	−178
Pt–P(3)–C(33)–C(34)	−56	47	−41	63
Pt–P(3)–C(35)–C(36)	54	−64	−65	−65
X–Pt–P(3)–C(31)			−134	180
X–Pt–P(2)–C(21)			158	−179
P(1)–Pt–P(2)–C(21)	4	3	−28	0
P(1)–Pt–P(3)–C(31)	173	25	52	0
P(2)–Pt–P(1)–C(11)	180	−174	−169	179
P(3)–Pt–P(1)–C(11)	−1	5	16	−4

It is surprising that angles X–Pt–P(2) and X–Pt–P(3) do not increase as the radius of X increases. Presumably the steric crowding between the three *cis*-PEt_3 groups does not allow the P–Pt–P angles to become much less than 96°. The size of X does have an affect on the *cis*-PEt_3 conformation. Only in the case of X = Cl (the largest X studied) does the size of X force both bonds P(2)–C(21) and P(3)–C(31) to eclipse Pt–P(1), thereby minimising contact between chlorine and the methylene hydrogens (at *ca.* 2.7 Å). The equivalent contact in (1; X = H) is not critical, which may well be why differing conformations of the phosphine ligand P(3) are observed in the two independent cations. In (1; X = F) the situation is intermediate and complicated by different conformations of the two *cis*-phosphine ligands. It may be that the high electronegativity of fluorine results in a small attractive interaction between methylene hydrogens of C(23), C(35), and fluorine (the appropriate H · · · F contacts are 2.40 Å). This could

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* The three numbers give the Pt–P–C–C torsion angles (°) defined in ref. 9.

result in a stabilisation of the (180, 60, 60) and (180, −60, −60) conformations relative to the usual (180, 60, −60) conformation, possibly also accounting for the marked tetrahedral distortion of the Pt co-ordination plane in (1; X = F) (see Table 6).

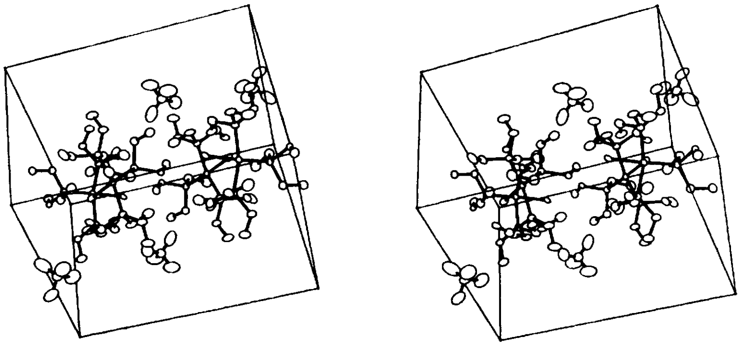

FIGURE 4 Stereoscopic pair view of the crystal structure of (1; X = Cl, Y = BF_4), approximately along {101}. Hydrogen atoms omitted

The cis *and* trans *Influences.*—The Pt–P bond lengths *trans* to X in the series (1; X = H, F, or Cl) follow the usual *trans*-influence order, *i.e.* Pt–P(*trans* to H) $\gg$ Pt–P(*trans* to Cl) > Pt–P(*trans* to F). It has been shown[11] that Pt–PEt_3 bond lengths correlate with platinum–phosphorus coupling constants ^1J(Pt–P). Using reported values for ^1J(Pt–P) and the bond lengths from this work, the correlation is further substantiated [although there is a marginal discrepancy in the order of *trans* influence for X = F and Cl when based on ^1J(Pt–P) or Pt–P distance]. The correlation also extends to the Pt–P(*cis* to X) bonds (see Table 7).

TABLE 6

Deviations (Å) of atoms from the platinum co-ordination plane in complexes (1)

Complex	Atoms defining plane	Deviations from plane
(1; X = H, Y = PF_6) (Cation A)	Pt, P(1), P(2), P(3)	Pt, 0.013; P(1), −0.002; P(2), −0.005; P(3), −0.005
(Cation B)	Pt, P(1), P(2), P(3)	Pt, 0.009; P(1), −0.002; P(2), −0.004; P(3), −0.004
(1; X = F, Y = BF_4)	Pt, P(1), P(2), P(3), F(1)	Pt, 0.000; P(1), 0.004; P(2), 0.101; P(3), 0.105; F(1) −0.229
(1; X = Cl, Y = BF_4)	Pt, P(1), P(2), P(3), Cl	Pt, −0.001; P(1), −0.007; P(2), 0.068; P(3), 0.041; Cl, −0.030

TABLE 7

Coupling constants ^1J(Pt–P) and bond lengths *l*(Pt–P) in complex cations $[Pt(PEt_3)_3X]^+$ (X = H, F, or Cl)

Complex cation	^1J(Pt–P)/Hz	*l*(Pt–P)/Å
$[Pt(PEt_3)_3H]^+$		
(*cis* P)	2 515 [a]	2.299(7) (mean of 4)
(*trans* P)	2 037	2.335(4), 2.291(7)
$[Pt(PEt_3)_3F]^+$		
(*cis* P)	2 382 [b]	2.337(4) (mean of 2)
(*trans* P)	3 455	2.239(3)
$[Pt(PEt_3)_3Cl]^+$		
(*cis* P)	2 261 [b] (2 233) [c]	2.354(3) (mean of 2)
(*trans* P)	3 474 (3 499)	2.251(3)

[a] T. W. Dingle and K. R. Dixon, *Inorg. Chem.*, 1974, **13**, 846. [b] M. A. Cairns, K. R. Dixon, and J. J. McFarland, *J.C.S. Dalton*, 1975, 1159. [c] G. G. Mather, A. Pidcock, and G. J. N. Rapsey, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 567.

The two Pt–P bonds *cis* to X, although essentially equal in length within a given compound, are significantly different between compounds and follow the order Pt–P(*cis* to Cl) > Pt–P(*cis* to F) > Pt–P(*cis* to H). Thus within the series of cations examined there is no straightforward correlation between *cis* and *trans* influences of the ligand X on the Pt–P bond length. Neither is there a correlation between *cis* influence and the electronegativity of X, so the variation in Pt–P (*cis* to X) bond length is unlikely to be caused primarily by a change in the charge on the metal with consequential metal-orbital contraction. Furthermore, it does not seem reasonable that hybridisation differences at platinum, caused by preferred orbital requirements for formulation of the Pt–X bond, could account for the order because one would then expect a correlation between *cis* and *trans* influences. Similarly, differences in metal–phosphorus π bonding may be neglected.

An obvious factor which does correlate with the observed order of *cis* influence is the size of X. The lack of influence of the size of X on *cis* X–Pt–P and P–Pt–P angles has been noted above. Because of crowding in the $Pt(PEt_3)_3$ unit, relief of strain between X and *cis*-PEt_3 groups can only be overcome either by distortion towards tetrahedral geometry, which is not observed (except for X = F, see above), or lengthening of the *cis* Pt–P bonds, which is observed. Lengthening of Pt–P bonds by steric interaction with large *cis* ligands has already been observed[12] in the case of *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$. It must be concluded that the *cis*-Pt–P bond lengths in (1) are controlled by steric interaction with *cis*-ligand atoms as small as Cl and possibly even F. For (1; X = Br or I), the correlation of $^1J(\text{Pt–P})$ with Pt–P bond lengths would suggest that the *cis*-Pt–P bond lengths in (1; X = Cl, Br, or I) are approximately equal. However, our work suggests that Pt–P[*cis* to I in (1; X = I)] should be longer than Pt–P[*cis* to Cl in (1; X = Cl)]. A breakdown in the correlation between $^1J(\text{Pt–P})$ and Pt–P bond lengths has already been recognised for *trans*-$[\text{PtI}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$ [13] where steric interactions are large. Structural data on (1; X = Br and I) are necessary to decide this point.

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