cis- and *trans*-Influences in Platinum(II) Complexes. *X*-Ray Crystal-structure Analysis of *cis*-Dichloro(triethylphosphine)(trifluorophosphine)-platinum(II) †

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Crystals of *cis*-$[PtCl_2(PEt_3)(PF_3)]$ are monoclinic, $P2_1/n$, with a = 11.813(6), b = 17.27(6), c = 6.67(3) Å, β = 91.29(2)°, and Z = 4. Least-squares refinement based on 1 957 reflection intensities has converged at R = 0.038. The co-ordination at platinum is approximately square planar with angle P–Pt–P 101.3(1)° and bond lengths Pt–PEt_3 2.272(3), Pt–PF_3 2.141(3), Pt–Cl 2.357(3) (*trans* to PEt_3), and 2.305(3) Å (*trans* to PF_3). The shorter Pt–P bond to PF_3 is at least partly due to the effect of electronegative substituents on the phosphorus lone-pair orbital, and the difference in the Pt–Cl lengths can be accounted for by changes in the σ orbitals of the complex. Correlations are noted between the lengths of mutually *trans* Pt–PX_3 and Pt–Cl bonds and between the lengths of mutually *trans* Pt–PEt_3 and Pt–Cl bonds in complexes *cis*-$[PtCl_2L(PEt_3)]$.

ALTHOUGH a number of structure determinations and accurate bond-length measurements have been made for transition-metal complexes of PF_3,[1] none of the available results permits a direct comparison to be made between PF_3 and a triorganophosphine in a similar molecular environment. In view of the importance of PF_3 in the foundation and continuing application of the theory of transition-metal–phosphorus π bonding, it appeared desirable to provide such a comparison. Since there is a wealth of structural information for triorganophosphine complexes of Pt^{II}, we have, therefore, made an accurate *X*-ray crystal-structure determination of the complex *cis*-$[PtCl_2(PEt_3)(PF_3)]$.

EXPERIMENTAL

The complex *cis*-$[PtCl_2(PEt_3)(PF_3)]$ was obtained by passing PF_3 through a dichloromethane solution of *sym,trans*-$[Pt_2Cl_4(PEt_3)_2]$ in the presence of a small amount of PCl_3.[2] Crystals (deliquescent) were obtained from dichloromethane–diethyl ether.

Crystal Data.—$C_6H_{15}Cl_2F_3P_2Pt$, M = 472.08, Monoclinic, a = 11.813(6), b = 17.27(6), c = 6.67(3) Å, β = 91.29(2)°, U = 1 366.5 Å^3, Z = 4, D_c = 1.33 g cm^{-3}, $F(000)$ = 880, Mo-K_α radiation, μ(Mo-K_α) = 114.5 cm^{-1}, space group $P2_1/n$ from systematic absences, $0k0$ for k odd and $h0l$ for $h + l$ odd.

Crystallographic Measurements.—The crystal was bounded by faces of the form {100}, {010}, and {001} with distances between parallel faces of 0.20, 0.48, and 0.40 mm. It was sealed in a quartz capillary and accurately centred on a Y290 Hilger and Watts four-circle diffractometer (graphite crystal monochromator) and unit-cell parameters were determined by least-squares treatment of the accurate setting angles of 12 strong reflections [λ(Mo-$K_{\alpha1}$) 0.709 26 Å]. Data were collected by an ω—2θ scan in 80 steps of 0.5 s to a maximum 2θ of 50°; backgrounds at either side of each peak were counted for 20 s. The intensities of three standard reflections, remeasured after every 100 reflections, varied by only ±2%, so corrections for crystal decay were unnecessary. Lorentz and polarization corrections were applied and the data were corrected for absorption with the program ABSCOR.[3] Symmetry-equivalent reflections were averaged to give 2 311 independent reflections of which 1 957 with $I > 3\sigma(I)$ were used in the structure analysis.

Structure Determination.—The positions of all the non-hydrogen atoms were obtained by the usual Patterson and Fourier methods. Scattering-factor curves for non-hydrogen atoms were taken from ref. 4 and that for hydrogen from ref. 5. The anomalous-dispersion factors for chlorine, fluorine, phosphorus, and platinum were taken from ref. 6. Atoms other than hydrogen were refined by full-matrix least squares with anisotropic Debye–Waller factors to R 0.049. Six low-angle reflections which were assumed to be affected by extinction were removed from further refinement. A difference-Fourier map did not clearly reveal hydrogen-atom positions; calculated positions [l(C–H) 1.08 Å, HCH 109.5°] with $U_{\text{iso.}}$ = 0.038 Å^2 were included in further cycles of refinement as fixed contributions, to give R 0.038 and R' 0.048. The final weighting scheme was determined from $w = 1/\{1 + [(F_o - 45.0)/41.9]^2\}$ which gave approximately constant averages of $w(|F_o| - |F_c|)^2$ against $|F_o|$. The final maximum change to error was 0.17 and the final difference-Fourier map was everywhere less than 0.48 eÅ^{-3}. Structure solution and refinement were carried out using the '*X*-RAY' program system.[7]

RESULTS AND DISCUSSION

Final atomic co-ordinates are given in Table 1 and a diagram of the molecular structure with the numbering scheme is given in Figure 1. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22134 (13 pp.).‡

The crystals are composed of discrete units separated by normal van der Waals contacts. Bond lengths, angles, and selected intramolecular non-bonded distances

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† No reprints available.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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[2] B. T. Heaton, D.Phil. Thesis, University of Sussex, 1967.

[3] 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

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

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

[7] '*X*-RAY system,' Computer Science Center, University of Maryland, Technical Report TR 72–193, version of July 1972.

are given in Table 2. The platinum, chlorine, and phosphorus atoms are nearly coplanar (Table 3) and F(2) and the C(3) methylene group also lie close to the plane, evidently to minimize the interactions between Cl(1) and F(1), F(3) and between Cl(2) and H(22), H(62). The conformation of the PEt_3 ligand, for which there is an approximate plane of symmetry through P(1), C(3), and C(4), is similar to that in other square-planar complexes.

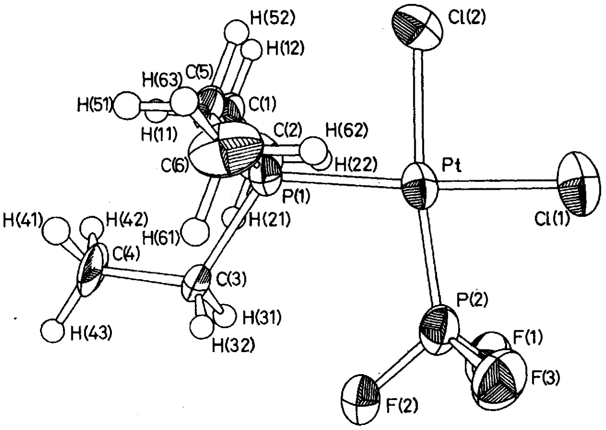

FIGURE 1 A view of the molecular structure; thermal-vibration ellipsoids enclose 50% probability. Hydrogen-atom positions were calculated.

TABLE 1

Fractional atomic co-ordinates (× 10^4) with standard deviations in parentheses

Atom	x	y	z
Pt	2 416.5(3)	2 181.3(2)	1 134.4(5)
Cl(1)	2 863(3)	906(2)	2 128(5)
Cl(2)	3 334(3)	2 637(2)	3 985(5)
P(1)	2 039(2)	3 442(1)	411(3)
P(2)	1 596(2)	2 608(2)	−1 347(5)
F(1)	2 326(7)	1 084(5)	−2 639(13)
F(2)	982(6)	2 034(4)	−3 061(11)
F(3)	659(7)	1 040(5)	−827(14)
C(1)	3 318(8)	4 033(6)	299(15)
C(2)	4 082(12)	3 829(10)	−1 424(23)
C(3)	1 242(8)	3 641(6)	−1 877(14)
C(4)	1 043(11)	4 501(7)	−2 307(17)
C(5)	1 231(8)	3 870(6)	2 448(14)
C(6)	143(10)	3 446(7)	2 844(18)
H(11)	3 016	4 683	42
H(12)	3 774	4 076	1 720
H(21)	3 640	3 879	−2 823
H(22)	4 398	3 272	−1 145
H(23)	4 829	4 237	−1 484
H(31)	1 669	3 445	−3 155
H(32)	400	3 412	−1 816
H(41)	599	4 788	−1 020
H(42)	1 868	4 821	−2 359
H(43)	571	4 697	−3 630
H(51)	1 747	3 871	3 786
H(52)	1 056	4 471	2 002
H(61)	−378	3 480	1 442
H(62)	313	2 880	3 226
H(63)	−345	3 738	3 986

The Cl(1)–Pt–Cl(2) angle (89.4°) is very close to 90°, indicating that the chlorine ligands are essentially unperturbed by steric interaction with the phosphorus ligands. Consistently, the distances Cl(1) · · · F(1), Cl(1) · · · F(3), Cl(2) · · · H(12), and Cl(2) · · · H(52) (Table 2) correspond to normal van der Waals contacts (Cl · · · F 3.20, Cl · · · H 2.90 Å).[8] Angles Cl(1)–Pt–P(2) and Cl(2)–Pt–P(1) smaller than those found would result in steric interactions between the phosphine and chlorine ligands. The angle P(1)–Pt–P(2) (101.3°) thus appears to have increased from the square-planar value of 90° to an extent limited by the development of phosphine–chlorine interactions, and the angles Cl(1)–Pt–P(2) (83.1°) and Cl(2)–Pt–P(2) (172.4°) for the PF_3 ligand in comparison with angles Cl(2)–Pt–P(1) (86.2°) and Cl(1)–Pt–P(1) (175.6°) for the PEt_3 ligand show that the smaller PF_3 ligand deviates from an ideal square-planar position to a greater extent than the larger PEt_3 ligand. The interactions between F(2) and C(3), H(31), and H(32) are substantially reduced by the opening of the P(1)–Pt–P(2) angle, but the presence of

TABLE 2

Selected interatomic distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Bond lengths			
Pt–Cl(1)	2.357(3)	C(1)–C(2)	1.515(18)
Pt–Cl(2)	2.305(3)	C(3)–C(4)	1.530(15)
Pt–P(1)	2.272(3)	C(5)–C(6)	1.508(15)
Pt–P(2)	2.141(3)	P(2)–F(1)	1.529(9)
P(1)–C(1)	1.827(11)	P(2)–F(2)	1.529(8)
P(1)–C(3)	1.808(9)	P(2)–F(3)	1.526(8)
P(1)–C(5)	1.834(10)		
(*b*) Bond angles			
Cl(1)–Pt–Cl(2)	89.4(1)	C(3)–P(1)–C(5)	106.2(4)
P(1)–Pt–P(2)	101.3(1)	P(1)–C(1)–C(2)	114.5(8)
Cl(1)–Pt–P(2)	83.1(1)	P(1)–C(3)–C(4)	114.7(7)
Cl(2)–Pt–P(1)	86.2(1)	P(1)–C(5)–C(6)	113.2(7)
Cl(1)–Pt–P(1)	175.6(1)	Pt–P(2)–F(1)	117.3(3)
Cl(2)–Pt–P(2)	172.4(1)	Pt–P(2)–F(2)	123.7(3)
Pt–P(1)–C(1)	112.7(3)	Pt–P(2)–F(3)	116.1(4)
Pt–P(1)–C(3)	117.2(3)	F(1)–P(2)–F(2)	97.3(4)
Pt–P(1)–C(5)	109.4(3)	F(1)–P(2)–F(3)	99.7(4)
C(1)–P(1)–C(3)	105.9(5)	F(2)–P(2)–F(3)	98.3(4)
C(1)–P(1)–C(5)	104.4(5)		
(*c*) Intramolecular non-bonded distances			
Cl(1) · · · Cl(2)	3.279(5)	Cl(1) · · · F(1)	3.242(9)
Cl(1) · · · P(2)	2.987(5)	Cl(1) · · · F(3)	3.237(9)
Cl(2) · · · P(1)	3.128(4)	F(2) · · · C(3)	2.90(1)
Cl(2) · · · H(12)	2.96	F(2) · · · H(31)	2.57
Cl(2) · · · H(52)	2.84	F(2) · · · H(32)	2.62

TABLE 3

Deviations (Å) of atoms from the least-squares plane * for Cl(1), Cl(2), P(1), and P(2)

Atom		Atom	
Pt	0.021	C(3)	0.024
Cl(1)	0.011	C(4)	0.065
Cl(2)	−0.011	C(5)	−1.456
P(1)	0.010	C(6)	−2.756
P(2)	−0.011	F(1)	1.140
C(1)	1.411	F(2)	−0.032
C(2)	2.801	F(3)	−1.211

* Equation of the plane: $0.8602x + 0.0589y - 0.5066z = 2.2586$.

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[8] J. E. E. Huheey, 'Inorganic Chemistry,' Harper and Row, New York, 1972, p. 184.

some strain is indicated by the fact that these distances (Table 2) are slightly shorter than normal van der Waals contacts (F $\cdots$ C 3.15, F $\cdots$ H 2.70 Å),[8] and by the larger than normal angles Pt–P(1)–C(3) and Pt–P(2)–F(2) (Table 2).

The lengths of the *trans*-related bonds Pt–Cl and Pt–PEt_3 in *cis*-$[PtCl_2(PEt_3)(PF_3)]$ are compared in Figure 2 with those in the similar complexes *cis*-$[PtCl_2(PEt_3)L]$ [L = PEt_3,[9] CNPh,[10] C(NHPh)(OEt),[10] or $C(NPhCH_2)_2$ [11]], *cis*-$[PtCl_2(PEt_2Ph)(CNEt)]$,[12] *cis*-$[PtCl_2(CO)(PPh_3)]$,[13] $[PtCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}]$,[14] and $[PtCl_3(PEt_3)]^-$.[15] As has been noted previously,[16] the Pt–P lengths show significant variation with L. The variation with L in the Pt–Cl lengths is smaller and in the opposite sense from the Pt–P lengths, and it has become recognisable only from recent structure determinations of high accuracy. The suggested correlation in Figure 2 is not accurately defined because of the uncertainties in the bond lengths, but it may be noted that the mean position of the points for the very closely related complexes *cis*-$[PtCl_2(CNPh)(PEt_3)]$ and *cis*-$[PtCl_2(CNEt)(PEt_2Ph)]$ would lie close to the correlation indicated. Incorporation of the results for the PPh_3 complex, *cis*-$[PtCl_2(CO)(PPh_3)]$, has been on the basis that bonds to PPh_3 are likely to be *ca.* 0.01 Å *shorter* than to PEt_3,[9] and that the Pt–Cl bond *trans* to PPh_3 may be somewhat shorter than when *trans* to PEt_3, since the *trans*-influence order for these ligands is $PPh_3 < PEt_3$.[17] The Pt–Cl bond lengths *cis* to L in the anions $[PtCl_3L]^-$ [L = CO,[16] 2.292(4); L = PEt_3,[15] 2.301(4); L = Cl,[18] 2.308(2) Å] show significantly less variation than in *cis*-$[PtCl_2(L)L']$ [L′ = phosphine], and an analysis of Pt–Cl lengths in complexes with mutually *trans* chloride ligands showed that any influence of *cis* ligands on the Pt–Cl lengths is smaller than the uncertainties in the *X*-ray determinations.[15]

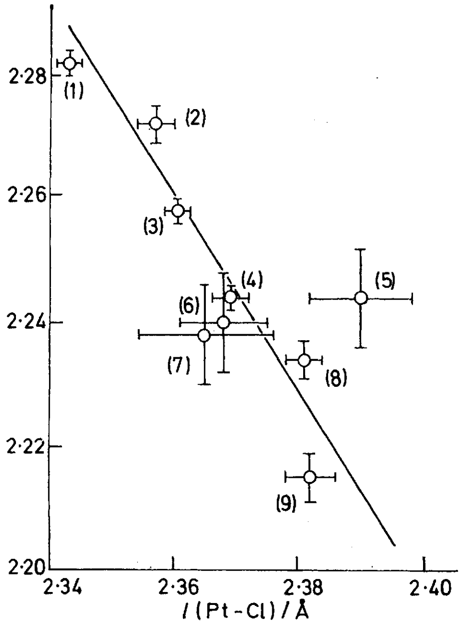

FIGURE 2 Correlation between l(Pt–P) and l(Pt–Cl) for mutually *trans* Pt–PR_3 and Pt–Cl bonds in complexes of type *cis*-$[PtCl_2L(PR_3)]$: (1) *cis*-$[PtCl_2(CO)(PPh_3)]$;[13] (2) *cis*-$[PtCl_2(PF_3)(PEt_3)]$ (this work); (3) *cis*-$[PtCl_2(PEt_3)_2]$;[9] (4) $[PtCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}]$;[14] (5) *cis*-$[PtCl_2(CNEt)(PEt_2Ph)]$;[12] (6) *cis*-$[PtCl_2\{C(NHPh)(OEt)\}(PEt_3)]$;[10] (7) *cis*-$[PtCl_2(CNPh)(PEt_3)]$;[10] (8) *cis*-$[PtCl_2\{C(NPhCH_2)_2\}(PEt_3)]$; and (9) $[PtCl_3(PEt_3)]^-$.[15] The error limits indicated for the bond lengths are the quoted standard deviations (*i.e.* $l \pm 1\sigma$)

It therefore appears that the lengths of Pt–Cl bonds *cis* to L show a greater dependence on L when the Pt–Cl bond is *trans* to P than when *trans* to Cl. A possible explanation for the results is that variation of L directly influences Pt–P but not Pt–Cl bonds *cis* to L. The variation in the Pt–Cl lengths when *trans* to P is in response to the Pt–P length variation, and the trend in Figure 2 is consistent with *trans*-influence theory, where a shorter Pt–PR_3 bond would be expected to be associated with a longer *trans*-Pt–Cl bond.[1,17] It should be noted that if a ' *cis* influence ' of a ligand L is defined as the power of the ligand to weaken bonds in *cis* relationship,[19] the ordering of ligands L based on the correlation of Figure 2 is opposite for the Pt–P and the Pt–Cl bonds.

It has been suggested that ligands L may affect M–P lengths *cis* to L *via* competition for the d_π electrons of M. Thus, the mutually *trans* Rh–P bonds are shorter when *cis* to PPh_3 (weak π acceptor) than when *cis* to C_2F_4 (strong π acceptor) in $[RhCl(L)(PPh_3)_2]$ (L = PPh_3 or C_2F_4),[20] and in platinum(II) complexes (ref. 16 and Figure 2) longer Pt–P bonds are found *cis* to the presumably strong π acceptors CO and PF_3. However, because the C–C axis of C_2F_4 in $[RhCl(C_2F_4)(PPh_3)_2]$ is approximately perpendicular to the plane of the complex, the C_2F_4 ligand interacts with a d_π orbital of Rh which is nearly orthogonal to the π-acceptor orbitals of the mutually *trans* PPh_3 ligands, so there can be very little direct competition between C_2F_4 and PPh_3 for electrons in any single d_π orbital of Rh. If competition for d_π electrons is the cause of the *cis* interaction, it must be assumed that removal of any metal d_π electrons

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by a π-acceptor ligand makes such electrons less available for all other ligands.[16] This is contrary to the usual interpretations of physical parameters of carbonyl complexes.[1]

Although these results for complexes of Rh^{I} and Pt^{II} can be explained in terms of π interactions, the majority of complexes studied have ligands L capable of significant σ and π interactions with the metal, so it is difficult to determine how the mutual influence of ligands is to be apportioned between effects through the σ and the π electrons of the complexes. As with the study of *trans* influence, it is necessary to examine complexes with ligands L for which π interactions with the metal can be presumed to be negligible. This allows the effects of variation in the σ system to be evaluated, so that the σ contribution to the mutual influence for a more general ligand L can be allowed for. A suitable series of complexes for the study of the *cis* influence on $Pt-PR_3$ bonds through the σ system would be *trans*-$[Pt(PR_3)_2(X)Y]$, where X or Y are essentially σ-bonding ligands such as H^-, Me^-, NH_3, amines, H_2O, $[OH]^-$, $[ONO_2]^-$, F^-, Cl^-, and probably $[NCS]^-$, Br^-, and I^-. Ideally, also, variations in the steric requirements of the ligands should be minimized, but this is not expected to be a serious limitation for complexes containing the less bulky phosphines. At present there are insufficient *X*-ray results for *trans*-bis(phosphine) complexes incorporating suitable ligands X,Y to determine whether the Pt–P lengths are sensitive to σ effects, so it is not yet possible to assess the relative importance of the σ and π contributions to the interactions between *cis* ligands.

In *cis*-$[PtCl_2(PEt_3)(PF_3)]$ the Pt–P bond to PF_3 is the shortest Pt–P bond known [2.141(3) Å] and the Pt–Cl bond *trans* to PF_3 [2.305(3) Å] is shorter than any known Pt–Cl bond *trans* to P. A similar but less extreme situation exists in $[PtCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}]$,[14] where the $Pt-P(CF_3)_2$ bond [2.168(3) Å] and the *trans*-Pt–Cl bond (2.317 Å) are both significantly shorter than in *cis*-$[PtCl_2(PEt_3)_2]$ [Pt–P, 2.258(2); Pt–Cl 2.361(2) Å].[9]

Although the Pt–P lengths in these complexes correlate roughly with the 'cone angle' of the ligands [PF_3, 104; $CH_2P(CF_3)_2$, 119; CH_2PPh_2, 125; PEt_3, 132°],[21] steric effects in these complexes appear unlikely to affect the Pt–P lengths significantly. In square-planar complexes bond lengthening resulting directly from steric interactions between ligands is expected principally when a ligand interacts strongly with *both cis* ligands as in *trans*-$[PtI_2\{P(C_6H_{11})_3\}_2]$ where the Pt–P bonds to $P(C_6H_{11})_3$ ('cone angle' 179°)[21] are 0.06 Å longer than the bonds to PMe_3 ('cone angle' 118°) in *trans*-$[PtI_2(PMe_3)_2]$.[22] In such strained complexes some of the interatomic distances between the *cis* ligands are found to be substantially shorter than van der Waals contacts, in contrast to those found in the *cis*-dichloro-complexes mentioned above.

It therefore appears that the short bond between platinum and PF_3 is a consequence of the presence of groups of high electronegativity on phosphorus, and it may be noted that qualitatively similar results have been obtained for the BH_3 adducts of PF_3 [B–P 1.836(12) Å][23] and PMe_3 [B–P 1.901(7)].[24] Phosphites are also known to give shorter bonds to transition metals than phosphines[1,25] and this has been demonstrated recently for the linearly co-ordinated gold(I) complexes [AuCl(L)] [L = PPh_3, Au–P 2.235(2); L = $P(OPh)_3$, Au–P 2.192(5) Å],[26] where the complete absence of steric pressure from *cis* ligands indicates an electronic origin for the bond-shortening effect.

There is considerable evidence (detailed below) that the *s* character of the σ-donor orbitals of ligands PX_3 increases with the electronegativity of X. Since the *s* orbital has a smaller mean radius than other orbitals used by phosphorus, at least part of the shortening of the $Pt-PF_3$ relative to the $Pt-PEt_3$ bond must derive from changes in the hybridization of the phosphorus σ orbitals. The bond angle X–P–X (θ) can be used to calculate the *s* character (α_P^2) of the phosphorus-donor orbital from the equation $\alpha_P^2 = (1 + 2\cos\theta)/(1 - \cos\theta)$,[27] which is derived from simple hybridization theory with the assumption that phosphorus uses only *s* and *p* orbitals. From the mean values of the angles C–P–C (105.3°) and F–P–F (98.4°), values of α_P^2 of 0.37 (PEt_3) and 0.62 (PF_3) are obtained for *cis*-$[PtCl_2(PEt_3)(PF_3)]$. Corresponding to these lone-pair hybridization states, centroids of electron density $\sigma = \int r\psi^2 d\tau / \int \psi^2 d\tau$ (ψ = phosphorus hybrid orbital) have been calculated from Clementi–Raimondi wavefunctions, and that for PF_3 is 0.03 Å shorter than for PEt_3.[28] Although the centroids appear to be closely related to covalent radii for carbon,[29] this has not been established for phosphorus. Nevertheless, the calculated difference in the centroids is much less than the difference in the Pt–P bond lengths (0.13 Å), so it is probable that some additional electronic factor is affecting the Pt–P lengths.

Electronegative groups on phosphorus, as well as inducing high *s* character in the lone-pair orbital, are also expected to cause contraction of the atomic orbitals comprising the lone pair with a corresponding reduction in the effective covalent radius of phosphorus.[30] Some evidence for this can be adduced from magnetic-resonance measurements. Provided that changing the

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group X on phosphorus does not induce substantial changes in the orbitals used by the platinum atom, the ratio of the coupling constants ^1J(Pt–PX$_3$) : ^1J(Pt–PEt$_3$) in complexes *cis*-[PtCl$_2$(PEt$_3$)(PX$_3$)] can, with certain assumptions,[27] be used as a measure of the relative values of $\alpha_P{}^2|\psi_P(0)|^2$ where $|\psi_P(0)|$ is the magnitude of the 3*s* wavefunction evaluated at the phosphorus nucleus. Values of this ratio are[31] 1 (X = Et), 1.96 (OMe), and 2.57 : 1 (F) and rather similar ^1J(H–PX$_3$) : ^1J(H–PR$_3$) ratios are obtained from phosphonium salts [PHX$_3$]$^+$: 1 (X = Et), 1.76 (OMe), and 2.53 : 1 (F).[32] E.s.r. parameters of PX$_3$ adducts of cobalt(II) porphyrins have been used to derive values of $\alpha_P{}^2$ under the assumption that $|\psi_P(0)|$ is invariant,[33] but may also be used to calculate $\alpha_P{}^2|\psi_P(0)|^2$ without this assumption. Ratios of these parameters are 1 (X = Bu), 1.77 (OMe), and 2.19 : 1 (F), and they are in reasonably good agreement with the ratios derived from the n.m.r. measurements. A contribution of 1.65 to the ratio for X = F is expected from the values of $\alpha_P{}^2$ calculated previously from the X–P–X bond angles, so on this basis $|\psi_P(0)|^2$ must be larger for X = F than for R, indicating contraction of the phosphorus 3*s* orbital by the electronegative fluorine substituents. Similar contraction must occur also for the phosphorus 3*p* orbitals with a consequent shortening of co-ordinate bonds formed by PF$_3$, which is additional to the shortening resulting from changes in the hybridization of the donor orbital. Although a quantitative assessment of the effect of the changes in the donor orbital on the Pt–P lengths has not been obtained, it may be noted that the difference between the Pt–PEt$_3$ and Pt–PF$_3$ lengths in *cis*-[PtCl$_2$(PEt$_3$)(PF$_3$)] (0.13 Å) is larger than that between the B–P lengths [0.06(1) Å] in the adducts PX$_3$·BH$_3$ (X = Me or F).[23,24] It is possible that the Pt–P bond length is more sensitive to changes in the phosphorus σ-donor orbital than the B–P length, but on this evidence it is not possible to rule out an additional contribution to the Pt–PF$_3$ bonding from back donation from platinum into virtual orbitals of PF$_3$.

The Pt–Cl bond *trans* to PF$_3$ (2.305 Å) is shorter than that *trans* to PEt$_3$ (2.357 Å). Although *trans*-influence theory[17] leads to the expectation that shorter Pt–P bonds to a given phosphorus donor should be associated with longer bonds in the *trans* position, the theory also appears capable of explaining the shortening of the *trans* bond as the Pt–P bond is shortened through the presence of electronegative substituents on phosphorus (Figure 3). As the electronegativity of the groups on phosphorus increases, the Pt–P bond shortens primarily because of the decrease in the phosphorus radius discussed above. The energy of the phosphorus lone pair changes also, however, and photoelectron spectra and *ab initio* SCF calculations show that the energies of the phosphorus lone pairs for PMe$_3$ (−8.5) and PF$_3$ (−12.7 eV)[34] are such that the energy separation (ΔE) between the lone pair and the metal-acceptor orbital is substantially greater for PF$_3$.* The contribution of the metal orbital to the phosphorus–metal bonding orbital will depend approximately on ΔE^{-1} and so will be smaller for Pt–PF$_3$ than Pt–PEt$_3$. This will allow a greater contribution of the metal orbital to the orbital binding the chloride ligand *trans* to PF$_3$,[17] so the Pt–Cl bond *trans* to PF$_3$ is expected to be shorter than that *trans* to PEt$_3$.

The mean P–F length in *cis*-[PtCl$_2$(PEt$_3$)(PF$_3$)] [1.528(8) Å] is significantly shorter than in free PF$_3$ [1.570(1) Å] and similar results have been obtained for other complexes of PF$_3$.[1] Donation of the lone pair of PF$_3$, which is antibonding with respect to the $2p_\sigma$ orbitals of fluorine, is expected to be accompanied by a shortening of the P–F bonds.[35]

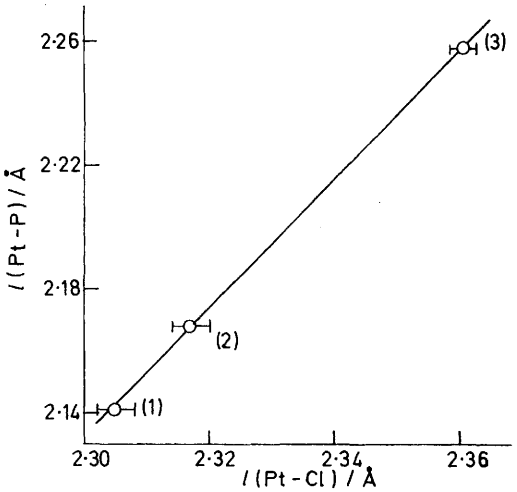

FIGURE 3 Correlation between l(Pt–P) and l(Pt–Cl) for mutually *trans* Pt–PX$_3$ and Pt–Cl bonds in complexes (1) *cis*-[PtCl$_2$(PEt$_3$)(PF$_3$)] (PX$_3$ = PF$_3$; this work), (2) [PtCl$_2${Ph$_2$PCH$_2$CH$_2$P(CF$_3$)$_2$}] [PX$_3$ = P(CF$_3$)$_2$],[14] and (3) *cis*-[PtCl$_2$(PEt$_3$)$_2$] (PX$_3$ = PEt$_3$).[9] The error limits indicated for the bond lengths are the quoted standard deviations (*i.e.* $l \pm 1\sigma$)

Although the Pt–PF$_3$ bond is shorter, it is likely to have lower intrinsic strength than the Pt–PEt$_3$ bond; the adduct PF$_3$·BH$_3$ has a shorter B–P bond than PMe$_3$·BH$_3$, but is much more extensively dissociated.[26,30] In this context it should also be noted that the variation in length of Pt–Cl bonds *trans* to phosphorus donors may indicate the presence of a levelling effect on the apparent basicity of phosphorus donors with respect to Pt^{II} and similar acceptors. For example, in *cis*-[PtCl$_2$(PEt$_3$)(PF$_3$)] the PEt$_3$ ligand is associated with a long and presumably weak *trans*-Pt–Cl bond, whereas PF$_3$ is associated with a short and presumably stronger *trans*-Pt–Cl bond. Neglecting other factors, such as

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

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cis effects, steric effects, and changes in the bonds within the phosphorus donors, the enthalpy of formation of a linear X_3P–Pt–Cl moiety from PX_3 and Pt–Cl is given by $-D(\text{Pt–PX}_3) + \delta D(\text{Pt–Cl})$, where $D(\text{Pt–PX}_3)$ is the intrinsic energy of the Pt–PX_3 bond and $\delta D(\text{Pt–Cl})$ is the energy required to change the Pt–Cl bond to its equilibrium length. Since the Pt–Cl bond *trans* to PEt_3 is weaker than that *trans* to PF_3, the enthalpies of association of PEt_3 and PF_3 with platinum will differ by less than the difference in the intrinsic Pt–P energies. In this respect, therefore, ligands of low *trans* influence, particularly the relatively ' weak ' neutral donors such as C_2H_4, PF_3, SbR_3, and CO, have a smaller unfavourable contribution to the enthalpy of association from $\delta D(\text{Pt–Cl})$ than ' strong ' donors of high *trans* influence such as PEt_3.

Conclusions.—The Pt–P and Pt–Cl bond lengths in $[PtCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}]$,[14] which are qualitatively similar to those in *cis*-$[PtCl_2(PEt_3)(PF_3)]$, have been explained on the basis that the bond to the $P(CF_3)_2$ group is shortened by Pt–P π bonding, which also removes d_π-electron density from the *trans*-Pt–Cl region and shortens the Pt–Cl bond. Since, however, σ effects are known to be dominant in other situations in platinum(II) complexes [1,17] and there is evidence for substantial variations in the orbital constitutions and energies of the phosphorus σ-donor orbitals, it appears to us to be reasonable to expect the variations in the σ system to contribute significantly to the observed differences in bond lengths.

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