Effects of Phosphine and Phosphite Substituents on Metal–Ligand Bonding. The Crystal and Molecular Structure of *cis*-Dichloro(triethylphosphine)(triphenyl phosphite)platinum(II) †

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The molecular structure of *cis*-$[PtCl_2(PEt_3)\{P(OPh)_3\}]$ has been determined by *X*-ray diffraction methods. The crystals are monoclinic, space group $P2_1/n$, with a = 8.614, b = 37.100, c = 9.207 Å, β = 116.21°, and Z = 4. The structure has been solved by the heavy-atom method and refined to R 0.034 for 4 206 diffractometric intensity data. The crystals contain discrete molecules, with platinum in tetrahedrally distorted square-planar co-ordination. The Pt–$P(OPh)_3$ and Pt–PEt_3 bond lengths are 2.182(2) and 2.269(1) Å. The Pt–Cl distances [2.344(2) Å *trans* to $P(OPh)_3$ and 2.355(2) Å *trans* to PEt_3] indicate that the *trans* influence of $P(OPh)_3$ is weaker than that of PEt_3. It is shown that the platinum(II)–ligand bond lengths in complexes with *cis*-Cl_2P_2 donor sets are related to the electronic properties of the substituents at the phosphorus atoms. The observed variations in the bond lengths are discussed in terms of σ- and π-electronic effects.

It is now recognised that the chemical behaviour and spectroscopic properties of tertiary phosphine and phosphite complexes of transition metals depend on the nature of the substituents at the phosphorus atom.[1-4] However, the relative importance of the effects of steric and electronic properties of the substituent groups on metal–ligand bonding is not well understood. Crystallographic studies of the variation in metal–phosphorus bond lengths, arising only from the change in character of the phosphorus-donor ligands, are still rare.

In this context we have shown that in the complexes *cis*-$[MCl_2\{(F_3C)_2PCH_2CH_2PPh_2\}]$ (M = Pd or Pt) the electron-withdrawing trifluoromethyl substituents shorten not only the adjacent M–P bond but also the *trans*-Pt–Cl bond.[5,6] In order to extend this study over a wider range of phosphorus-donor ligands we have determined accurately the crystal structures of another three complexes containing *cis*-$Pt^{II}Cl_2P_2$ chromophores.[7] We report here the *X*-ray analysis of *cis*-$[PtCl_2(PEt_3)\{P(OPh)_3\}]$, the first square-planar platinum(II) phosphite species to be crystallographically characterised.

The results of this work allow the effect of electron withdrawal at the ligating phosphorus atom on metal–phosphorus bond lengths to be assessed quantitatively. They are also of interest in view of the proposed correlation between Pt–P bond lengths and $^1J(^{195}Pt-^{31}P)$ n.m.r. coupling constants.[8] In addition, they permit a direct comparison of the *trans* influence of phosphine and phosphite on Pt–Cl bond lengths.

EXPERIMENTAL

Crystal Data.—$C_{24}H_{30}Cl_2O_3P_2Pt$, M = 694.4, Monoclinic, a = 8.614, b = 37.100, c = 9.207 Å, β = 116.21°, U = 2 640 Å^3, Z = 4, D_c = 1.747 g cm^{-3}, $F(000)$ = 1 360, space group $P2_1/n$ (C^5_{2h}, no. 14), equivalent positions $\pm(x, y, z)$, $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$; Mo-$K_\alpha$ radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 57.2 cm^{-1}.

Measurements.—The space group and preliminary unit-cell dimensions were determined from rotation and Weissenberg photographs. Final values of the unit-cell parameters and the intensities of all the independent reflections with θ(Mo-K_α) ⩽ 28° were measured on a Hilger and Watts Y290 four-circle diffractometer equipped with a graphite monochromator. A symmetrical θ—2θ scan was employed: 2-s counts were taken at 0.02° intervals over a range of 0.50° in θ, and stationary crystal–stationary counter backgrounds were measured for 10 s at each end of the scan. The intensities of two strong reflections, periodically remeasured during the experiment, varied by less than 2% of their mean values.

Structure amplitudes and their standard deviations were derived in the usual way (q 0.05).[9] A correction was made for the effects of absorption; the transmission factors on F, calculated by Gaussian integration, varied between 0.57 and 0.78. The subsequent calculations proceeded with the 4 206 reflections for which $I \geqslant 3\sigma(I)$.

Structure Analysis.—The platinum atom was located from the three-dimensional Patterson function. The positions of the remaining atoms, including those of hydrogen, were obtained from subsequent difference syntheses. The structure was refined by blocked-matrix least-squares minimisation of the function $\Sigma\{(|F_o| - |F_c|)/\sigma(F)\}^2$. Atomic-scattering factors were taken from ref. 10 apart from that for hydrogen.[11] Allowance was made for the anomalous scattering of the platinum, chlorine, and phosphorus atoms.[10]

Refinement of the positional and thermal parameters of all the atoms converged at R 0.034 and R' 0.042. For the final calculations, isotropic temperature factors were used for the hydrogen atoms and anisotropic temperature factors

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† No reprints available.

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TABLE 1

Final fractional co-ordinates of the non-hydrogen atoms

	x	y	z
Pt	0.013 36(3)	0.139 49(1)	0.218 32(3)
P(1)	−0.123 8(2)	0.108 68(4)	0.327 5(2)
P(2)	−0.220 9(2)	0.159 31(4)	−0.003 8(2)
Cl(1)	0.273 4(2)	0.127 37(6)	0.449 9(2)
Cl(2)	0.182 1(2)	0.165 46(5)	0.104 2(2)
O(1)	−0.021 9(5)	0.075 0(1)	0.430 9(5)
O(2)	−0.179 9(6)	0.128 0(1)	0.449 7(6)
O(3)	−0.295 3(5)	0.090 4(1)	0.194 7(5)
C(1)	0.016 2(8)	0.066 1(2)	0.591 4(8)
C(2)	−0.051 8(9)	0.034 7(2)	0.617 0(9)
C(3)	−0.009 2(10)	0.024 2(2)	0.774 3(11)
C(4)	0.098 1(12)	0.045 0(3)	0.900 6(10)
C(5)	0.165 2(12)	0.076 4(2)	0.874 3(9)
C(6)	0.126 1(9)	0.087 7(2)	0.716 4(8)
C(7)	−0.200 0(7)	0.165 1(1)	0.465 0(7)
C(8)	−0.362 2(8)	0.178 3(2)	0.416 6(8)
C(9)	−0.385 4(11)	0.213 8(2)	0.437 7(10)
C(10)	−0.242 6(15)	0.236 3(2)	0.514 2(12)
C(11)	−0.078 4(14)	0.222 3(3)	0.565 1(12)
C(12)	−0.054 6(9)	0.185 9(2)	0.539 8(9)
C(13)	−0.382 8(7)	0.062 4(2)	0.231 6(7)
C(14)	−0.492 2(7)	0.071 2(2)	0.298 6(8)
C(15)	−0.575 8(10)	0.041 2(2)	0.332 5(9)
C(16)	−0.548 5(11)	0.006 2(2)	0.293 4(9)
C(17)	−0.443 6(12)	−0.000 1(2)	0.222 3(10)
C(18)	−0.358 7(10)	0.028 1(2)	0.188 4(9)
C(19)	−0.431 6(8)	0.159 5(2)	−0.000 1(8)
C(20)	−0.577 4(9)	0.178 3(2)	−0.141 7(9)
C(21)	−0.252 3(10)	0.135 5(2)	−0.187 5(8)
C(22)	−0.310 1(11)	0.096 9(2)	−0.195 3(10)
C(23)	−0.190 1(10)	0.206 5(2)	−0.042 5(10)
C(24)	−0.147 7(13)	0.230 8(2)	0.100 8(13)

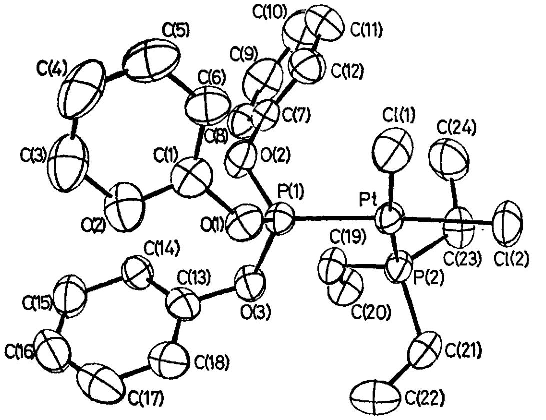

FIGURE 1 A view of the molecular structure. Hydrogen atoms are omitted for clarity. 50% Probability ellipsoids are displayed

TABLE 3

Deviations (Å) of atoms from the mean plane defined by Pt,P(1),P(2),Cl(1),Cl(2), whose equation, referred to orthonormal axes defined by a, b, and c *, is $-0.279X + 0.843Y + 0.460Z = 5.407$

Pt	0.001	P(1)	−0.095	P(2)	0.087	Cl(1)	0.141	Cl(2)	−0.156
O(1)	−0.88	O(2)	1.25	O(3)	−0.91	C(19)	0.62	C(21)	−1.49
C(23)	1.30								

for the remaining atoms. In the final difference-synthesis function, values lay between ±0.9 eÅ^{-3}, apart from peaks of ±1.5 eÅ^{-3} close to the platinum atom. The standard deviation of an observation of unit weight was 1.3, indicating that the weights were on a scale close to absolute. The relative weighting of the structure amplitudes was also satisfactory, mean values of $w\Delta^2$ showing little variation with either $|F_o|$ or sinθ. The final positional and thermal parameters of all the atoms, bond lengths, interbond angles, and torsion angles (including those involving the hydrogen atoms) are listed in Supplementary Publication No. SUP 22132 (23 pp.), together with the observed and calculated structure amplitudes.* The fractional co-ordinates of the non-hydrogen atoms and a selection of functions derived from them are presented in Tables 1—3. A perspective view of the molecule is shown in Figure 1.

TABLE 2

Selected interatomic distances (Å) and angles (°)

(*a*) Bond lengths

Pt–P(1)	2.182(2)	O(2)–C(7)	1.404(7)
Pt–P(2)	2.269(1)	O(3)–C(13)	1.411(8)
Pt–Cl(1)	2.355(2)	P(2)–C(19)	1.831(8)
Pt–Cl(2)	2.344(2)	P(2)–C(21)	1.821(8)
P(1)–O(1)	1.583(4)	P(2)–C(23)	1.829(8)
P(1)–O(2)	1.579(6)	C(19)–C(20)	1.523(8)
P(1)–O(3)	1.595(4)	C(21)–C(22)	1.504(11)
O(1)–C(1)	1.404(9)	C(23)–C(24)	1.505(14)
Mean C–C (Phenyl)	1.380(5)	Mean C–H	0.96(2)

(*b*) Interbond angles

P(1)–Pt–P(2)	97.9(1)	Cl(1)–Pt–Cl(2)	87.4(1)
P(1)–Pt–Cl(1)	88.6(1)	P(2)–Pt–Cl(2)	86.7(1)
P(1)–Pt–Cl(2)	172.3(1)	P(2)–Pt–Cl(1)	171.6(1)
Pt–P(1)–O(1)	114.9(2)	Pt–P(2)–C(19)	118.6(2)
Pt–P(1)–O(2)	119.3(2)	Pt–P(2)–C(21)	112.8(2)
Pt–P(1)–O(3)	112.1(2)	Pt–P(2)–C(23)	109.8(2)
O(1)–P(1)–O(2)	101.2(3)	C(19)–P(2)–C(21)	106.1(3)
O(1)–P(1)–O(3)	101.8(2)	C(19)–P(2)–C(23)	103.4(4)
O(2)–P(1)–O(3)	105.5(3)	C(21)–P(2)–C(23)	105.0(4)
P(1)–O(1)–C(1)	128.9(4)	P(2)–C(19)–C(20)	115.8(5)
P(1)–O(2)–C(7)	127.4(5)	P(2)–C(21)–C(22)	114.6(6)
P(1)–O(3)–C(13)	122.8(4)	P(2)–C(23)–C(24)	113.7(7)
O(1)–C(1)–C(2)	117.5(6)	O(2)–C(7)–C(8)	118.4(5)
O(1)–C(1)–C(6)	119.8(6)	O(2)–C(7)–C(12)	118.5(6)
C(2)–C(1)–C(6)	122.6(7)	C(8)–C(7)–C(12)	122.9(6)
O(3)–C(13)–C(14)	118.5(5)	C(7)–C(8)–C(9)	119.9(6)
O(3)–C(13)–C(18)	116.5(7)	C(7)–C(12)–C(11)	117.2(8)
C(14)–C(13)–C(18)	124.9(7)	C(13)–C(14)–C(15)	115.0(6)
C(1)–C(2)–C(3)	118.9(7)	C(13)–C(18)–C(17)	118.0(8)
C(1)–C(6)–C(5)	117.0(7)		

(*c*) Torsion angles

Pt–P(1)–O(1)–C(1)	127(1)	Pt–P(2)–C(19)–C(20)	171(1)
Pt–P(1)–O(2)–C(7)	21(1)	Pt–P(2)–C(21)–C(22)	70(1)
Pt–P(1)–O(3)–C(13)	164(1)	Pt–P(2)–C(23)–C(24)	−54(1)
P(1)–O(1)–C(1)–C(6)	−66(1)	P(1)–O(3)–C(13)–C(14)	81(1)
P(1)–O(2)–C(7)–C(12)	−75(1)		

The computer programs used were J. M. Stewart's 'X-RAY '72' system, C. K. Johnson's ORTEP2, the HILGER data-processing program of P. R. Mallinson and K. W. Muir, and the GEOM molecular-geometry program of P. R. Mallinson and D. N. J. White.

DISCUSSION

The crystals contain discrete molecules with the expected *cis*-square-planar co-ordination around the

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

platinum atom. The shortest distances between atoms in different molecules are close to the sum of the appropriate van der Waals radii.

The hydrogen atoms lie in positions which, although not accurately determined, are in accord with the established stereochemistry of the trigonal and tetrahedral carbon atoms to which they are attached. Thus the C–H bond lengths range from 0.7(1) to 1.2(1) Å, with a mean of 0.96(2) Å.*

Bond lengths and angles in the PEt_3 ligand are in good agreement with corresponding values in, for example, *cis*- and *trans*-$[PtCl_2\{C(PhNCH_2)_2\}(PEt_3)]$.[12] The conformations about the CH_2–CH_3 bonds are approximately staggered, the P(2)–C–C–H torsion angles lying within 15° of 180 or ±60°. Staggered conformations are also found about the P(2)–C bonds, as shown by the Pt–P(2)–C–C torsion angles listed in Table 2. As a result, the planes defined by the atoms P(2), C(21), and C(22), and by P(2), C(23), and C(24), are nearly coincident (dihedral angle 12°), and both are normal (dihedral angles 89 and 91°) to the plane through P(2), C(19), and C(20). The last plane is close to the co-ordination plane of platinum (dihedral angle 17°). The conformation of the PEt_3 ligand and its orientation with respect to the metal co-ordination plane are therefore similar to those we have observed in *cis*- and *trans*-$[PtCl_2\{C(PhNCH_2)_2\}(PEt_3)]$ [12] and in *cis*-$[PtCl_2\{C(OEt)(NHPh)\}(PEt_3)]$.[13] From an inspection of models this appears to be a favourable conformation for the minimisation of non-bonded repulsions when triethylphosphine is attached to a metal with square-planar co-ordination.

Bond lengths and angles within the triphenyl phosphite ligand are close to expected values. The mean P–O, O–C, and C–C distances, respectively 1.586(5), 1.406(5), and 1.380(5) Å, and also the P–O–C angles of 122.8(4)—128.9(4)°, agree well with corresponding values in $[Cr(CO)_5\{P(OPh)_3\}]$.[14] The internal ring angles at the phenyl-carbon atoms C(1), C(7), and C(13) are 3—5° greater than 120°, as expected when the exocyclic substituents of these atoms are electron withdrawing.[15] The conformations about the P–O bonds, as revealed by the torsion angles, display no obvious pattern: however, those about the O–C(phenyl) bonds are such as to prevent close approaches between P(1) and the *ortho*-carbon and hydrogen atoms of each ring (Table 2).

The square-planar co-ordination around the platinum atom shows a substantial tetrahedral distortion, evident both from the displacements of the atoms from the $PtCl_2P_2$ plane (Table 3) and from the *trans*-P–Pt–Cl angles of 172.3(1) and 171.6(1)°. The mutually *cis* phosphorus atoms subtend a rather large angle of 97.9(1)° at the metal. These deformations are likely to arise from steric interactions between the ligands, which are also obvious from an inspection of the non-bonded distances within the molecule. Thus the hydrogen atom attached to C(6) is 2.7 Å from Cl(1), and a hydrogen atom attached to C(23) is 2.6 Å from Cl(2). Between the phosphine and phosphite ligands the most significant approaches appear to be the O(3) • • • C(19) contact of 3.05 Å and an O(3) • • • H contact of 2.3 Å involving a hydrogen atom attached to C(19).†

In view of the steric crowding in the molecule, it is interesting to note that the cone angles for PEt_3 and $P(OPh)_3$, calculated from the observed molecular geometry using the expression suggested by Tolman,[3] are 152 and 146°, respectively. Both angles are substantially larger than the corresponding values of 130 and 128° which were obtained by Tolman using molecular models.[3] Such a discrepancy is perhaps to be expected in square-planar complexes, where bulky substituents can twist away from the co-ordination plane, close to which steric crowding tends to be most severe. This results in conformations which do not necessarily give minimum values of the cone angles. Thus, in *cis*-$[PtCl_2(PEt_3)\{P(OPh)_3\}]$ the phenyl group attached to O(2), which lies in a sterically unhindered region of the molecule, has a minimum half-cone angle of 98°. We feel that these effects should not be neglected when attempting, for example, to relate the enthalpies of substitution reactions of platinum(II) species to the cone angles of the entering ligands.[16]

The Pt–$P(OPh)_3$ bond is 0.087(3) Å shorter than the Pt–PEt_3 bond. A similar difference (0.11 Å) is found between the Cr–P bond lengths in the complexes $[Cr(CO)_5L]$ [L = $P(OPh)_3$ or PPh_3].[14] The $^1J(^{195}Pt-^{31}P)$ coupling constants in *cis*-$[PtCl_2(PEt_3)\{P(OPh)_3\}]$ [6 255 Hz for $P(OPh)_3$ and 3 210 Hz for PEt_3] [17] show the trend expected from the bond lengths. It should however be noted that ^1J(Pt–P) (coupling constant across the Pt–$P(CF_3)_2$ bond in *cis*-$[PtCl_2\{(F_3C)_2PCH_2CH_2PPh_2\}]$) is 4 013 Hz,[6] although the Pt–$P(CF_3)_2$ bond length of 2.168(3) Å is shorter by 0.014(4) Å than the Pt–$P(OPh)_3$ distance found here. It therefore appears that the variations in Pt–P coupling constants are not necessarily reflected by the bond lengths.

The mean O–P(1)–O angle [103(1)°] is very similar to the mean C–P(2)–C angle [105(1)°]. If these angles are used as an index of the hybridisation state of the phosphorus atoms, as suggested by Bent,[18] one would be forced to conclude that the phosphorus orbitals used in

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* Unweighted arithmetic means, $\bar{x}$, are used throughout the paper; the standard deviation of $\bar{x}$ is the greater of (*i*) $(\sum\sigma_i^{-2})^{-\frac{1}{2}}$ and (*ii*) $\sum_{i=1}^{n}[(x_i-\bar{x})^2/n(n-1)]^{\frac{1}{2}}$, where individual x_i have standard deviations σ_i derived from the inverse least-squares matrix.

† Non-bonded distances involving hydrogen atoms given here are based on refined hydrogen positions. Corresponding values based on calculated hydrogen positions, assuming normal stereochemistry at sp^2 and sp^3 carbon and C–H 1.08 Å, agree to within 0.1 Å.

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the Pt–P(OPh)$_3$ and Pt–PEt$_3$ bonds contain about the same amount of 3*s* character. Obviously, the observed difference in the lengths of these bonds cannot then be related to changes in the phosphorus-atom hybridisation.

The Pt–Cl bond *trans* to P(OPh)$_3$ is 0.011(3) Å shorter than the Pt–Cl bond *trans* to PEt$_3$. Thus our bond-length data support the conclusion, already made both from Pt–Cl stretching frequencies and from n.m.r. coupling constants,[19] that in platinum(II) complexes P(OPh)$_3$ exerts a weaker *trans* influence than PEt$_3$. This contrasts with the situation in the chromium(0) complexes [Cr(CO)$_5$L] where the Cr–C bond *trans* to P(OPh)$_3$ is found to be slightly longer than that *trans* to PPh$_3$.[14]

TABLE 4

Selected bond lengths in platinum(II) complexes containing *cis*-Cl$_2$P$_2$ donor sets

Complex	Bond length/Å		Cone angle (°) [a]	$\sum_{i=1}^{3} \chi_i$ [b]	Ref.
	Pt–P	Pt–Cl			
cis-[PtCl$_2$(PEt$_3$)$_2$] [c]	2.258(2)	2.361(6)	130	5.4	7
cis-[PtCl$_2$(PMe$_2$Ph)$_2$]·HgCl$_2$ [c]	2.255(5)	2.371(11)	127	9.5	21
cis-[PtCl$_2$(PMe$_3$)$_2$] [c]	2.248(9)	2.376(12)	118	7.8	22
cis-[PtCl$_2${PMe$_2$(C$_6$F$_5$)}$_2$] [c]	2.236(6)	2.344(12)	130	16.4	7
cis-[PtCl$_2$(PEt$_3$){P′(OPh)$_3$}] [d]	2.182(2)	2.344(2)	128	29.1	*e*
cis-[PtCl$_2${(F$_3$C)$_2$P′CH$_2$CH$_2$PPh$_2$}] [d]	2.168(3)	3.317(3)	119	41.0	6
cis-[PtCl$_2$(PEt$_3$)(P′F$_3$)] [d]	2.141(3)	2.305(3)	104	54.6	23

[a] Tolman cone angle, see refs. 3 and 16. [b] See text and ref. 2. [c] Mean bond lengths are given. [d] Pt–P and Pt–Cl (*trans* to P) bonds refer to primed phosphorus atom. [e] This work.

A discussion of the *cis* influences of the ligands L in the complexes *cis*-[PtCl$_2$(PEt$_3$)L], including that with L = P(OPh)$_3$, will be presented elsewhere.[7] We note here that the *cis* influence of P(OPh)$_3$ resembles that of carbon monoxide: the Pt–PEt$_3$ and Pt–Cl(*trans* to PEt$_3$) distances are respectively 2.269(1) and 2.355(2) Å in the P(OPh)$_3$ complex and 2.265(3) and 2.368(3) Å in the complex with L = CO,[7] and they present an interesting contrast with comparable distances [2.215(4) and 2.382(4) Å] in the [PtCl$_3$(PEt$_3$)]$^-$ anion.[20]

The Electronic Effect of the Phosphorus-ligand Substituents.—Recent crystallographic studies, in this laboratory [6,7] and elsewhere,[21–23] permit for the first time a detailed examination of the relation between the properties of the substituents at the phosphorus atom and the metal–ligand bonding in phosphine and phosphite complexes of Pt^{II}.

We note that in complexes with *cis*-Cl$_2$P$_2$ donor sets (Table 4) the Pt–P bond lengths display a variation of *ca.* 0.12 Å and decrease along the series PEt$_3$ ~ PMe$_2$Ph ~ PMe$_3$ > PMe$_2$(C$_6$F$_5$) > P(OPh)$_3$ > P(CF$_3$)$_2$$^-$ > PF$_3$. This series is not well related to the size of the ligands as measured, for example, by minimum cone angle.[3,16] Furthermore, in *cis*-[PtCl$_2$(PEt$_3$){P(OPh)$_3$}] the difference in length of the Pt–P bonds cannot be explained in terms of the steric demands of PEt$_3$ and P(OPh)$_3$. We therefore do not consider that in these complexes the variation in Pt–P bond lengths arises from the steric requirements of the ligands. Rather we believe that the trend is determined predominantly by the electron-withdrawing ability of the substituents on phosphorus. A convenient measure of this property, $\Sigma\chi_i$, has been proposed by Tolman, who showed that in [Ni(CO)$_3$(PR^{1}R^{2}R^3)] complexes the ν(CO) (A_1) stretching frequency can be predicted from the relation 2 056.1 + $\Sigma\chi_i$, where χ_i is the enhancement of the stretching frequency attributed to the R^i substituent of phosphorus.[2] We find that there is a linear correlation between the Pt^{II}–P bond lengths in Table 4 and the parameter $\Sigma\chi_i$ (Figure 2). A similar, although less-extensive, correlation has been observed for the complexes [Cr(CO)$_5$L] [L = PPh$_3$, PH$_3$, or P(OPh)$_3$], where the Cr–P bond lengths vary linearly with the ν(CO)(E) stretching frequency.[14] The Pt–Cl(*trans* to P) bond lengths in Table 4 are also linearly related to $\Sigma\chi_i$ (Figure 2), but their rate of variation is about half that of the Pt–P distances.

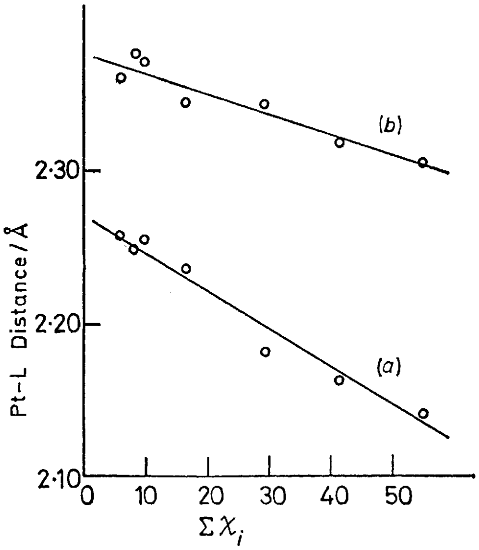

FIGURE 2 Variation in the Pt–P (*a*) and Pt–Cl(*trans* to P) (*b*) bond lengths in complexes having *cis*-PtCl$_2$P$_2$ chromophores with $\Sigma\chi_i$, a measure of the electron-withdrawing ability of the phosphorus substituents (see text)

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The observed changes in Pt–P and Pt–Cl(*trans* to P) bond lengths can be understood in terms of π-bonding effects. Electron withdrawal by phosphorus substituents would be expected to favour more d_π–d_π back donation from platinum to phosphorus, leading to a shortening of the Pt–P bond. The flow of electron density in the metal d_π orbitals, away from chloride and towards the phosphorus atom, would increase the electrostatic interaction between the metal and chloride ions, resulting in a contraction of the Pt–Cl(*trans* to P) bond. We have previously demonstrated that a similar effect operates in platinum(II) complexes with carbon-donor ligands, increased back donation from platinum to carbon being accompanied by shortening of the Pt–Cl bond *trans* to carbon.[24] We note also that the enhancement of carbonyl-stretching frequencies in nickel(0) complexes, which we have related to platinum(II)–ligand bond lengths, may be interpreted in terms of decreased Ni–C multiple bonding.

The observed variations in metal–ligand bond lengths may also be ascribed to σ-bonding effects. Electron withdrawal at phosphorus would then be expected to contract the phosphorus σ-donor orbital. A contraction of the platinum acceptor orbitals, arising from the higher formal charge of the metal when attached to a less basic phosphine, may also be anticipated. These effects would result in a shortening of both Pt–P and Pt–Cl(*trans* to P) bonds, but the latter, sensitive only to the decrease in the metal radius, would be less affected. A difficulty with this argument is that an isotropic contraction of the metal orbitals might be expected, with a consequent shortening of the *cis* bonds which is not evident in the experimental results.

It should also be pointed out that the molecular-orbital theory of *trans* influence would predict that in a linear P–Pt–Cl system a shortening of the Pt–Cl bond leads to lengthening of the Pt–P σ bond. Against this, the theory indicates that the *trans* influence of the phosphorus-donor ligand diminishes as the electronegativity of the phosphorus atom increases.[25]

The alternative rationalisations of the results discussed here, based on π and σ effects, are not mutually exclusive and both have some predictive value. We feel that the ambiguity of interpretation will only be resolved when a quantitative theory of bonding in transition-metal complexes becomes available.

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