cis- And *trans*-Influences in Platinum(II) Complexes. *X*-Ray Crystal Structure Analysis of Tetraethylammonium Trichloro(triethylphosphine)-platinate(II)

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Crystals of the title compound are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions a = 1·03232(17), b = 0·92006(20), c = 2·27101(55) nm, β = 97·33(3)°. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to R 3·9%. The anion has bond angles at platinum within 1·4° of 90° and perturbations by interionic forces appear negligible. The 4° fold about the approximately linear P–Pt–Cl axis and the orientation of the PC_3 moiety with respect to the complex plane are explained by C ··· Cl repulsions. The bond lengths Pt–P [221·5(4)], Pt–Cl (*trans* to P) [238·2(4)], and Pt–Cl [230·2(4), 229·9(4) pm] are compared with those in *cis*-$[PtCl_2(PMe_3)_2]$ and the Pt–P lengths are consistent with n.m.r. coupling constants ^1J(Pt–P). Complexes of form $[PtCl_3L]$ are shown to be suitable as a basis for measurements of *cis*- and *trans*-influences of ligands L.

ALTHOUGH the existence of weaker bonds *trans* to certain ligands was formalised as the *trans*-influence in the context of platinum(II) compounds,[1] and many bond-length determinations have been made for platinum(II) complexes, there is still no extensive set of measurements of lengths *cis* and *trans* to ligands (L) in otherwise identical complexes. The bond lengths Pt–Cl for both terminal and bridging chlorine ligands *cis* to L in *sym-trans*-$[Pt_2Cl_4L_2]$ are not significantly dependent on L (L = Pr_3P,[2] Me_3As[3]), but the Pt–Cl bond *trans* to P is slightly longer than that *trans* to As. Such compounds are, however, not ideal as a basis for a standard set of measurements, because the bridging chlorine atoms are subject to the *cis*-influence of one L and the *trans*-influence of the other L. Also, in the complex $[Pt_2Cl_4(Et_2S)_2]$ the Et_2S ligands occupy bridging rather than terminal positions.[4]

Other possibly suitable complexes are *trans*-$[PtClLY_2]$ (Y = phosphine) which are cationic with neutral ligands L, and uncharged with anionic ligands L. However, this series would have the disadvantage that the ligands *cis* and *trans* to L are different, and the crystal structure determination [5] of *cis*-$[PtCl_2(PMe_3)_2]$ has shown that there would generally be considerable steric interaction between L and the organic groups of the phosphine ligands. Accordingly, we decided to examine the suitability of compounds of type $[PtCl_3L]^-$ using Et_4N^+ as counter ion in the hope of reducing ionic interactions to minor proportions, and, to facilitate comparisons with as many other structures as possible, we selected the complex with L = Et_3P for initial study. A wide range of compounds containing ions $[PtCl_3L]^-$ is known (L = NH_3, RNH_2, py, C_2H_4, NO, CO, Me_2S, thiourea, R_3P, and R_3As) [6] as well as $[PtCl_3L]^{2-}$ (L = Cl or NO_2) [7] and there is little doubt that crystals could be obtained for tetraethylammonium or similar salts.

EXPERIMENTAL

Preparation.—The complex was prepared by addition of tetraethylammonium chloride to a dichloromethane solution of *sym-trans*-$[Pt_2Cl_4(Et_3P)_2]$ and recrystallised from a solution of dichloromethane and acetone (Found: C, 30·3; H, 6·25; N, 2·60. Calc. for $C_{14}H_{35}Cl_3NPPt$: C, 30·58; H, 6·42; N, 2·55%).

Crystal Data.—$C_{14}H_{35}Cl_3NPPt$, M = 549·86, Monoclinic, a = 1·03232(17), b = 0·92006(20), c = 2·27101(55) nm, α = γ = 90°, β = 97·33(3)°, U = 2·1394(8) nm³, D_m = 1·73 g cm⁻³ (by flotation), Z = 4, D_c = 1·707, $F(000)$ = 1080. Space group $P2_1/c$ (No. 14). Mo-K_α radiation, λ = 0·071069 pm, μ(Mo-K_α) = 73·4 cm⁻¹. Boundary planes of the crystal in the form (h,k,l), length of perpendicular from the origin to the face: (0, 0, ±1), 0·105 mm; (±1, 0, 0), 0·183 mm; (1, 0, 2), 0·152 mm; $(\bar{1}, 0, \bar{2})$, 0·180 mm; $(\bar{1}, 0, 2)$, 0·149 mm; $(1, 0, \bar{2})$, 0·159 mm; (0, ±1, 0), 0·25 mm.

Crystallographic Measurements.—A set of 57 2θ measurements was obtained on a Picker four-cycle diffractometer and used for cell refinement by least-squares. The crystal was mounted on its b axis. Diffractometer measurements were obtained manually, in the bisecting position with ω centred at zero. Each measurement was obtained by scanning ω for 1 min at 1° min⁻¹. For reflections >10° in 2θ, background counts were collected for 30 s at the extremities of the scan. For reflections <10° in 2θ the *X*-ray photographs showed that this method would have been unsatisfactory due to streaking effects, and the background readings were taken with ω = 0 and 2θ ± 1° from the reflection centre. This procedure was adopted when the θ—2θ scan motor failed during the first few measurements. Three axial reflections were used for checking the crystal orientation, and reflection (2,1,2) was measured hourly as the standard reflection. All measurements were scaled using the current value of the standard reflection. A total of 1401 reflections was measured up to 2θ 35°. Lorentz and polarisation corrections were applied and a list of F_o derived. Estimates of the standard deviations of the measurements and F_o were made using the formulae given in ref. 8, and an instrument instability constant of 0·04. The data-reduction programme assigned unobserved status to 42 reflections by use of the criterion that the net count was less than the standard deviation of the background count (σ). Measurements between −σ and σ were squeezed by a factor of 0·5 into the 0 to σ range. Measurements below −σ were given a value very close to zero. The unobserved reflections were

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[1] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1707.

[2] M. Black, R. H. B. Mais, and P. G. Owston, *Acta Cryst.*, 1969, **B25**, 1760.

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[5] G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 725.

[6] Gmelin, ' Handbuch der Anorganischen Chemie,' 8th edn., no. 68, Platinum (D), pp. 419—445.

[7] Ref. 6, Platinum (C), pp, 187, 213.

[8] G. H. Stout and L. H. Jensen, ' *X*-Ray Structure Determination,' Macmillan, New York, 1968, p. 456.

included in the structure-factor calculations but not in the least-squares refinement. Absorption corrections were calculated by Gaussian grid numerical integration using 8, 10, and 6 points in the *a*, *b*, and *c* directions.

Structure Determination.—Calculations were performed with an IBM 370/145 computer at the University of Victoria. The position of the platinum atom was obtained from the three-dimensional Patterson function. Scattering-factor curves for uncharged atoms were taken from ref. 9, and the anomalous dispersion correction for platinum from ref. 10. The phosphorus and chlorine atoms were placed by means of a Fourier map phased by platinum. The five heavy atoms were refined by least-squares to R 0·169. The light atoms were located from a difference map and the structure was refined by three cycles of full-matrix least-squares with isotropic temperature factors, and introducing an algebraic weighting scheme (R 0·059). The five heavy atoms were then given anisotropic temperature factors and three more least-squares cycles gave R 0·042 and R' 0·052. Two final refinement cycles were performed with all atoms anisotropic, giving R 0·039 and R' 0·044. In the final cycle of refinement the greatest change-to-error ratio was 0·21, and the largest atom shift was 0·2 pm for carbon. The final weighting scheme was determined from: $\sigma^2(F_o) = 26{\cdot}44 - 0{\cdot}3941F_o + 0{\cdot}00246F_o^2$ using $\omega = 1/\sigma^2$. The quantity $(\Sigma\omega\Delta^2)/(NO - NV)$ was *ca.* 1·0 and did not vary with F_o. Hamilton's R' ratio test [11] showed the best model to be that with all atoms anisotropic.

The final difference synthesis indicated that no atoms were misplaced or had been omitted. The maximum positive and negative peak heights were 0·65 and 0·69 × 10^{-6} e pm^{-3}. The full variance–covariance matrix was used in estimating the standard deviations in bond lengths and angles.

A mean-plane calculation [12] was carried out for the five heavy atoms using an orthogonal axis system with X along *a*, Y in the *a*,*b* plane, and Z along c^*. The equation of the plane was $0{\cdot}5310X + 0{\cdot}8262Y + 0{\cdot}1883Z = 322{\cdot}12$. Distances from the plane were Pt −0·21(6), Cl(1) −1·3(5), Cl(2) 7·2(5), Cl(3) 7·0(5), and P −0·9(4) pm. The significant non-planarity of this set of atoms is due to a fold along the P–Pt–Cl(1) line, of *ca.* 4°.

RESULTS AND DISCUSSION

Final atomic parameters are given in Table 1 and a diagram of the structure is given in Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21185 (2 pp., 1 microfiche).* Bond lengths and angles are listed in Table 2, and interionic distances to chlorine of <400 pm in Table 3.

Examination of the non-bonded distances from points in the Et_4N^+ ion to Cl(1), Cl(2), and Cl(3) (Table 3) clearly shows that there are no significant differences in the (interionic) environments of the chlorine atoms, and the excellent agreement obtained between the values of Pt–Cl(2) and Pt–Cl(3) (Table 2) is a further indication that perturbation of the ion $[PtCl_3(PEt_3)]^-$ by interionic forces has been reduced to an insignificant level by use of Et_4N^+ as counter ion.

The deviation from planarity of the platinum and co-ordinated atoms of the complex may be described as a fold of *ca.* 4° about the P–Pt–Cl(1) axis, and a further feature of the structure of the ion is that the P–C bonds of the phosphine all lie out of the plane of the complex (Figure 2). Both phenomena are clearly derived from repulsion between the carbon atoms attached to phosphorus and the chlorine ligands Cl(2) and Cl(3): the fold is derived from the imbalance about the plane of the complex of the repulsions between the carbon and chlorine atoms, and the orientation of the PC_3 group with respect to the plane is such that there are no very short

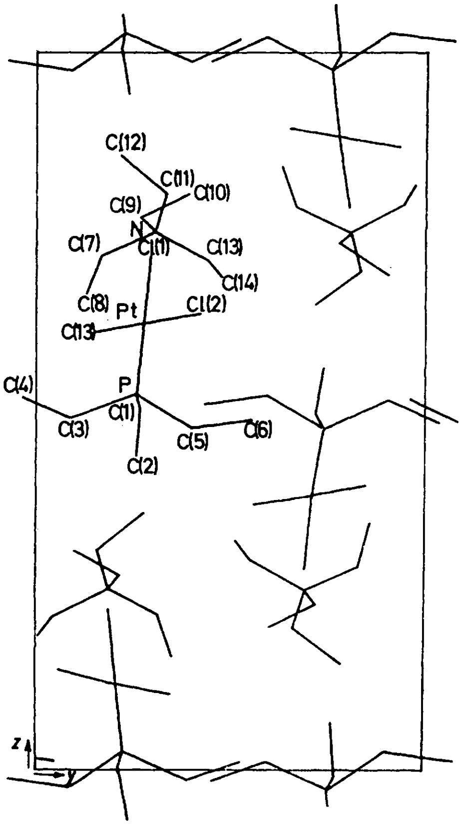

FIGURE 1 The crystal structure of $[Et_4N][PtCl_3(PEt_3)]$

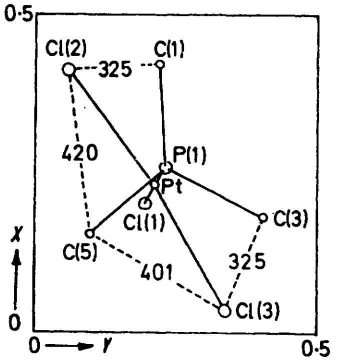

FIGURE 2 Non-bonded intramolecular distances in the anion nearest to the origin in Figure 1. The *z* axis is perpendicular to the paper and down, the *x* axis lies above the plane of the page

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

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

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

[11] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[12] D. M. Blow, *Acta Cryst.*, 1960, **13**, 168.

C ··· Cl distances and the distances C(1) ··· Cl(2) and C(3) ··· Cl(3) are equal (Figure 2). That these interactions, between the phosphine and the ligands in *cis*-positions, are relatively weak is evident from the small degree of folding and from the closeness of the P–Pt–Cl(2) and P–Pt–Cl(3) angles to 90° (Table 2).

TABLE 1

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

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Pt	2312(1)	2149(1)	1195(0·3)
Cl(1)	2109(5)	1944(5)	2224(2)
Cl(2)	4134(4)	686(5)	1340(2)
Cl(3)	409(4)	3474(5)	1060(2)
P	2493(4)	2368(4)	237(2)
N	−2435(11)	1909(13)	2494(5)
C(1)	4170(15)	2239(19)	56(7)
C(2)	4285(18)	2391(23)	−617(9)
C(3)	1814(16)	4042(17)	−119(7)
C(4)	2514(22)	5376(19)	143(9)
C(5)	1537(16)	999(16)	−234(7)
C(6)	2055(19)	−587(18)	−116(8)
C(7)	−1975(18)	3259(18)	2173(8)
C(8)	−2817(19)	3633(24)	1584(8)
C(9)	−3822(16)	2236(21)	2681(7)
C(10)	−4317(18)	1040(22)	3035(8)
C(11)	−1422(17)	1621(20)	3039(7)
C(12)	−1418(19)	2803(21)	3527(8)
C(13)	−2529(16)	540(18)	2108(7)
C(14)	−1254(18)	199(20)	1861(8)

(*b*) Anisotropic temperature parameters (× 10^4) *

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	96(1)	100(1)	17(0·2)	−7(0·7)	3(0·3)	−0·2(0·3)
Cl(1)	214(7)	165(7)	19(1)	−19(6)	11(2)	−2(2)
Cl(2)	117(6)	206(8)	27(1)	36(5)	−8(2)	10(3)
Cl(3)	124(6)	195(8)	28(1)	34(5)	18(2)	11(3)
P	87(5)	95(6)	19(1)	2(5)	8(2)	−3(2)
N	87(16)	120(22)	19(3)	12(14)	3(6)	9(8)
C(1)	117(21)	202(31)	26(5)	−15(22)	12(8)	7(10)
C(2)	158(26)	291(41)	38(7)	30(27)	39(10)	20(13)
C(3)	171(24)	92(27)	18(4)	32(20)	18(8)	15(8)
C(4)	328(39)	86(28)	36(6)	−33(27)	48(13)	−10(11)
C(5)	156(23)	79(27)	25(5)	−17(19)	−4(8)	−6(8)
C(6)	246(31)	92(29)	31(5)	−3(24)	22(10)	−8(9)
C(7)	196(28)	100(28)	35(6)	−11(22)	19(11)	17(10)
C(8)	210(30)	269(39)	22(5)	43(28)	11(10)	31(12)
C(9)	113(24)	268(37)	23(5)	22(25)	14(9)	4(11)
C(10)	175(27)	249(37)	30(5)	−80(27)	37(10)	14(12)
C(11)	144(24)	232(35)	19(5)	5(23)	−17(9)	0(11)
C(12)	204(28)	211(34)	27(5)	−40(26)	−2(10)	−35(12)
C(13)	153(26)	130(28)	26(5)	3(21)	14(9)	−29(10)
C(14)	159(26)	209(34)	30(5)	40(24)	25(10)	−24(11)

* In the form: $T = \exp[-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hkb_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table 4 lists Pt–Cl distances for structures having approximately linear arrangements Cl–Pt–Cl with terminal chlorine ligands and with different *cis* groups. Application of Cruickshank's test [13] shows that there is no significant difference in bond lengths between neutral and anionic complexes (a further indication of negligible interionic perturbations), and it is also clear that any influence of *cis* ligands on the Pt–Cl bond lengths is smaller than the uncertainties in the *X*-ray determinations.

The Pt–P bond [221·5(4) pm] in $[PtCl_3(PEt_3)]^-$ is shorter than the mean, [224·7(8) pm] in *cis*-$[PtCl_2(PMe_3)_2]$.[5] This result is consistent with an analysis of n.m.r. coupling constants, ^1J(Pt–P), in similar compounds, which are 3704 for $[PtCl_3(PEt_3)]^-$ and 3520 Hz for *cis*-$[PtCl_2(PEt_3)_2]$.[14] Larger values of ^1J(Pt–P) can, for similar complexes, generally be associated with shorter Pt–P bonds and explanations [1,14] in terms of changes in the *s* components of the bonds now appear to have gained acceptance.[15] Theory of *trans*-influence [15] predicts that the shorter Pt–P bond in $[PtCl_3(PEt_3)]^-$ should utilise a greater share of platinum σ-orbitals and cause some lengthening of the *trans*-Pt–Cl bond compared with that in *cis*-$[PtCl_2(PMe_3)_2]$. In fact the Pt–Cl *trans* to phosphorus in $[PtCl_3(PEt_3)]^-$ is 238·2(4) pm, not significantly different from the average value 237·6(8) pm

TABLE 2

(*a*) Bond lengths (pm) and their standard deviations

(i) Pt co-ordination			
Pt–P	221·5(4)	Pt–Cl(1)	238·2(4)
Pt–Cl(2)	230·2(4)	Pt–Cl(3)	229·9(4)
(ii) Et_3P ligand			
P–C(1)	183·4(16)	C(1)–C(2)	155·5(25)
P–C(3)	183·7(15)	C(3)–C(4)	150·8(24)
P–C(5)	185·4(15)	C(5)–C(6)	156·6(23)
(iii) Et_4N			
N–C(7)	154·5(19)	C(7)–C(8)	153·8(24)
N–C(9)	157·4(19)	C(9)–C(10)	149·1(24)
N–C(11)	153·9(19)	C(11)–C(12)	155·2(24)
N–C(13)	153·1(19)	C(13)–C(14)	152·7(23)

(*b*) Bond angles (°) with standard deviations

(i) Pt co-ordination			
P–Pt–Cl(1)	179·29(15)	Cl(2)–Pt–Cl(3)	176·14(16)
Cl(1)–Pt–Cl(2)	89·19(17)	P–Pt–Cl(3)	89·92(15)
P–Pt–Cl(2)	91·37(15)	Cl(3)–Pt–Cl(1)	89·55(16)
(ii) PEt_3 ligand			
Pt–P–C(1)	114·5(6)	P–C(3)–C(4)	111·8(12)
P–C(1)–C(2)	114·1(12)	Pt–P–C(5)	113·6(5)
Pt–P–C(3)	115·7(5)	P–C(5)–C(6)	112·9(11)
(iii) Et_4N ion			
C(7)–N–C(9)	108·6(12)	C(11)–C–C(13)	107·8(12)
C(9)–N–C(11)	111·3(12)	N–C(9)–C(10)	113·0(14)
N–C(7)–C(8)	114·6(15)	C(7)–N–C(13)	113·1(11)
N–C(13)–C(14)	112·6(13)	C(13)–N–C(9)	108·6(11)
C(7)–N–C(11)	107·5(12)	N–C(11)–C(12)	113·2(14)

TABLE 3

Interionic distances (pm)* to chlorine <400 pm

Atom	Symmetry position	Distance from Cl(1)	Symmetry position	Co-ordinates †
C(13)	*a*	364	*a*	$\bar{x}, \frac{1}{2} + y, (\frac{1}{2} - z)$
C(7)	*b*	367	*b*	$\bar{x}, y - \frac{1}{2}, (\frac{1}{2} - z)$
C(14)	*a*	381	*c*	x, y, z
C(14)	*c*	382	*d*	$1 + x, y, z$
C(10)	*d*	399	*e*	$1 - x, \bar{y}, \bar{z}$
			f	$\bar{x}, 1 - y, \bar{z}$

Atom	Symmetry position	Distance from Cl(2)	Atom	Symmetry position	Distance from Cl (3)
C(13)	*d*	366	C(11)	*a*	362
C(2)	*e*	375	C(8)	*c*	368
C(9)	*d*	376	C(3)	*f*	372
C(12)	*b*	390	C(7)	*c*	375
C(9)	*b*	391	C(4)	*f*	395
C(10)	*d*	399			

* Standard deviations all 2 pm. † With respect to *x*, *y*, *z* in Table 1.

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[15] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335; A. Pidcock, 'Transition-Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' ed. C. A. McAuliffe, Macmillan, London, 1973, Part 1.

for *cis*-[$PtCl_2(PMe_3)_2$],[5] so it seems probable that the metal–ligand bond lengths in *cis*-[$PtCl_2(PMe_3)_2$] are affected by steric factors. In particular, the distortion away from a square-planar structure towards a tetrahedral form,[5] which is mainly a consequence of steric interactions involving the methyl groups of the phosphines, may cause the platinum σ orbitals to be distributed between the metal–ligand bonds in a way that is significantly different from that for a relatively undistorted square-planar complex. It would thus be of considerable interest to obtain structural data for the analogous platinum(IV) compounds [$PtCl_5(PR_3)$]$^-$ and *cis*-[$PtCl_4(PR_3)_2$], since for these, the coupling constants ^1J(Pt–P) are closely similar,[14] and the extra ligands and the longer Pt–P bonds of Pt^{IV} complexes [16] may reduce distortion in the *cis*-complex.

TABLE 4

Lengths (pm) of Pt–Cl bonds

Compound	Pt–Cl (*trans* to Cl)	*cis*-Groups	Pt–Cl (*trans* to L)
$K_2[PtCl_4]$ [a]	231·7(2)	Cl, Cl	
[$Pt(MeNH_2)_4$][$PtCl_4$] [b]	229(14)	Cl, Cl	
[$Pt(EtNH_2)_4$][$PtCl_4$] [b]	233(1) 241(4)	Cl, Cl	
K[$PtCl_3(C_2H_4)$],H_2O [c]	231·4(7) 229·6(7)	Cl, C_2H_4	232·7(5)
[NMe_3Et]$_2$[$Cl_3PtC_4H_6PtCl_3$] [d]	232(1) 229(1)	Cl, C_4H_6	229(1)
[Ph_4P][$PtCl_3$(*cis*-but-2-ene-1,4-diol)] [e]	229·1(9) 230·1(8)	Cl, olefin	229·6(9)
[$PtCl_3$(*trans*-but-2-ene-1,4-diammonium)]Cl,$\frac{1}{2}H_2O$ [f]	231·1(2) 229·3(2)	Cl, olefin	234·2(2)
[$PtCl_3$(*trans*-MeCH:CHCH$_2$NMe$_3$)] [g]	230·7(6) 228·8(7)	Cl, olefin	233·9 (7)
[$PtCl_3$(*cis*-MeCH:CHCH$_2$NMe$_3$)] [g]	230·1(6) 229·3(6)	Cl, olefin	232·0(6)
[Et_4N][$PtCl_3(PEt_3)$] [h]	230·2(4) 229·9(4)	Cl, PEt_3	238·2(4)
trans-[$PtCl_2(C_2H_4)(NHMe_2)$] [i]	230(4) 233(4)	C_2H_4, amine	
trans-[$PtCl_2(Bu^tC{:}CBu^t)(MeC_6H_4NH_2)$] [j]	230·0(2)	Amine, acetylene	
trans-[$PtCl_2(C_5H_5N)$(pyridinium propylide)] [k]	235(2) 230(2)	C_5H_5N, ylide	
trans-[$PtCl_2(PEt_3)\{C(NPhCH_2)_2\}$] [l]	230(1) 232(1)	PEt_3, carbene	
trans-[$PtCl_2(PEt_3)_2$] [m]	230·0(19)	PEt_3, PEt_3	

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Conclusions.—The complexes of type [$PtCl_3L$]$^-$ appear to be very suitable for the determination of *cis*- and *trans*-influences based on measurements of Pt–Cl bond lengths. The simplicity of structure of the complexes facilitates the recognition of intramolecular steric interactions, and it is clear that the relative importance of steric compared with electronic effects is much greater for the *cis*- than for the *trans*-influence. The *trans*-influence order, as determined from Pt–Cl bond lengths in complexes [$PtCl_3L$], is: $R_3P >$ olefin, Cl^- (Table 4).

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