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SYNTHESIS AND ^{31}P NMR SPECTRA OF SOME PLATINUM(II) COMPLEXES OF THE PHOSPHA-ALKENE, (MESITYL)P=CPh$_2$

CRYSTAL AND MOLECULAR STRUCTURE OF *cis*-[PtCl$_2$(PEt$_3$)(C$_6$H$_2$Me$_3$P=CPh$_2$)]·CHCl$_3$

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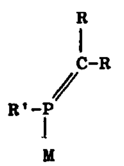
Abstract—Syntheses of the phospha-alkene complexes *cis*- and *trans*-[PtCl$_2$(PEt$_3$)(mesityl)P=CPh$_2$], and *cis*-[PtX$_2${(Mesityl)P=CPh$_2$}$_2$](X=Cl, I, Me) complexes are reported. ^{31}P NMR spectra indicate that bonding of the phospha-alkene to the metal is via the phosphorus lone pair and this is confirmed by a single crystal X-ray diffraction study of *cis*-[PtCl$_2$(PEt$_3$){(mesityl)P=CPh$_2$}]CHCl$_3$.

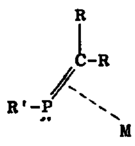
INTRODUCTION

There is current interest in the chemistry of trivalent phosphorus compounds in which phosphorus is one or two coordinate. Recently we and others[1–4] have developed synthetic routes to novel compounds containing carbon multiply bonded to phosphorus, viz. phospha-alkenes, R$_2$C=PR′, and phospha-alkynes, RC≡P.

In a preliminary report[5] we described a number of transition metal complexes of the phosphaalkene C$_6$H$_2$Me$_3$P=CPh$_2$,[3] (C$_6$H$_2$Me$_3$ = mesityl). NMR studies on complexes of tungsten(O), rhodium(I) and platinum(II) indicated that in all cases the bonding of the phospha-alkene to the transition metal was via the phosphorus lone pair as in (A) rather than as in (B).



(A)



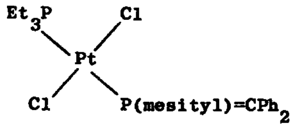
(B)

These results complemented observations by Niecke[6] and Scherer[7] on complexes containing the isoelectronic R′PNR and RPO ligands.

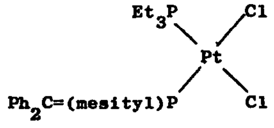
We now report details of a number of platinum(II) complexes of (mesityl)P=CPh$_2$ and the crystal and molecular structure of the chloroform solvate of *cis*-[PtCl$_2$(PEt$_3$) (mesityl)P=CPh$_2$] which confirms the nature of the metal–ligand bonding.

RESULTS AND DISCUSSION

Many amine and phosphine ligands, L, cleave the bridge of the dinuclear complex [Pt$_2$Cl$_4$(PEt$_3$)$_2$] to afford *trans*-complexes [PtCl$_2$(PEt$_3$)L]. The ^{31}P{^{1}H} NMR spectrum of a dichloromethane solution of [Pt$_2$Cl$_4$(PEt$_3$)$_2$] and (mesityl)P=CPh$_2$, shown in Fig. 1, consists of two "triplets" from coupling to ^{195}Pt each line exhibiting a further large ^{2}J(PP′) coupling (544 Hz) typical of formation of the *trans*-isomer of [PtCl$_2${(mesityl)P=CPh$_2$)}(PEt$_3$)], (I), in which the phosphaalkene is coordinated via the phosphorus lone pair. Coupling constant data are listed in Table 1.



(I)



(II)

Removal of solvent from the solution of (I) gave a yellow oil from which a yellow solid, (II), can be obtained from pentane. The ^{31}P{^{1}H} NMR spectra of (II) shown in Fig. 2 indicated that it was the *cis*-isomer of (I) since the magnitude of ^{1}J(PtP) was greatly increased while ^{2}J(PP′) was only 23 Hz (Table 1). The IR spectrum of (II) exhibited two (Pt–Cl) bands at 315 and 290 cm^{-1} expected for a *cis*-complex. A solid sample of (I) could not be obtained pure but the IR of a mixture of (I) and (II) exhibited an additional band at 335 cm^{-1} which is assigned as ν(Pt–Cl) for (I).

The complex *trans*-[PtCl$_2$(PEt$_3$){PCl(mesityl)CHPh$_2$}], (III), was also prepared from [Pt$_2$Cl$_4$(PEt$_3$)$_2$] and its reaction with dbu (dbu = 1,5 - diazabicyclo - [5,4,0]*trans* -

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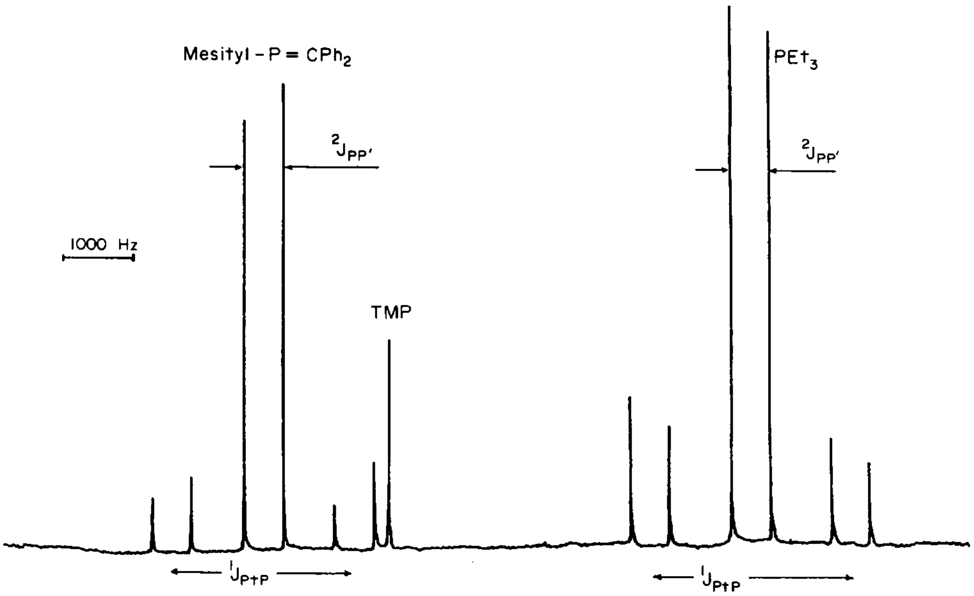

Fig. 1. ^{31}P NMR spectrum of *trans*-[PtCl$_2$(PEt$_3$)(mesityl)P=CPh$_2$)].

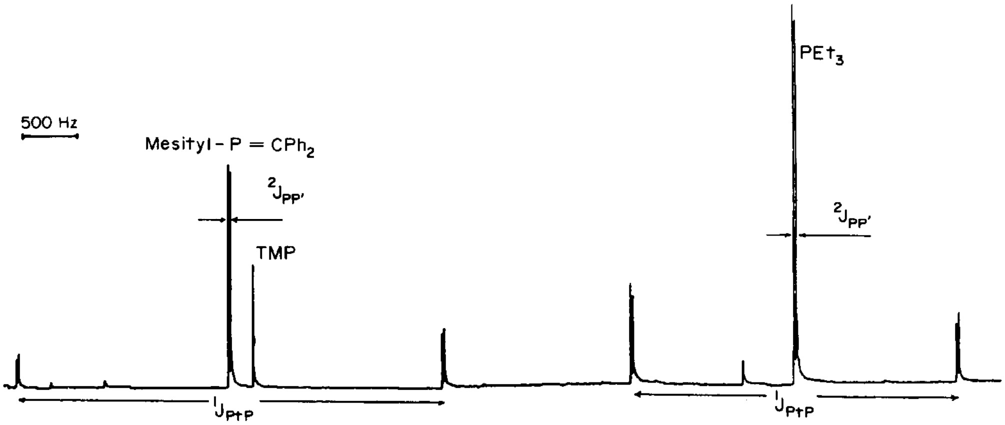

Fig. 2. ^{31}P NMR spectrum of *cis*-[PtCl$_2$(PEt$_3$)(mesityl)P=CPh$_2$)].

Table 1. ^{31}P NMR data for some PtCl$_2$LL', complexes

L	L'		$^1J_{PtL}$[c]	$^1J_{Pt(PEt_3)}$[c]	$^2J_{PP'}$[c]
(mesityl)P=CPh$_2$[a]	PEt$_3$	cis	4294	3269	23
(mesityl)P=CPh$_2$[a]	PEt$_3$	trans	2590	2844	544
PF$_3$[b]	PEt$_3$	cis	7388	2869	19
P(OPh)$_3$[b]	PEt$_3$	cis	6249	3197	22
P(OPh$_3$)$_2$[b]	PBu$_3$	trans	4116	2570	715
PCl$_3$[b]	PEt$_3$	cis	6054	2977	17
PPh$_2$Cl[b]	PEt$_3$	cis	5077	3164	17
PPh$_3$[b]	PEt$_3$	cis	3815	3373	17
PEt$_3$[b]	PEt$_3$	cis	3520	3520	17
P(Cl)(mesityl)(CHPh$_2$)[a]	PEt$_3$	trans	2539	2647	547

(a) This work. (b) Data from refs.8, 10, 20, 21. (c) In Hz.

undec - 5 - ene) was studied to see if hydrogen chloride could be eliminated from the coordinated chlorophosphine to afford (I). This type of reaction has been previously established by us for PCl(mesityl)CHPh$_2$ coordinated to zerovalent tungsten.[5]

The ^{31}P{^{1}H} NMR spectrum of the reaction mixture, however, showed only the presence of PCl(mesityl)CHPh$_2$, (mesityl)P=CPh$_2$ (+some phosphine oxide) and a platinum complex tentatively identified as *trans*-[PtCl$_2$(PEt$_3$)(dbu)], (IV), since the same product was obtained directly from [Pt$_2$Cl$_4$(PEt$_3$)$_2$] and dbu. In the presence of small amounts of moisture the complex hydro - 1,5 - diazabicyclo - [5,4,0] - undec - 1 - ene trichloro(triethylphosphine) platinate(II), [[dbuH] [PtCl$_3$·(PEt$_3$)]], is also formed.

Displacement of coordinated cyclo-octadiene (COD) from [PtX$_2$(COD)], (X=Cl, I, Me) by

$$[\mathrm{PtX_2(COD)}] \rightarrow cis\text{-}[\mathrm{PtX_2\{(mesityl)P{=}CPh_2\}_2}]$$

(mesityl)P=CPh$_2$ readily afforded the corresponding phospha-alkene complexes *cis*-[PtX$_2${(mesityl)P=CPh$_2$}$_2$], (X=Cl, (V), X=I, (VI) and X=Me (VII)). The ^{31}P{^{1}H} NMR spectra of these complexes were simple "triplet" patterns as expected. Coupling constant data are listed in Table 2 the values of ^{1}J(PtP) being typical for *cis*-[PtX$_2$P$_2$] complexes.

^{1}J(PtP) for *cis*-[PtCl$_2${(mesityl)P=CPh$_2$}$_2$], (V), (3950 Hz) is slightly greater than the value found in *cis*-[PtCl$_2$(PEt$_3$)$_2$], (3250 Hz), and much larger than that in *trans*-[PtCl$_2$(PEt$_3$)$_2$], (2500 Hz). The *cis*-geometry in (V) is also confirmed by the observation of two ν(Pt–Cl) stretching bands at 320 and 298 cm^{-1} in the IR spectrum. Substitution of chloride by iodide to form *cis*-[PtI$_2${(mesityl)R=CPh$_2$}$_2$] (VI), results in an increase in ^{1}J(PtP) (4009 Hz) consistent with the poorer *trans*-influence of iodide. The *cis*-geometry for (VII), [PtMe$_2${(mesityl)P=CPh$_2$}$_2$], is inferred by the very small value of ^{1}J(PtP) (1816 Hz) (see ^{1}J(PtP) for *cis*-[PtMe$_2$(PEt$_3$)$_2$], 1856 Hz). Bands at 550 and 522 cm^{-1} in the IR spectrum of (VII) are assigned to Pt–C stretching modes.

The magnitude of ^{1}J(PtP) in phosphine complexes of platinum is given by the expression[8]

$$^1\mathrm{J(PtP)} = \gamma_P\gamma_{Pt}\frac{h}{2\pi}\frac{256\pi^2}{9}\beta^2\frac{a^2(1-a^2)\alpha_P{}^2}{n} \times \frac{|S_P(O)|^2|S_{Pt}(O)|^2}{^3\Delta E}$$

where γ_X is the magnetogyric ratio of nucleus X, $S_X(O)^2$ is the s-electron density of X evaluated at the nucleus, $\alpha_P{}^2$ is the s-character of the phosphorus lone pair orbital, a^2 is the s-character of the metal hybrid orbital, n is the number of ligands and $^3\Delta E$ is an average triplet excitation energy. Changes in the magnitude of ^{1}J(PtP) within a series of platinum-phosphine complexes are largely dependent on changes in $|S(O)|^2$ and $\alpha_P{}^2$.

Inspection of the coupling constant data in Tables 1 and 2 indicates that in complexes in which the (mesityl)P=CPh$_2$ is *trans* to a ligand of weak *trans* influence (e.g. in *cis*-[PtX$_2$L$_2$], X=Cl, I or *cis*-[PtCl$_2$L(PEt$_2$)]), the values of ^{1}J$_{(PtP)}$ for (mesityl)P=CPh$_2$ are larger than those of PR$_3$ (or PAr$_3$) but lower than those of P(OR)$_3$ or PX$_3$ (X = halogen).

The former can be readily interpreted in terms of the greater s-character of the lone pair of (mesityl)P=CPh$_2$ (sp^2) compared with PR$_3$ (sp^3), which produces a larger $\alpha_P{}^2$ term in the equation for ^{1}J(PtP). The s-character of the lone pair of PF$_3$, however, has been calculated to be *ca.* 35%[9] approximately the same as that expected for an sp^2 hybrid. Since ^{1}J$_{(PtP)}$ for PF$_3$ complexes, and those of

Table 2. ^{31}P NMR data for some *cis*-[PtX$_2$L$_2$] complexes (X-Cl, Me)

L	^{1}J(PtP)^a	^{1}J$_{(PtCH_3)}$^{a}	Ref
X = Cl			
PF$_3$	6462	-	22
P(OPh)$_3$	5793	-	23
(Mesityl) P = CPh$_2$	3950	-	This work
PPh$_3$	3684	-	8
PBuPh$_2$	3641	-	24
PBu$_2$Ph	3551	-	24
PBu$_3$	3500	-	24
PEt$_3$	3520	-	10
X = Me			
PPh$_2$Me	1851	68.0	25
PEt$_3$	1855	67.6	10
(mesityl) P = CPh$_2$	1816	75.0	This work

[a] In Hz.

$P(OR)_3$ where the lower electronegativity of the substituents reduces the s-character of the lone pair, are larger than those of (mesityl)P=CPh_2 it appears that the charge on phosphorus, and hence the $|\Psi_{S(P)}(O)|^2$ term also plays an important part in determining $^1J_{(PtP)}$.

In complexes where (mesityl)P=CPh_2 is *trans* to a ligand of high *trans*-influence (e.g. Me, PR_3) the magnitude of $^1J_{(PtP)}$ falls below those of the analogous PR_3 complexes. This would indicate that (mesityl)P=CPh_2 has a lower *trans* influence than PR_3, in line with their relative donor properties.[10,11]

Some support for this view comes from consideration of the Pt–Cl stretching frequencies in the complexes *cis*-$[PtCl_2L_2]$ and the magnitudes of $^2J_{(PtCH_3)}$ in the complexes *cis*-$[PtMe_2L_2]$. For *cis*-$[PtCl_2L_2]$ complexes the average νPt–Cl stretching frequency (in cm^{-1}) increases along the series:

$$L{=}PEt_3(294) < PPh_3(305) \sim \{(\text{mesityl})P{=}CPh_2\}(309) < P(OPh_3)(322) < COD(327);$$

which is the *opposite* order of the *trans*-influence of these ligands. Likewise $^2J_{(PtCH_3)}$ (Hz) in the complexes *cis*-$[PtMe_2L_2]$ show a similar behaviour viz.

$$L{=}PEt_3(67.6) < PPh_3(69) < \{(\text{mesityl})P{=}CPh_2\}(75) < COD(83.4).$$

SINGLE CRYSTAL X-RAY STUDIES

The results of a single-crystal X-ray analysis of the chloroform solvate of *cis*-$[PtCl_2(PEt_3)L]$, {L =(mesityl)P=CPh_2}, (II), are presented in Fig. 3 and in Table 3. Together with those recently reported for $[Cr(CO)_5L]$[12] they permit a tentative discussion of the nature of the bonding in L and of its properties as a ligand.

In both metal complexes L behaves as a mono-dentate P-donor ligand. The significant structural features of L in the two complexes are broadly similar and they are fully compatible with the proposed formulation of L as a phosphalkene with a localised P=C bond.[5] In the chromium complex the central CrCP=CC_2 skeleton deviates only slightly from planarity—the Cr–P=C–C(Ph) and C(mesityl)–P=C–C(Ph) torsion angles are 3 and 6°, respectively, whereas in the platinum complex the corresponding torsion angles are 12 and 22°. The greater distortions from planarity in the platinum complex arise both from slight deviations from planarity of the bonds radiating from P(1) and C(1) but also (and more seriously) from a twisting of the two coordination planes by *ca.* 17° about the P=C bond (see Table 3c). However, the P(1)–C(1) and P(1)–C(1C) bond lengths [1.660(9) and 1.794(10) Å] do not differ significantly from the corresponding values in the chromium complex [1.679(4) and 1.822(5) Å]. Valency angles at the donor phosphorus atom also show nearly identical distortions from an ideal trigonal-planar arrangement: in the platinum complex the C–P–C angle of 112.5(5)° is narrowed at the expense of the Pt–P–C angle of 127.5(3)° [see 109.8(2) and 130.8(2)° for corresponding angles in the chromium compound]. An implication of these narrow C–P–C angles is that the phosphorus lone pair has more s-character than would be expected from ideal sp^2-hybridisation; a not unexpected conclusion since the lone pair of a monotertiary phosphine is usually thought to have more s-character than would be expected from sp^3-hybridisation in view of the tendency for C–P–C angles in phosphine complexes to be less than 109.5° and M–P–C angles to be greater. In

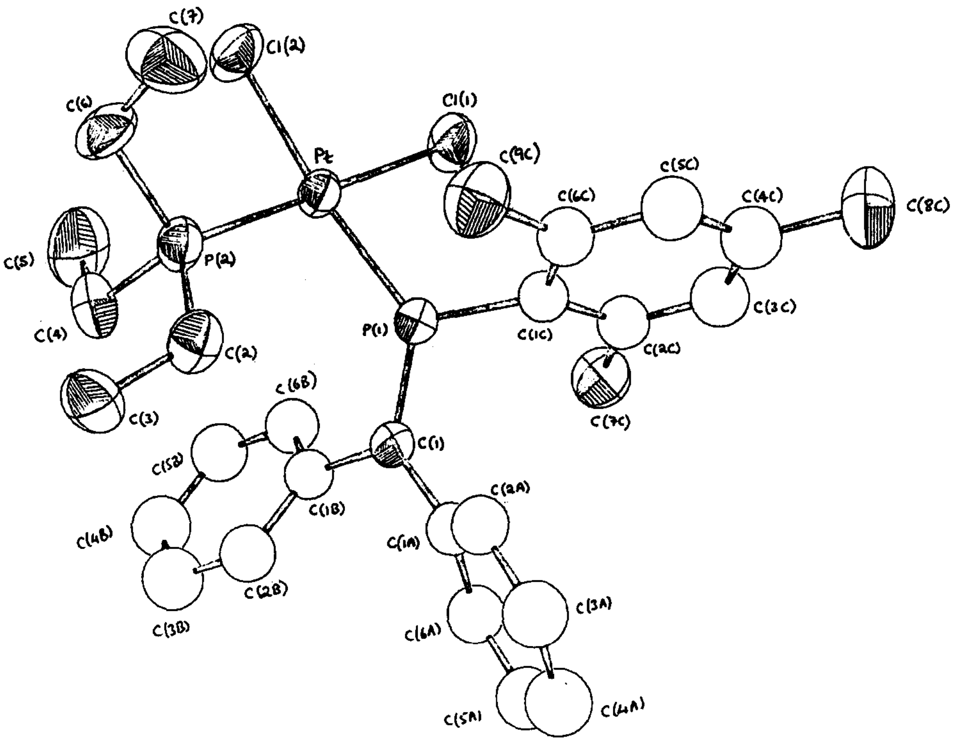

Fig. 3. A perspective view of the *cis*-$[PtCl_2(PEt_3)(C_6H_2Me_3P{=}CPh_2)]$ molecule showing the atom numbering and 50% probability ellipsoids. Anisotropic vibrational parameters were used only for shaded atoms.

Table 3. Selected distances (Å) and angles (°) in *cis*-[PtCl$_2$(PEt$_3$)(C$_6$H$_2$Me$_3$P=CPh$_2$)]

(a) Bond lengths			
Pt-Cl(1)	2.358(3)	C(4)-C(5)	1.51(2)
Pt-Cl(2)	2.335(3)	C(6)-C(7)	1.49(2)
Pt-P(1)	2.199(2)	C(1C)-C(2C)	1.42(2)
Pt-P(2)	2.256(3)	C(2C)-C(3C)	1.35(2)
P(1)-C(1)	1.660(9)	C(3C)-C(4C)	1.43(2)
P(1)-C(1C)	1.794(10)	C(4C)-C(5C)	1.38(2)
P(2)-C(2)	1.821(12)	C(5C)-C(6C)	1.39(2)
P(2)-C(4)	1.828(12)	C(6C)-C(1C)	1.41(2)
P(2)-C(6)	1.843(12)	C(2C)-C(7C)	1.53(2)
C(1)-C(1A)	1.50(2)	C(4C)-C(8C)	1.50(2)
C(1)-C(1B)	1.49(2)	C(6C)-C(9C)	1.52(2)
C(2)-C(3)	1.53(2)		
(b) Bond angles			
Cl(1)-Pt-Cl(2)	88.7(1)	Pt-P(1)-C(1)	127.5(3)
Cl(1)-Pt-P(1)	85.2(1)	Pt-P(1)-C(1C)	119.8(3)
Cl(2)-Pt-P(2)	89.6(1)	C(1)-P(1)-C(1C)	112.5(5)
P(1)-Pt-P(2)	96.6(1)	P(1)-C(1)-C(1A)	122.0(7)
Cl(1)-Pt-P(2)	177.9(1)	P(1)-C(1)-C(1B)	119.9(6)
Cl(2)-Pt-P(1)	173.4(1)	C(1A)-C(1)-C(1B)	117.9(7)
Pt-P(2)-C	111.9(4)-116.2(4)	P(2)-C-C	115(1) -117(1)
C-P(2)-C	103.8(5)-106.6(5)	At C(aromatic)	118(1) -122(1)
(c) Torsion angles			
Pt-P(2)-C(2)-C(3)	-166(1)	P(2)-Pt-P(1)-C(1)	53.7(5)
Pt-P(2)-C(4)-C(5)	-50(1)	Pt-P(1)-C(1)-C(1A)	-163(1)
Pt-P(2)-C(6)-C(7)	-56(1)	Pt-P(1)-C(1)-C(1B)	12(1)
P(1)-Pt-P(2)-C(2)	18.1(4)	C(1C)-P(1)-C(1)-C(1A)	22(1)

the platinum complex the olefinic carbon atom C(1) subtends valency angles which are all within 2 of 120°. In the chromium complex the corresponding angles are more variable with the C(Ph)–C–C(Ph) angles being narrowed to 114.8(4)°. The differences in the planarity of the central skeleton of L and in the valency angles at the olefinic carbon atom found between the platinum and chromium complexes probably have a steric origin. In the chromium complex the mesityl ring makes an angle of 81° to the central CrCP=CC$_2$ plane whereas the corresponding value in the platinum complex is 67°. The phenyl rings are tilted at 70 and 37° to the central plane in the chromium complex whereas the corresponding values are 47 and 51° in the platinum complex.

The Pt–PEt$_3$ and *trans* Pt–Cl (1) bond lengths of 2.256(3) and 2.358(3) Å are normal, being virtually identical to the mean values of 2.258(2) and 2.361(6) Å found in *cis*-[PtCl$_2$(PEt$_3$)$_2$].[13] These values may be compared with the Pt–P(1) and *trans* Pt–Cl(2) bond lengths of 2.199(2) and 2.335(3) Å. Differences in the nature of the phosphorus hybridisation would be expected to cause some shortening of the Pt–P(1) distance relative to the Pt–P(2) distance. This shortening is accompanied by a slight but detectable diminution of *trans*-influence as judged by the Pt–Cl bond lengths. The different *trans*-influences of the two P-donor ligands may reflect the different types of phosphorus hybridisation, although we have previously[14] shown that the *trans*-influences of C-donor ligands on Pt–Cl bond lengths are insensitive to the state of hybridisation of the donor carbon atom, a result in accord with current theories of σ-*trans*-influence. An alternative explanation for the slightly lower *trans*-influence of L relative to PEt$_3$ would be that L is a slightly better π-acceptor. This conclusion contrasts somewhat with the suggestion, based on the structural results for [Cr(CO)$_5$L], that L has fairly strong π-acid properties relative to other P-donor ligands.[12]

Whatever view is taken of the relative importance of σ- and π-effects in determining the platinum-ligand bond lengths in *cis*-[PtCl$_2$(PEt$_3$)L] it is interesting to note that the Pt–P and Pt–Cl distances are in accord with our previous discussion of bond lengths in complexes with *cis*-[PtCl$_2$P$_2$] donor sets.[13] The Pt–P(1) bond length is shorter than the Pt–P(2) bond length by 0.06 Å and as expected the *trans* Pt–Cl bond length is also shorter, but by roughly half this amount. Since the bond length variations can be related empirically to the electron-withdrawing of the P-donor ligand, in the sense defined by Tolman,[15] it would appear that L can be compared with P(OPh)$_3$ in terms of electron-withdrawing ability and *trans*-influence.

EXPERIMENTAL

All manipulations were carried out under an atmosphere of dry nitrogen gas or *in vacuo*. Solvents were dried by standard methods and freshly distilled before use and degassed by the repeated freeze–thaw method. ^{31}P NMR spectra were obtained using a JEOL PFT 100 Fourier transform spectrometer operating at 40.49 MHz with broad band noise irradiation at 99.9984 MHz to decouple ^{1}H. Chemical shifts are quoted relative to H_3PO_4 with downfield positive. ^{1}H NMR spectra were recorded on Varian T60 or Varian EM360 instruments. IR spectra in the range 4000–250 cm^{-1} were recorded on a Perkin-Elmer 457 grating spectrometer. Elemental analyses were obtained by Mr. and Mrs. A. G. Olney of this laboratory.

(Mesityl)P=CPh$_2$ was prepared by a modification of the method of Ref. 3. It was imperative to dry dbu which is very hygroscopic. This was best done by adding benzene, removing the C_6H_6/H_2O azeotrope followed by distillation and storage under dry nitrogen over fresh 4 Å molecular sieve. The following platinum complexes were prepared by standard procedures, [PtCl$_2$(COD)],[16] [PtMe$_2$(COD)][16] and [Pt$_2$Cl$_4$(PEt$_3$)$_2$].[17]

Reaction of (*mesityl*)P=CPh$_2$ *with* [Pt$_2$Cl$_4$(PEt$_3$)$_2$]

(i) [Pt$_2$Cl$_4$(PEt$_3$)$_2$] (0.153 g, 0.2 mmol) in 5 cm^3 of CH$_2$Cl$_2$ was stirred for 1 hr at R.T. with (mesityl)P=CPh$_2$ (0.15 g, 0.474 mmol) to produce a solution of *trans dichloro* (*triethyl phosphine*) (*P-mesityl diphenylmethylene phosphine*)*platinum*(*II*), (I), ^{31}P δ_p 186.9 (d of t, $^1J_{(PtP)} = 2590$ Hz), 14.7 (d of t, $^1J_{(PtP)} = 2844$ Hz), $^2J_{(PP')} = 544$ Hz. Removal of solvent produced a yellow oil which was stirred with hexane to produce the *cis* isomer, (II), as a pale yellow solid. m.p. 210–212°. Found, C, 47.7; H, 5.2; $C_{28}H_{36}P_2Cl_2Pt$ requires C, 48.00; H, 5.18%. IR (KBr) 2970(m), 2940(m, br), 1650(m), 1605(m), 1490(m), 1450(s), 1410(m), 1380(m), 1260(w), 1075(w), 1035(s), 920(w, br), 890(w), 850(w), 800(w, br), 765(s), 759(s), 740(m), 695(s), 555(s), 461(m), 420(m), 315(m), 290(m) cm^{-1}. ^{1}H δ 0.8–3.0(m, 24H), 6.8–8.0(m, 12H). ^{31}P δp 149 (d of t, $^1J_{(PtP)} = 4294$ Hz); 8.6 (d of t, $^1J_{(PtP)} = 3269$ Hz), $^2J_{(PP')} = 23$ Hz. A crystalline sample suitable for the x-ray diffraction study was obtained by recrystallisation from chloroform/hexane.

(ii) As above with THF as solvent. ^{31}P NMR spectrum revealed both *cis* and *trans* isomers. IR (KBr) was identical to the *cis* isomer above except for an extra ν(Pt–Cl) band at 335(m) cm^{-1}.

(iii) As in (i) above, except the phosphine was contaminated with dbu. Crystallisation from CH$_2$Cl$_2$/hexane yielded hydro - 1,5 - diazabicyclo[5,4,0] - undec - 1 - ene trichloro(triethylphosphine)platinate(II), (DBUH)(PtCl$_3$(PEt$_3$)] as yellow plates, m.p. 117–120°. Found C, 31.5; H, 6.0; N, 4.8; $C_{14}H_{30}N_2PCl_3Pt$ requires C, 31.51; H, 5.58; N, 4.91%. IR (KBr) 3270(s), 3140(w), 2935(m), 1645(s), 1580(m), 1105(w), 1039(w), 980(w), 780(s), 750(w), 728(w), 330(m). ^{1}H 3.8–1.0(m). ^{31}P δ_p10 (t, $^1J_{(PtP)} = 3747$ Hz). (Lit. for [Et$_4$N](PtCl$_3$(PEt$_3$) 3704 Hz.[19]

Reaction of [Pt$_2$Cl$_4$(PEt$_3$)$_2$] *with mesityl* (CHPh$_2$)PCl

[Pt$_2$Cl$_4$(PEt$_3$)$_2$] (0.187 g, 0.243 mmol) in 5 cm^3 of CH$_2$Cl$_2$ was stirred at R.T. with mesityl (CHPh$_2$)PCl (0.18 g, ≃ 0.51 mmol) for 2 hr. Removal of solvent yielded a yellow solid which was washed with 2 cm^3 of hexane, identified as *trans dichloro* (*triethylphosphine*)(*mesityl*(*diphenylmethyl*)*chlorophosphine platinum*(*II*), (III), by ^{31}P NMR spectroscopy. ^{31}P δ_p 102.8 (d of t, $^1J_{(PtP)} = 2539$ Hz); 15.2 (d of t, 2647 Hz), $^2J_{(PP')} = 547$ Hz.

Reaction of trans-[PtCl$_2$(PEt$_3$)[PCl(CHPh$_2$)(*mesityl*)]] *with dbu*

Trans-[PtCl$_2$(PEt$_3$)[PCl(CHPh$_2$)(mesityl)] (0.15 g, 0.204 mmol) in 1 cm^3 of THF was stirred with dbu (0.03 g, 0.2 mmol) for 2 hr with the formation of a white precipitate. The ^{31}P NMR spectrum of the reaction mixture showed δ_p 235(s), 131(s), 120(s), 85(s), and (IV) 0.0 (t, $^1J_{(PtP)} = 3340$ Hz).

Reaction of [Pt$_2$Cl$_4$(PEt$_3$)$_2$] *with dbu*

[Pt$_2$Cl$_4$(PEt$_3$)$_2$] (0.05 g, 0.065 mmol) in 1 cm^3 of CH$_2$Cl$_2$ was stirred with a few drops (excess) of dbu to yield *trans dichloro*(*triethylphosphine*)(1,4 - *diazabicyclo trans* - *unde* - 1 - *ene*) *platinum*(*II*), δ_p 0.1 (t $^1J_{(PtP)}$ 3272 Hz).

Reaction of (*mesityl*)P=CPh$_2$ *with* PtX$_2$ (COD), (X=Cl, I)

[PtCl$_2$(COD)] (0.04 g, 0.11 mmol) in 2 cm^3 of CH$_2$Cl$_2$ was stirred overnight with (mesityl)P=CPh$_2$ (0.095 g, 0.3 mmol). The initial colourless solution became yellow and yielded a yellow oil on removal of solvent. This was washed with 2 × 2 cm^3 of Et$_2$O and recrystallised from CH$_2$Cl$_2$/pentane to produce *cis dichloro di*(*P-mesityldiphenylmethylene phosphine*) *platinum*(*II*), (V), m.p. 230–233°. Found C, 55.9; H, 4.7; $C_{40}H_{42}P_2Cl_2Pt$ requires C, 58.80; H, 4.71%. IR (KBr) 2910(w), 1602(m), 1489(m), 1445(s), 920(w), 892(w), 853(w), 761(s), 691(s), 637(m), 600(m), 558(s), 530(w), 451(m), 425(m), 320(m), 298(m). ^{1}H δ 2.2(s, 3H), 2.45(s, 6H), 6.5–7.8(m, 12H). ^{31}P δ_p 131.5 (t, $^1J_{(PtP)} = 3950$ Hz).

Similarly PtI$_2$(COD) gave (VI), δ_p 138.9 (t, $^1J_{(PtP)} = 4009$ Hz).

Reaction of (*mesityl*)P=CPh$_2$ *with* [PtMe$_2$(COD)]

(Mesityl)P=CPh$_2$ (0.095 g, 0.3 mmol) in 2 cm^3 to toluene was stirred with [PtMe$_2$(COD)] (0.038 g, 0.12 mmol) for 2 hr. The initial colourless solution became yellow, which yielded a yellow oil on removal of solvent. This was washed with 2 cm^3 of pentane to produce *cis dimethyl di*(*P-mesityl diphenylmethylenephosphine*)*platinum*(*II*), (VII), which could not be isolated analytically pure and was identified by NMR spectroscopy. m.p. 205–208°. IR (KBr) 2920(m, br), 1645(m), 1608(m), 1495(m), 1485(m), 1445(m), 1250(m, br), 1975(w), 1030(w), 910(w, br), 845(m), 755(s), 690(s), 630(s), 600(w), 550(m), 522(m, br), 435(m). ^{1}H δ 0.8 (t, $^2J_{(PtCH_3)} = 75$ Hz), 2.35(s, 3H), 2.4(s, 6H), 6.8–7.8(m, 12H). ^{31}P δ_p 208.1 (t, $^1J_{(PtP)} = 1816$ Hz).

X-Ray structure analysis of cis-[PtCl$_2$(PEt$_3$)(C$_6$H$_2$Me$_3$P=CPh$_2$)]·CHCl$_3$

Crystal data. $C_{28}H_{36}Cl_2P_2Pt \cdot CHCl_3$, $M = 819.9$, monoclinic, $a = 10.904(2)$, $b = 14.351(4)$, $c = 21.560(4)$ Å, $\beta = 91.01(2)°$, $U = 3373$ Å, $Z = 4$, $D_c = 1.614$ g cm^{-3}, F(000) = 1615.8, space group P2$_1$/n, Mo-K$_\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 44.6$ cm^{-1}.

Measurements. The unit cell dimensions and the intensities of all independent reflections with θ(Mo-K$_\alpha$) < 28° were determined by standard experimental methods using an Enraf-Nonius CAD4F diffractometer equipped with a graphite monochromator. Corrections were applied for Lorentz, polarization, crystal decomposition, and absorption effects. The wide variation in the calculated transmission factors (0.19–0.96) is a consequence of the platy morphology of the specimen, which measured 0.94 × 0.25 × 0.08 mm. 4585 Reflections with I ≥ 3σ(I) were used in the subsequent analysis.

Structure analysis. The structure was solved by the heavy-atom method and the atomic parameters were refined by full-matrix least-squares. In the final calculations contributions for geometrically-positioned hydrogen atoms were included in the structure factors and phenyl rings A and B were constrained to be hexagons of side 1.395 Å. Anisotropic temperature factors were assigned to all atoms except the 18 phenyl ring carbon atoms and the hydrogen atoms. The refinement converged at R 0.050 and R$_w$ 0.068. Function values in the final difference synthesis did not exceed 1.0 eÅ^{-3} except close to the platinum atom. Final atomic coordinates and a list of F_0/F_c values have been deposited with the Editor as supplementary material.† Atomic scattering factors and anomalous dispersion corrections were taken from Ref. 17.

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†Copies are available, on request from the Editor at Queen Mary College. Atomic co-ordinates have also been deposited with the Cambridge Crystallographic Data Centre.

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