Base-Induced Coupling of Acetylenes Held Proximate to a Metal: Structures of Unsymmetrical Diphosphine Complexes of Platinum(II) Containing Strong Vinyl Alcohol–Amine Hydrogen Bonds

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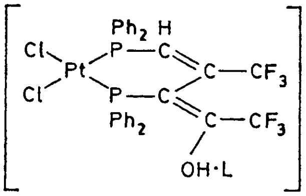
The complexes *cis*-[Pt(Cl$_2$)Y]·L [where Y = diphosphine Ph$_2$P·CH:C(CF$_3$)·C(PPh$_2$):C(OH)·CF$_3$; L = Et$_2$NH, Et$_3$N, Me$_3$N, or Pr$_3$N] have been synthesised by base-promoted coupling of phosphinoacetylene ligands in the complex *cis*-[PtCl$_2$(Ph$_2$PC:CCF$_3$)$_2$], and characterised by microanalysis, i.r. spectroscopy, and a single-crystal *X*-ray diffraction study of the diethylamine derivative (II). Crystals of (II) are monoclinic, space group $P2_1/n$, a = 18.707(13), b = 11.102(18), c = 19.383(13) Å, β = 111.48(10)°, D_m = 1.60 g cm^{-3}, Z = 4, D_c = 1.618 g cm^{-3}. The structure was solved by conventional heavy-atom methods and refined to R 0.065 for 3 384 observed diffractometer intensity data. The molecule contains an unsymmetrical diphosphine ligand formed *via* dimerisation of two alkyne fragments. The molecule of diethylamine is strongly hydrogen bonded to the oxygen atom of a vinyl alcohol moiety in the diphosphine ligand [N···O 2.74(2) Å]. Relevant metal–ligand distances are: Pt–Cl(1) 2.367(5), Pt–Cl(2) 2.357(5), Pt–P(1) 2.248(4), and Pt–P(2) 2.202(5) Å. The i.r. spectra of all four complexes are similar and characteristic of hydrogen-bonded systems with predominantly ion-pair C–$\bar{\mathrm{O}}$···H–$\overset{+}{\mathrm{N}}$(H)Et$_2$ character.

THE coupling of heteroatom-substituted alkynes *via* electrophilic or nucleophilic attack on triple bonds held proximate to one another in a *cis*-square or octahedral complex has attractive synthetic potential.

We report the facile synthesis of amine adducts of the diphosphine complex *cis*-$[PtCl_2Y]$ [where Y = $PPh_2{\cdot}CH{:}C(CF_3){\cdot}C(PPh_2){:}C(OH){\cdot}CF_3$] *via* base-promoted coupling of the unco-ordinated triple bonds in (I), *cis*-$[PtCl_2(Ph_2PC{:}CCF_3)_2]$. I.r. measurements and a single-crystal *X*-ray diffraction study of (II), the diethylamine addition complex, have revealed that these complexes contain hydrogen-bonded ion pairs derived from a vinyl alcohol and the nitrogen base. The complexes also provide an insight into the mechanism previously postulated to explain the synthesis of diphosphine complexes of the type $[MCl_2(Ph_2P{\cdot}CH{:}C(CF_3){\cdot}CH_2{\cdot}PPh_2)]$ [1,2] *via* hydrolysis of *cis*-$[MCl_2(Ph_2P{\cdot}C{:}C{\cdot}CF_3)_2]$ (M = Pd or Pt).



(II) L = Et_2NH
(III) L = Et_3N
(IV) L = Pr_3N
(V) L = Me_3N

EXPERIMENTAL

The complex *cis*-$[PtCl_2(Ph_2PC{:}CCF_3)_2]$ (I) was prepared as previously described.[2]

Synthesis of Amine Addition Complexes.—Complexes (II)—(IV) were prepared by adding the amine (0.5 mmol) to an ice cold solution of (I) (0.41 g, 0.5 mmol) in reagent-grade chloroform (30 cm^3). The almost colourless solution became lemon yellow over a period of several hours. The volume of solvent was reduced to a few cm^3, diethyl ether (5 cm^3) added, and crystals of the complexes obtained when the solution was set aside. In the synthesis of the analogous trimethylamine complex (V), a stream of gaseous trimethylamine was passed for several minutes through the solution of (I) giving a yellow solution which was treated as before. Microanalytical data for the complexes are listed in Table 1.

TABLE 1

Microanalytical data and i.r. spectra (cm^{-1}) in the ν(N–H), ν(O–H), ν(C=O), and ν(Pt–Cl) regions

		Analyses (%)											
		Found				Calc.							
L	Complex	C	H	N	P	C	H	N	P	ν(O–H···N)	$\nu(\bar{O}\cdots H\overset{+}{N})$	ν(C=O)	ν(Pt–Cl)
Et_2NH *	(II)	44.65	3.55		6.65	44.70	3.64		6.78	3 044s	2 766m, br, 2 492w, br, 2 384vw, br	1 577m, sh, 1 550vs, br	308m, 285m
Me_3N	(V)	43.8	3.45	1.65	6.7	44.04	3.50	1.56	6.88	3 075sh, 3 044s	2 720sh, 2 665m, br, 2 520sh, 2 450m, br	1 572m, 1 542vs, br	302m, 279m
Et_3N	(III)	46.05	4.05	1.6	6.05	45.90	3.99	1.48	6.58	3 059s	2 722m, br, 2 500w, br, 2 760w, br, 2 600m, br	1 572m, 1 540vs, br	307m, 280m
Pr_3N	(IV)	47.5	4.5	1.6	6.2	47.62	4.41	1.42	6.50	3 058s	2 760w, br, 2 660m, br, 2 538w, br	1 572m, 1 546vs, br	308m, 285m

* %Cl: Found 7.70; Calc. 7.76. w = weak, m = medium, s = strong, br = broad, sh = shoulder, v = very.

I.r. spectra were measured as Nujol and halogenocarbon mulls between caesium iodide plates on a Perkin-Elmer 180 instrument.

Platelike crystals of the diethylamine complex (II), were obtained on recrystallisation from acetonitrile. Preliminary Weissenberg and precession photographs established the space group. Accurate unit-cell parameters were refined from the 2θ values for 21 reflections measured on a General Electric XRD 6 Datex-automated diffractometer.

Crystal Data.—$C_{34}H_{33}Cl_2F_6NOP_2Pt$, $M = 913.58$, Monoclinic, $a = 18.707(13)$, $b = 11.102(18)$, $c = 19.383(13)$ Å, $\beta = 111.48(10)°$, $U = 3\,745.9$ Å^3, D_m (flotation) = 1.60 g cm^{-3}, $Z = 4$, $D_c = 1.618$ g cm^{-3}, $F(000) = 1\,792$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 42.3 cm^{-1}. Space group $P2_1/n$.

Both because absorption should not substantially affect atom positions and because the maximum variation in any F_o was estimated to be ±10%, no absorption correction was applied.

Intensity Data Collection and Reduction.—A crystal of dimensions 0.20 × 0.25 × 0.07 mm was mounted with b^* parallel to the ϕ axis of a General Electric XRD 6 automatic diffractometer equipped with scintillation counter and pulse-height analyser. Zirconium filtered Mo-K_α radiation was employed with the θ—2θ scan width determined by the equation $\Delta\theta = \pm(0.9 + 0.43 \tan\theta)$ and with a scan rate of 2° min^{-1}. Background counts of 10 s were measured before and after each scan. The intensities of the three standard reflections, monitored every 100 reflections, diminished 10% during data collection and were used to scale the data to a common level. Of 6 593 independent reflections measured ($2\theta \leqslant 50°$), 3 384 with intensities $> 2.5\sigma$ were considered observed and used for the structure determination. Lorentz and polarisation factors were applied to the derivation of structure amplitudes.

Structure Solution and Refinement.—The non-hydrogen atoms were found by standard heavy-atom methods. With all atoms having isotropic temperature coefficients, the structure was refined by full-matrix least-squares methods to *R* 0.121. Scattering factors used, including anomalous dispersion corrections for platinum, were taken from ref. 3. Conversion to anisotropic temperature factors followed by two further cycles of refinement reduced *R* to 0.069. An empirical weighting scheme of the form $w^{-1} = 1.7132 -$

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[1] R. T. Simpson, S. E. Jacobson, A. J. Carty, M. Mathew, and G. J. Palenik, *J.C.S. Chem. Comm.*, 1973, 388.

[2] A. J. Carty, S. E. Jacobson, R. T. Simpson, and N. J. Taylor, *J. Amer. Chem. Soc.*, 1975, **97**, 7254.

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

$0.0170|F| + 0.001|F|^2$ was introduced to obtain constant errors in the different ranges of $|F_o|$ values. Final refinement gave convergence at an R value of 0.065 with R', the weighted residual, of 0.076. A final difference Fourier revealed no significant electron density except in the region of the heavy atom ' ripple.' All calculations were carried out in the University of Waterloo Computing Centre on an IBM 360 model 75 system. Locally modified versions of least squares (Doedens and Ibers) , Fourier (Zalkin), and Ranger (Corfield) programmes were used. The plotting programme ORTEP II (Johnson) was used for perspective views of the molecular structure. Other programmes were originally developed at Waterloo. Final positional parameters are listed in Table 2. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 21707 (21 pp., 1 microfiche).*

TABLE 2

Atomic co-ordinates (fractional × 10^4)

	x	*y*	*z*
Pt	4 214.7(4)	1 898.1(6)	1 257.5(4)
Cl(1)	3 234(3)	1 998(5)	67(2)
Cl(2)	4 769(3)	3 629(4)	956(2)
P(1)	5 238(2)	1 729(4)	2 320(2)
P(2)	3 694(3)	251(4)	1 500(2)
F(1)	5 133(8)	156(15)	4 307(6)
F(2)	4 012(9)	−521(19)	3 894(8)
F(3)	4 193(14)	1 338(18)	3 874(9)
F(4)	5 222(7)	−1 795(11)	3 553(6)
F(5)	6 353(9)	−1 489(14)	4 299(9)
F(6)	6 160(9)	−2 097(14)	3 203(11)
O	6 565(7)	326(13)	3 463(7)
N	7 971(9)	261(13)	4 598(9)
C(1)	3 817(11)	99(17)	2 465(10)
C(2)	4 496(10)	227(13)	3 003(8)
C(3)	4 472(13)	291(24)	3 769(11)
C(4)	5 202(10)	507(16)	2 891(9)
C(5)	5 886(12)	−43(18)	3 338(9)
C(6)	5 906(13)	−1 357(22)	3 604(12)
C(7)	8 351(12)	561(23)	3 521(11)
C(8)	8 485(13)	−175(19)	4 229(11)
C(9)	8 008(12)	−466(22)	5 273(13)
C(10)	7 553(17)	56(27)	5 692(17)
C(11)	6 048(11)	1 488(18)	2 056(9)
C(12)	6 078(13)	361(23)	1 733(12)
C(13)	6 701(14)	160(27)	1 486(11)
C(14)	7 247(13)	1 057(29)	1 562(14)
C(15)	7 204(17)	2 182(23)	1 880(16)
C(16)	6 571(12)	2 339(19)	2 113(12)
C(21)	5 431(10)	3 069(19)	2 879(9)
C(22)	6 093(12)	3 151(23)	3 496(12)
C(23)	6 245(14)	4 211(22)	3 946(13)
C(24)	5 722(16)	5 122(20)	3 780(12)
C(25)	5 035(13)	5 033(20)	3 159(10)
C(26)	4 885(13)	4 004(18)	2 703(11)
C(31)	2 674(11)	114(17)	1 130(10)
C(32)	2 218(14)	1 061(24)	1 133(14)
C(33)	1 396(11)	892(33)	934(14)
C(34)	1 099(13)	−285(27)	720(14)
C(35)	1 562(14)	−1 218(26)	659(12)
C(36)	2 363(12)	−1 042(26)	875(12)
C(41)	4 115(10)	−1 062(19)	1 211(9)
C(42)	4 167(13)	−993(19)	535(11)
C(43)	4 509(12)	−1 905(21)	293(10)
C(44)	4 832(12)	−2 869(18)	744(13)
C(45)	4 773(13)	−2 961(21)	1 435(13)
C(46)	4 365(12)	−2 033(16)	1 653(11)

RESULTS AND DISCUSSION

Description of the Structure of (II).—The crystal structure consists of discrete molecules. A view of the molecular structure is given in Figure 1 together with the atomic numbering scheme. Figure 2 illustrates the molecular packing. Interatomic distances and angles are detailed in Table 3.

TABLE 3

Bond lengths (Å) and angles (°)

(*a*) Distances

Pt–Cl(1)	2.367(5)	C(4)–C(5)	1.40(3)
Pt–Cl(2)	2.357(5)	C(5)–C(6)	1.54(3)
Pt–P(1)	2.248(4)	C(5)–O	1.27(3)
Pt–P(2)	2.202(5)	C(3)–F(1)	1.30(3)
P(1)–C(4)	1.77(2)	C(3)–F(2)	1.33(3)
P(1)–C(11)	1.79(2)	C(3)–F(3)	1.32(3)
P(1)–C(21)	1.80(2)	C(6)–F(4)	1.34(3)
P(2)–C(1)	1.81(2)	C(6)–F(5)	1.31(3)
P(2)–C(31)	1.78(2)	C(6)–F(6)	1.33(3)
P(2)–C(41)	1.84(2)	N–C(8)	1.47(3)
C(1)–C(2)	1.32(3)	N–C(9)	1.52(3)
C(2)–C(3)	1.50(3)	C(7)–C(8)	1.54(3)
C(2)–C(4)	1.45(3)	C(9)–C(10)	1.49(4)

(*b*) Angles

Cl(1)–Pt–Cl(2)	88.6(1)	P(1)–C(4)–C(2)	120.3(6)
Cl(1)–Pt–P(1)	173.3(1)	P(1)–C(4)–C(5)	119.1(8)
Cl(1)–Pt–P(2)	90.1(1)	C(2)–C(4)–C(5)	120(1)
Cl(2)–Pt–P(1)	89.5(1)	C(4)–C(5)–C(6)	122(1)
Cl(2)–Pt–P(2)	177.9(1)	C(4)–C(5)–O	127.1(9)
P(1)–Pt–P(2)	91.7(1)	C(6)–C(5)–O	110(1)
Pt–P(1)–C(4)	115.0(5)	C(2)–C(3)–F(1)	115.0(9)
Pt–P(1)–C(11)	106.1(6)	C(2)–C(3)–F(2)	113.8(9)
Pt–P(1)–C(21)	113.5(6)	C(2)–C(3)–F(3)	111(1)
C(4)–P(1)–C(11)	107.2(8)	F(1)–C(3)–F(2)	105(1)
C(4)–P(1)–C(21)	107.6(8)	F(1)–C(3)–F(3)	107(1)
C(11)–P(1)–C(21)	107.0(8)	F(2)–C(3)–F(3)	105(1)
Pt–P(2)–C(1)	113.6(6)	C(5)–C(6)–F(4)	114.4(9)
Pt–P(2)–C(31)	118.5(6)	C(5)–C(6)–F(5)	112(1)
Pt–P(2)–C(41)	108.7(5)	C(5)–C(6)–F(6)	111(1)
C(1)–P(2)–C(31)	96.9(8)	F(4)–C(6)–F(5)	105.6(9)
C(1)–P(2)–C(41)	109.6(8)	F(4)–C(6)–F(6)	105.6(9)
C(31)–P(2)–C(41)	109.0(8)	F(5)–C(6)–F(6)	108(1)
P(2)–C(1)–C(2)	121.8(7)	C(7)–C(8)–N	110(1)
C(1)–C(2)–C(3)	115(1)	C(8)–N–C(9)	114(1)
C(1)–C(2)–C(4)	125(1)	N–C(9)–C(10)	114(1)
C(3)–C(2)–C(4)	120(1)		

(*c*) Mean phenyl ring dimensions

	Av. C–C (Å)	Av. C–C–C (°)
Ring 1	1.40(3)	120.0(14)
Ring 2	1.40(3)	120.0(13)
Ring 3	1.41(4)	120.0(15)
Ring 4	1.38(3)	119.9(13)

The platinum atom is co-ordinated in square-planar fashion by two chloride ions and the phosphorus atoms of a chelating diphosphine ligand formed *via* α,β-dimerisation of the original alkynes in (I), *cis*-[$PtCl_2(Ph_2P{\cdot}C{\vdots}C{\cdot}CF_3)_2$]. The Pt–P(2) bond length [2.202(5) Å] is appreciably shorter than Pt–P(1) [2.248(4) Å; $\underset{\sigma}{\triangleq}$ 10], probably for steric reasons. Thus the Pt–P(1)–C(Ph) angles (mean 109.8°) are smaller than the corresponding Pt–P(2)–C(Ph) angles (mean 113.6°) indicating that the phenyl rings on P(1) are forced closer to the metal atom by the substituent on C(4) [C(1) is unsubstituted]. However the mean Pt–P distance (2.225 Å) in the puckered six-membered ring is not significantly different from the Pt–P(*trans* to Cl) bond length in *cis*-[$PtCl_2\{C(PhNCH_2)_2\}(PEt_3)$] [2.234(3) Å] [4] or from the mean [2.237(2) Å] found in a range of platinum(II)–phosphine

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* See Notice to Authors, No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[4] Lj. Manojlović-Muir and K. W. Muir, *J.C.S. Dalton*, 1974, 2427.

complexes.[5] Similarly the Pt–Cl distances in (II) (mean 2.36 Å) compare favourably with values of 2.381(3) Å in *cis*-[$PtCl_2\{C(PhNCH_2)_2\}(PEt_3)$] [4] and a mean of 2.376(5) Å in several other platinum(II) complexes where Cl ligands are *trans* to phosphines.[6] The platinum–ligand bond lengths in (II) are thus consistent with the expected *trans* bond-lengthening influences of Cl and phosphorus.

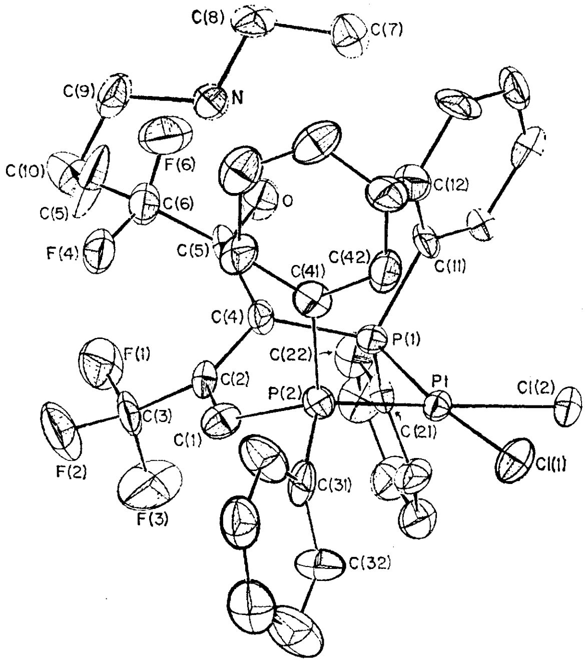

FIGURE 1 A perspective view of the molecular structure of (II) showing the atom numbering. Thermal ellipsoids represent 30% probability

Within the PtP_2C_3 ring, the C(1)–C(2) [1.32(3) Å] and C(2)–C(4) [1.45(3) Å] bond lengths are significantly different and indicative of double and single bonds respectively. For comparison, the standard C(sp^2)–C(sp^2) double bond and single bond lengths are listed as 1.337(6) and 1.53(1) Å respectively.[7] These bond distances imply planar stereochemistry at C(2) and C(4), a fact substantiated by the least-squares planes listed (Table 4) and by the bond angles subtended by adjacent atoms at C(2) (mean 120°) and C(4) (mean 119.8°). The C(4)–C(5) bond length [1.40(3) Å] is considerably shorter than that expected for a carbon–carbon single bond while the C(5)–C(6) distance [1.54(4) Å] is a typical of a single bond.[7] Together with the C(5)–O distance [1.27(3) Å], which is identical to the average carboxylate C–O bond length in zwitterionic amino-acids,[7] these structural parameters suggest that there is some delocalisation over the C(4)–C(5)–O portion of the ligand skeleton. These bond lengths are rather similar to the corresponding distances in the π-vinyl alcohol complex [PtCl(acac)($H_2C{\cdot}CH{\cdot}OH$)] (acac = anion of acetylacetone) [8] where a structure intermediate between that of vinyl alcohol $CH_2{:}CH(OH)$ and acetaldehyde $CH_3{\cdot}CH({:}O)$, albeit co-ordinated, has been suggested. The diethylamine molecule is not co-ordinated to platinum. However, the non-bonded N ··· O distance [2.74(2) Å] is at the lower end of the range for strong O ··· H ··· N hydrogen bonds [9-11]

TABLE 4

Atom displacement (Å) from least-squares planes

Plane (1): Pt 0.222, P(1) 0.080, P(2) −0.422, C(1) 0.271, C(2) 0.219, C(4) −0.369

Plane (2): C(1) 0.021, C(2) −0.058, C(3) 0.017, C(4) 0.020

Plane (3): P(1) 0.019, C(2) 0.024, C(4) −0.067, C(5) 0.024

Plane (4): C(4) −0.025, C(5) 0.068, C(6) −0.019, O −0.025

Plane (5): Pt −0.065, Cl(1) 0.064, Cl(2) −0.032, P(1) 0.066, P(2) −0.032

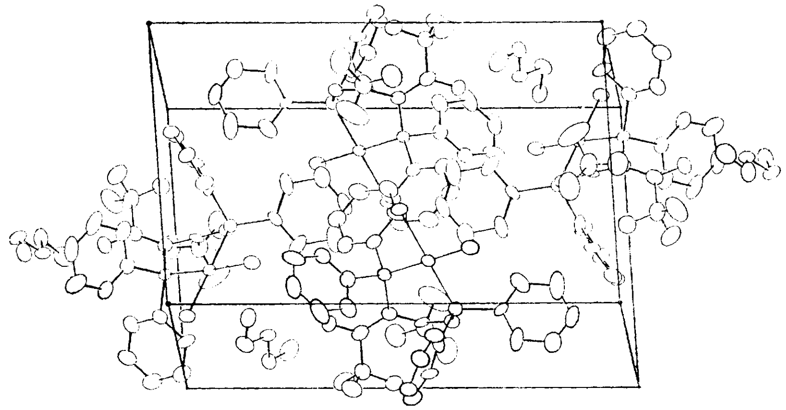

FIGURE 2 Packing diagram illustrating the arrangement of the molecules in the unit cell

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[5] For a compilation of Pt–P distances, see Lj. Manojlović-Muir, K. W. Muir, and R. Walker, *J. Organometallic Chem.*, 1974, **66**, *C*21.

[6] Lj. Manojlović-Muir and K. W. Muir, *Inorg. Chim. Acta*, 1974, **10**, 47.

[7] 'Molecular Structures and Dimensions,' eds. O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Petterson, and W. G. Town, N.V.A. Oosthoek, Utrecht, 1972, vol. *A*1, *S*2.

[8] F. A. Cotton, J. N. Francis, B. A. Frenz, and M. Tsutsui, *J. Amer. Chem. Soc.*, 1973, **95**, 2483.

[9] K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.

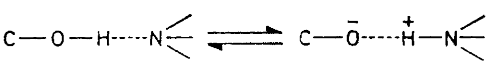
[10] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968.

[11] S. N. Vinogradov and R. H. Linnell, 'Hydrogen Bonding,' Van Nostrand, New York, 1971.

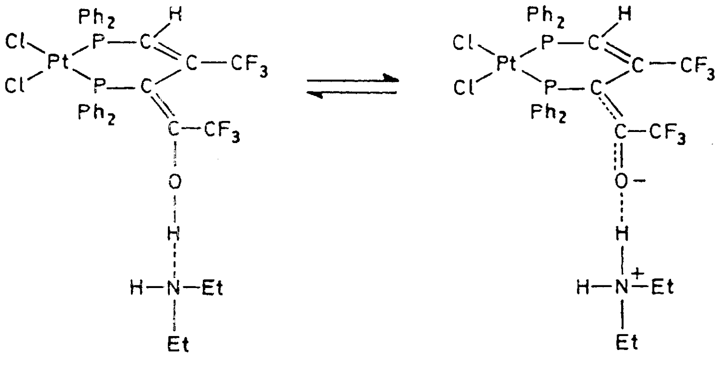
suggesting that the amine plays a vital role in stabilising the co-ordinated phosphine. It is notable that neither diethylamine nor the other amines can be removed from these complexes *in vacuo* or on repeated recrystallisation from acetonitrile. The foregoing structural features reinforce the conclusion that the ligand in the synthesised diphosphine complex is derived from a stabilised vinyl alcohol, 3,5-bis(diphenylphosphino)-1,1,1-trifluoro-4-(trifluoromethyl)penta-2,4-dien-2-ol. The *X*-ray data were not unfortunately of sufficiently high quality to allow unequivocal identification of the hydrogen atom position in the O ··· H ··· N hydrogen bond. The foregoing conclusions are however strongly supported by i.r. data (see below).

There are several other intramolecular non-bonded contacts <3.0 Å, involving fluorine atoms of trifluoromethyl groups (Table 5), but none appear to be structurally significant.

I.r. Spectra.—The i.r. spectra of the amine complexes (II)—(V) in the regions of ν(O-H), ν(N-H), ν(C-O), and ν(Pt-Cl) absorptions are given in Table 1. The spectra of all four compounds are closely similar indicating similar structures. For each complex there are two ν(Pt-Cl) bands between 270—310 cm^{-1} characteristic of *cis*-square-planar stereochemistry[12] and an intense band near 1 550 cm^{-1}, absent in *cis*-$[PtCl_2(Ph_2PC_2CCF_3)_2]$ and the diphosphine complexes $[MCl_2\{Ph_2P{\cdot}CH{:}C(CF_3){\cdot}CH_2{\cdot}PPh_2\}]$. We assign this band to ν(C=O) of the hydrogen-bonded C(5)-O group. The frequency of this band is much lower than for a typical aldehyde or ketone but higher than expected for ν(C-O) of a simple alcohol.[13] This observation is consistent with the *X*-ray data which suggests some double-bond character in the C(5)-O bond.



(A) (B)



(C) (D)

TABLE 6

Intra- and inter-molecular non-bonded contacts

(*a*) Intramolecular distances			
P(1) ··· C(1)	3.31(2)	P(2) ··· C(2)	2.75(1)
P(1) ··· C(2)	2.79(2)	P(2) ··· C(4)	3.12(2)
P(1) ··· C(5)	2.74(2)	O ··· N	2.74(2)
P(1) ··· O	3.08(1)	O ··· C(11)	2.85(2)
(*b*) Intramolecular distances			
Cl(1) ··· N	3.16(2)	F(1) ··· F(5)	2.93(2)
F(1) ··· F(1)	2.93(2)	F(2) ··· F(4)	2.94(2)
F(1) ··· F(2)	3.29(2)	F(5) ··· O	2.71(2)
F(1) ··· F(4)	2.65(2)	F(6) ··· O	2.79(2)

Free diethylamine has ν(N-H) at 3 334 cm^{-1}.[14] There is no absorption band at this frequency in (II). However all four amine derivatives exhibit a medium intensity band close to 3 050 cm^{-1} and two or more bands in the region 2 500—2 800 cm^{-1}. Similar spectra have been observed for various combinations of amine acceptors with alcohol[15] or benzoic acid[16] donors where strong hydrogen-bonding is known to occur. For example i.r. bands at 3 050 cm^{-1} [ν(O-H ··· N)] and at 2 740 and 2 690 cm^{-1} [$\nu(\overset{+}{N}\text{-}H \cdots O)$] are characteristic of hydrogen bonding in the phenol–propylamine complex.[15] The appearance of a band at *ca.* 3 050 cm^{-1} in both the secondary and tertiary amine derivatives described herein strongly suggests that this band is due to ν(O-H ··· N).[15] We assign the bands between 2 400 and 2 800 cm^{-1} to $\nu(\overset{-}{O} \cdots H\text{-}\overset{+}{N})$. Our i.r. results thus suggest that the hydrogen atom in the O ··· H ··· N hydrogen bond lies closer to nitrogen than oxygen, there being a greater contribution from a structure of type (B) than type (A). The disappearance of ν(N-H) of diethylamine in the platinum complex is explicable from the fact that protonated secondary and tertiary amines have ν(N-H) bands substantially <3 000 cm^{-1}. The salt $[Et_3HN]^+[Cl]^-$ for example has an average ν(N-H) frequency of 2 540 cm^{-1}.[17] When considered in conjunction with the i.r. spectral data, the bond lengths,

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angles, and ligand stereochemistry found in the structure determination indicate that the ground-state configuration of the molecule is more closely represented by (D) than by the stabilised vinyl alcohol structure (C).

Finally it should be pointed out that the isolation of the four amine addition complexes confirms the hypothesis[2] that formation of the diphosphine complexes $[MCl_2(Ph_2P{\cdot}CH{:}C(CF_3){\cdot}CH_2{\cdot}PPh_2)]$ ($M = Pd$ or Pt) proceeds *via* initial attack by base (H_2O or OH^-) on a β-acetylenic carbon followed by dimerisation and protonation to yield an intermediate analogous to (C) or (D) without the molecule of amine. Hydrolysis of this intermediate and elimination of trifluoroacetic acid then yields the final diphosphine complex. To provide additional evidence for this mechanism, the diethylamine–platinum complex (II) was treated with aqueous acid (1 mol) to remove the stabilising base. The product which was obtained quantitatively was the expected complex $[PtCl_2\{Ph_2P{\cdot}CH{:}C(CF_3){\cdot}CH_2{\cdot}PPh_2\}]$.[2]

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