Unsaturated σ-Hydrocarbyl Transition-metal Complexes. Part 3.[1] Crystal and Molecular Structure of *trans*-Chlorobis(diethylphenylphosphine)(vinyl)platinum(II) †

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The molecular structure of *trans*-[$PtCl(CH{=}CH_2)(PEt_2Ph)_2$] has been determined by *X*-ray diffraction methods. The crystals are orthorhombic, space group *Pbcn*, with a = 10.686(2), b = 13.832(4), c = 16.129(4) Å, and Z = 4. The structure has been solved by the heavy-atom method and refined by full-matrix least squares to R 0.044 for 1 420 diffractometric intensity data. The crystals contain discrete molecules in which the platinum co-ordination is square planar. The Pt–Cl bond vector coincides with a crystallographic diad axis about which the atoms of the vinyl group are disordered. Selected bond lengths (Å) are Pt–Cl 2.398(4), Pt–P 2.295(3), and Pt–C 2.03(2). The Pt–C=C angle is 127(2)°. From a survey of the available structural data it is concluded that there is little, if any, back donation from platinum to carbon in platinum–alkenyl linkages.

AN earlier part of this series[1] described the synthesis, reactivity, and spectroscopic properties of a group of related alkynyl- and alkenyl-platinum(II) compounds. We have undertaken a crystal structure analysis of one of these compounds, *trans*-[$PtCl(CH{=}CH_2)(PEt_2Ph)_2$], because of our interest in the relation between the *trans* influence and hybridization state of carbon atoms σ-bonded to platinum(II). This analysis, together with an earlier study of *trans*-[$PtCl(CH_2SiMe_3)(PMe_2Ph)_2$],[2] permits the *trans* influences of σ-alkyl and σ-alkenyl ligands on Pt^{II}–Cl bonds to be compared directly. The extension of this comparison to include σ-alkynyl ligands and full discussion of the results in the light of current theories of *trans* influence is postponed until Part 4,[3] in which a diffraction study of *trans*-[$PtCl(C{\equiv}CPh)(PEt_2Ph)_2$] will be presented.

This work was also prompted by recent speculation on the nature of transition-metal–alkenyl bonds. According to Churchill,[4] such bonds are on average 0.10 Å shorter than corresponding M–C(alkyl) bonds, when M is a first-row transition metal. To explain this contraction it appears to be necessary to ascribe some multiple character to M–C(alkenyl) bonds, since the covalent radii of sp^3 and sp^2 carbon atoms differ by only 0.03 Å. Comparison of the Pt–C bond lengths in *trans*-[$PtCl(CH_2SiMe_3)(PMe_2Ph)_2$] and *trans*-[$PtCl(CH{=}CH_2)(PEt_2Ph)_2$] permits the first assessment of this feature for a third-row transition metal.

Most of the rather sparse structural information on transition metal–alkenyl compounds relates to substituted vinyls; only in the case of Co^{III} are we aware of results for the unsubstituted ligand.[5,6] Prior to our preliminary account of this work,[7] the only diffraction study available of an alkenylplatinum(II) compound was that of [$Pt(C_6H_9)(CH_2COPh)(Ph_2PCH_2CH_2PPh_2)$]

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(C_6H_9 = cyclohexenyl).[8] More recently other reports have appeared.[9-12]

EXPERIMENTAL

Crystal Data.—$C_{22}H_{33}ClP_2Pt$, $M = 590.0$, Orthorhombic, $a = 10.686(2)$, $b = 13.832(4)$, $c = 16.129(4)$ Å, $U = 2\,384.0$ Å^3, $D_m = 1.67$, $Z = 4$, $D_c = 1.644$ g cm^{-3}, $F(000) = 1\,160$, space group *Pbcn*, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 64.4 cm^{-1}.

Measurements.—The space group and preliminary unit-cell dimensions were determined from Weissenberg and precession photographs. Final values of the unit-cell parameters and the intensities of all the independent reflections with θ(Mo-K_α) $\leqslant 28°$ were measured on a Hilger and Watts Y290 diffractometer equipped with a graphite monochromator. A symmetrical θ—2θ step scan was employed for all the intensity measurements; 1.3-s counts were taken at intervals of 0.01° over a range of 0.55° in θ. The intensities of three strong reflections, periodically remeasured during the experiment, varied by less than $\pm 3\%$ of their mean values.

Structure amplitudes and their standard deviations were derived in the usual way (q 0.05).[13] Corrections were made for coincidence loss [14] and for absorption; [15] the transmission factors on F^2 varied between 0.11 and 0.20. 1 420 Reflections with $I \geqslant 3\sigma(I)$ were used in the subsequent analysis.

Structure Analysis.—The space-group symmetry implies that each platinum atom occupies a site of either $\bar{1}$ or two-fold point symmetry, neither arrangement being compatible with a fully ordered crystal structure. The unique platinum atom was located on a diad axis from the Patterson function. Subsequent difference syntheses allowed the positions of the other atoms, apart from hydrogen, to be deduced.

The structure was refined by least-squares minimization of $\Sigma[(|F_o| - |F_c|)/\sigma(F)]^2$. Atomic-scattering factors were taken from ref. 16 except for those of platinum [17] and hydrogen.[18] Allowance was made for the anomalous scattering of the platinum, chlorine, and phosphorus atoms.[19] Refinement of the positional and vibrational parameters of all the non-hydrogen atoms gave R 0.044 and R' 0.062. The structure factors contained contributions for the scattering of the phenyl and methylene hydrogen atoms, the hydrogen-atom positions being deduced from those of adjacent carbon and phosphorus atoms. Anisotropic temperature factors were used only for platinum, chlorine, and phosphorus atoms.

In the model thus obtained the terminal vinyl carbon atom C(2) was disordered about the diad axis whereas C(1) was constrained to lie on the axis. Removal of this constraint gave R 0.044 and R' 0.060. Disordering of C(1) about the diad axis thus led to a small but statistically significant decrease in R'. Additionally, the angle Pt–C(1)–C(2) decreased from 148 to 127°, a value more consistent with the expected trigonal hybridization at C(1).

In the final difference-synthesis function values lay between ± 0.9 eÅ^{-3} apart from extreme values of -2.0 and $+1.2$ eÅ^{-3} in the region of the disordered vinyl group. The weighting scheme was satisfactory, mean values of $w\Delta^2$ displaying little variation with either $|F_o|$ or sinθ. The standard deviation of an observation of unit weight was 1.8.

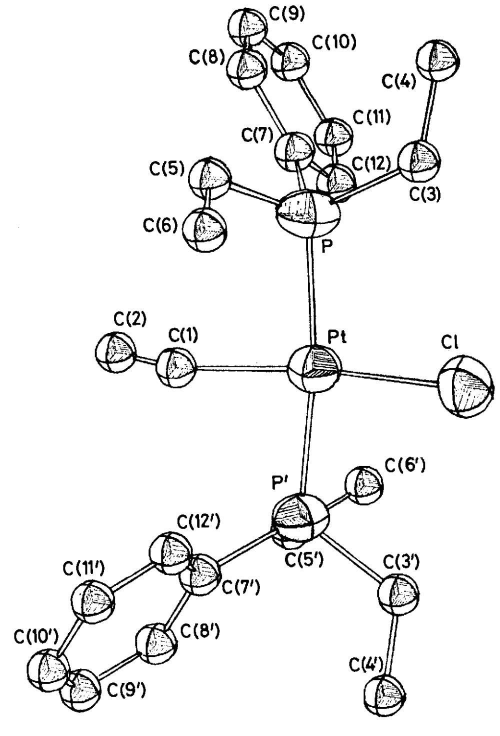

FIGURE Perspective view of the *trans*-[PtCl(CH=CH$_2$)(PMe$_2$Ph)$_2$] molecule. To aid clarity the disorder of the vinyl group is not shown. Thermal ellipsoids enclose 50% of probability

TABLE 1

Atomic parameters (fractional co-ordinates × 10^4)

Atom	x	y	z
Pt	0	236(1)	2 500
Cl	0	−1 498(3)	2 500
P	1 983(2)	353(2)	1 962(2)
C(1) *	−127(26)	1 682(17)	2 295(14)
C(2) *	199(15)	2 395(19)	2 823(16)
C(3)	2 720(15)	−860(11)	1 683(9)
C(4)	3 768(18)	−874(15)	1 069(12)
C(5)	3 038(13)	979(12)	2 655(8)
C(6)	3 073(12)	530(10)	3 529(9)
C(7)	2 058(10)	1 020(7)	994(6)
C(8)	3 144(11)	1 572(9)	787(8)
C(9)	3 131(15)	2 007(10)	−21(7)
C(10)	2 168(13)	1 895(10)	−560(8)
C(11)	1 145(8)	1 352(10)	−343(8)
C(12)	1 099(10)	910(7)	454(7)

* Assigned an occupancy factor of 0.5.

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

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TABLE 2

Selected interatomic distances (Å) and angles (°)

(*a*) Bond lengths

Pt–Cl	2.398(4)	C(5)–C(6)	1.54(2)
Pt–P	2.295(3)	C(7)–C(8)	1.43(2)
Pt–C(1)	2.032(23)	C(8)–C(9)	1.44(2)
C(1)–C(2)	1.35(4) [a]	C(9)–C(10)	1.36(2)
P–C(3)	1.906(16)	C(10)–C(11)	1.37(2)
P–C(5)	1.809(14)	C(11)–C(12)	1.42(2)
P–C(7)	1.816(10)	C(12)–C(7)	1.35(1)
C(3)–C(4)	1.50(3)		

(*b*) Bond angles [b]

Cl–Pt–P	94.0(1)	C(5)–P–C(7)	105.1(6)
Cl–Pt–C(1)	169.9(7)	P–C(3)–C(4)	118.3(12)
P–Pt–P′	171.9(1)	P–C(5)–C(6)	112.8(10)
P–Pt–C(1)	86.1(7)	P–C(7)–C(8)	120.6(8)
P–Pt–C(1′)	86.0(8)	P–C(7)–C(12)	117.6(8)
Pt–C(1)–C(2)	127(2)	C(8)–C(7)–C(12)	121.6(10)
Pt–P–C(3)	114.0(5)	C(7)–C(8)–C(9)	115.4(11)
Pt–P–C(5)	112.1(4)	C(8)–C(9)–C(10)	122.7(13)
Pt–P–C(7)	113.7(4)	C(9)–C(10)–C(11)	120.3(13)
C(3)–P–C(5)	107.9(7)	C(10)–C(11)–C(12)	119.6(11)
C(3)–P–C(7)	103.2(6)	C(11)–C(12)–C(7)	120.4(10)

(*c*) Torsion angles

Pt–P–C(3)–C(4)	158(1)	Pt–P–C(7)–C(12)	−37(1)
C(5)–P–C(3)–C(4)	−76(1)	C(3)–P–C(7)–C(12)	87(1)
C(7)–P–C(3)–C(4)	35(1)	C(5)–P–C(7)–C(12)	−160(1)
Pt–P–C(5)–C(6)	54(1)	Cl–Pt–P–C(3)	4(1)
C(3)–P–C(5)–C(6)	−72(1)	Cl–Pt–P–C(5)	−119(1)
C(7)–P–C(5)–C(6)	178(1)	Cl–Pt–P–C(7)	122(1)
Pt–P–C(7)–C(8)	148(1)	C(1)–Pt–P–C(3)	−166(1)
C(3)–P–C(7)–C(8)	−88(1)	C(1)–Pt–P–C(5)	71(1)
C(5)–P–C(7)–C(8)	25(1)	C(1)–Pt–P–C(7)	−48(1)

[a] In calculating the C(1)–C(2) bond length and Pt–C(1)–C(2) bond angle it is necessary to assume that C(1) is bonded to C(2) rather than C(2′). This assumption seems justified since the C(1)–C(2′) distance (1.0 Å) is well outside the expected range for bonds between carbon atoms. [b] Co-ordinates of primed atoms are related to those of the corresponding unprimed atoms in Table 1 by the transformation $\bar{x}, y, \frac{1}{2} - z$.

Final atomic parameters, including temperature factors, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22069 (9 pp.).* Fractional co-ordinates of atoms and a selection of functions derived from them are presented in Tables 1 and 2. A perspective view of the molecule is displayed in the Figure.

The computer programs used have been listed elsewhere,[2] apart from the Sussexray system for the University of Sussex ICL 1904A computer, and Dr. N. W. Alcocks' ABSORB analytical absorption-correction program.

RESULTS AND DISCUSSION

The crystals are built of discrete molecules with the expected *trans*-square-planar co-ordination. All the contacts between non-hydrogen atoms in different molecules are longer than 3.60 Å.

The co-ordination at the platinum atom is somewhat distorted from an ideal square-planar co-ordination, apparently in order to relieve steric interactions between the ligands. Thus, despite the opening of the Cl–Pt–P angle to 94° the Cl · · · C(3) contact is only 3.31 Å. Relief of this interaction by rotation of the phosphine about the Pt–P bond relative to the metal co-ordination plane, thus increasing the Cl–Pt–P–C(3) torsion angle from 4°, would decrease either the C(1) · · · C(5) or C(1) · · · C(7) distance, both of which are already short (3.26 and 3.27 Å respectively). The plane of the vinyl group [defined by atoms Pt, C(1), and C(2)] is normal to that passing through the atoms Pt, Cl, P, and P′, which are exactly coplanar. The displacement of C(1) from the latter plane is 0.36 Å. The metal co-ordination is thus similar to that found in *trans*-$[PtBr(CH{=}CHPh)(PPh_3)_2]$, where the Br–Pt–P angles are 93° and the ligating carbon atom is displaced by 0.23 Å from the metal co-ordination plane.[9]

The geometry of the phosphine ligand is normal. The carbon atoms of the phenyl group are coplanar to within ±0.006 Å. The conformation about the P–C(5) bond is close to staggered; that about the P–C(3) bond is intermediate between staggered and eclipsed. The Pt–P bond length [2.295(3) Å] agrees well with the value (2.302 Å) obtained by averaging results for 22 platinum(II) compounds containing mutually-*trans* tertiary phosphines with n-alkyl or phenyl substituents.

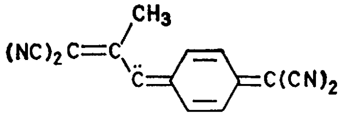
The *trans* influence of σ-hydrocarbyl ligands will be discussed in Part 4.[3] Here we note that the Pt–Cl distances in *trans*-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$ [2.415(5) Å][2] and in *trans*-$[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$ [2.398(4) Å] suggest that the *trans* influence of $CH{=}CH_2$ is slightly weaker than that of CH_2SiMe_3.

TABLE 3

Bond lengths and angles involving C_α in platinum(II)–alkenyl compounds

	Bond/Å		Angle/°	
Compound	Pt–C_α	$C_\alpha{=}C_\beta$	Pt–$C_\alpha{=}C_\beta$	Ref.
$[PtCl(Ph_2PC_6H_4CH{=}CC_6H_4PPh_2)]$	2.016 (8)	1.336 (12)	129.7(9)	10
trans-$[PtBr(CH{=}CHPh)(PPh_3)_2]$	2.022 (8)	1.347 (11)	123.8(6)	9
trans-$[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$	2.03(2)	1.35(4)	127(2)	*a*
trans-$[Pt(CCl{=}CH_2)_2(PMe_2Ph)_2]$	2.053 (5)	1.316 (7)	133.5	12
trans-$[Pt(C_{15}H_7N_4)(CCMe)(PMe_3)_2]$ [b]	2.057 (15)	1.35(2)	127.3(12)	11
$[Pt(C_6H_9)(CH_2COPh)(Ph_2PCH_2CH_2PPh_2)]$	2.068 (10)	1.32		8

[a] This work. [b] $C_{15}H_7N_4$ =



Bond lengths and angles within the Pt–$CH{=}CH_2$ unit are compared with those in other alkenylplatinum(II) compounds in Table 3. In all the alkenyl ligands the C=C bond lengths are close to the value (1.34 Å) found in ethylene.[20] However, the Pt–C=C angles lie in the range 124—134° and are all significantly more obtuse than 120°, the valency angle expected at sp^2 carbon. The Pt–C bond lengths in Table 3 vary slightly, depending on the nature of the *trans* ligand. The shortest three are *trans to* chloride or bromide; the remainder are *trans* to phosphine or σ-hydrocarbyl, both of which display a high *trans* influence compared with halide in platinum(II) compounds.[21]

The weighted mean of the shortest three Pt–C bond lengths in Table 3 is 2.020(5) Å. We suggest that this is the best estimate that can be made at present of the length of a Pt^{II}–C(alkenyl) bond subject to low *trans* influence. The corresponding mean for Pt^{II}–C(alkyl) bonds *trans* to chloride is 2.079(5) Å.* Thus, for Pt^{II} the difference between comparable M–C(alkenyl) and M–C(alkyl) bond lengths is 0.059(7) Å and half of this contraction is explained by the difference in covalent radii between sp^2 and sp^3 carbon atoms. Since it is thought that an M–C bond 0.10 Å shorter than a comparable M–C(alkyl) bond possesses *ca.* 20% multiple character,[4] we conclude that there is little, if any, $d \longrightarrow p$ back donation involved in the platinum(II)–alkenyl linkage. Moreover, such back donation would involve occupancy of the alkenyl π^* orbital and a consequent increase in the C=C bond lengths, compared with the value in ethylene, which the data in Table 3 do not support. A parallel conclusion on the absence of back donation in platinum(II)–phenyl bonds has been made from n.m.r. evidence.[25]

In our view the difference in length between Pt^{II}–C(alkyl) and Pt^{II}–C(alkenyl) bonds could be explained in terms of the hybridization states of the carbon atoms involved. The wide Pt–C=C angles in the alkenyl compounds suggest that more than two thirds of the carbon 2*s* orbital is distributed between the Pt–C and C=C bonds. Using arguments due to Coulson,[26] and assuming that the carbon 2*s* orbital is distributed approximately equally between the two bonds, it can be concluded that the carbon radius appropriate to these Pt–C(alkenyl) bonds is *ca.* 0.72 Å, compared with 0.74 and 0.77 Å for exact sp^2 and sp^3 hybridization.[27] On the further assumption that the carbon atoms in Pt–C(alkyl) bonds are sp^3 hybridized the calculated difference in length of Pt–C(alkyl) and Pt–C(alkenyl) bonds is 0.05 Å, in good agreement with the observed contraction of 0.06 Å. This argument does not, of course, take account of differences in hybridization at platinum. We believe that these differences are small in the compounds we have considered since there is no great disparity between the relative *trans* influences of alkyl and alkenyl ligands on the Pt–Cl bonds (see above).

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* Weighted mean of 2.079(14) Å in *trans*-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$,[2] 2.081(6) Å in *trans*-$[PtClMe(PMePh_2)_2]$,[10] 2.05(3) Å in two diastereoisomers of *cis*-$[PtCl_2(CH_2{=}CHCH_2CH_2CHCH_2NH_2CHMePh)]$,[22] and 2.08(3) Å in $[PtCl(CH_2{=}CHCH_2OCH_2CHCH_2OMe)(NH_2CHMePh)]$.[23] Although these bond lengths agree well it should be noted that the 19 values for Pt^{II}–C(alkyl) bond lengths available in the literature range from 2.03(1) to 2.18(1) Å.[10,24] The influence of the *trans* ligand does not seem to be a major factor in this large variation, for which there is no satisfactory explanation at present.

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