Journal of Organometallic Chemistry, 99 (1975) 315—328

STUDIES ON METAL—ACETYLENE COMPLEXES

V*. CRYSTAL AND MOLECULAR STRUCTURE OF BIS(TRIPHENYLPHOSPHINE)(1-PHENYLPROPYNE)PLATINUM(0), $[P(C_6H_5)_3]_2(C_6H_5C{\equiv}CCH_3)Pt^0$

BRIAN WILLIAM DAVIES** and NICHOLAS C. PAYNE*

Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7 (Canada)

(Received March 15th, 1975)

Summary

The acetylene complex $(P(C_6H_5)_3)_2Pt(C_6H_5C{\equiv}CCH_3)$ crystallizes in the monoclinic space group $P2_1$ with $a = 14.840(4)$, $b = 9.558(3)$, $c = 13.553(4)$ Å and $\beta = 102.74(2)°$. The observed density of 1.47(2) g cm^{-3} agrees with the value of 1.480 g cm^{-3}, calculated for $M = 835.8$ and $Z = 2$. Three dimensional X-ray diffraction intensity data were collected on an automatic four circle diffractometer using Mo radiation. The structure was solved by the heavy atom method and refined by Fourier and full matrix least-squares techniques on F. The final conventional agreement factor for the converged model is 0.042, using 2843 observations with $I > 3\sigma(I)$. The coordination geometry about the Pt atom is essentially trigonal, if the coordinated triple bond of the acetylene is assumed to occupy one coordination site. The acetylene ligand adopts a *cis*-bent configuration, with a mean departure from linearity of 40(1)°. The coordinated triple bond length is 1.277(25) Å. The plane of the phenyl substituent of the acetylene is inclined at an angle of 10.4° with the plane of the acetylene ligand. The mean Pt—C(acetylene) distance is 2.029(15) Å. The structural results indicate that the acetylene is considerably perturbed on coordination, consistent with the observation that $\Delta\nu(C{\equiv}C)$ is 478 cm^{-1}.

---

* For part IV see ref. 1.

** Present address: Chemistry Division (B429), A.E.R.E. Harwell, Oxfordshire, OX11 ORA (Great Britain).

Introduction

In 1957 Chatt et al. [2] prepared a series of acetylene complexes $(PPh_3)_2Pt$(acetylene), and since that time a number of workers [3-17] have prepared related complexes. In these compounds the coordinated triple bond was thought to resemble a double bond, as $\nu(C{\equiv}C)$ was reduced by some 500 cm^{-1}.

A ^1H NMR study on $(PPh_3)_2Pt(PhC{\equiv}CMe)$ [5,6] furnished useful structural information. The observation of two distinct couplings to the methyl H atoms of the acetylene, $J(P{-}H_{cis})$ 1.2 Hz and $J(P{-}H_{trans})$ 6.2 Hz, suggested that the coordinated triple bond lay in the plane of the Pt and the two P atoms, and that rotation about the Pt—acetylene bond was not detectable on the NMR time scale. That this geometry was preserved in the solid state was demonstrated for analogous complexes in preliminary reports of the X-ray structural determinations of $(PPh_3)_2Pt(PhC{\equiv}CPh)$ [19] and $(PPh_3)_2Pt(NCC{\equiv}CCN)$ [20]. The first complete account of the X-ray structural determination of such a compound, $(PPh_3)_2Pt(F_3CC{\equiv}CCF_3)$, has recently appeared [1], and structural results have been presented for $(PPh_3)_2Pt$(cyclo-C_6H_8) and $(PPh_3)_2Pt$(cyclo-C_7H_{10}) [21].

In an attempt to obtain further structural information for these complexes, we undertook a single crystal X-ray diffraction study of bis(triphenylphosphine)(1-phenylpropyne)platinum(0), $(PPh_3)_2Pt(PhC{\equiv}CMe)$. An $RC{\equiv}CR'$ acetylene ligand was chosen in order to see whether the difference in electron-withdrawing power of the substituents resulted in any discernible structural differences, and whether such a difference (if present) could be accounted for in terms of existing bonding theories.

Experimental

A crystalline sample was kindly furnished by Dr. J.E.H. Ward. Pale yellow prismatic crystals were obtained by recrystallisation from methylene chloride and n-pentane. Crystal data were obtained from a preliminary photographic examination, and are summarised in Table 1. The systematic absences observed are consistent with space groups $P2_1$ (C_2^2, No. 4) and $P2_1/m$ (C_{2h}^2, No. 11) [22]. With two formula units per cell, a mirror plane is imposed upon the molecule in $P2_1/m$, whereas no symmetry constraints exist in $P2_1$. Solution and refinement were initially attempted in $P2_1$, a choice which was later justified by a successful analysis.

The crystal chosen for data collection was mounted so that the long dimension [010] was offset from coincidence with the diffractometer ϕ axis to minimise the possibility of multiple reflections [23]. The mosaicity of the crystal was examined by the method of Furnas [24]. The mean width at half height was 0.09°. Refined cell parameters and an orientation matrix were obtained from a least-squares procedure* employing the angular setting values of 29

---

* Computing was performed on the DEC PDP-10 and the CDC Cyber 73/14 at the University of Western Ontario. Among the programs used were: cell refinement and orientation matrix, PICKTT, based on the logic of Hamilton's MODE 1; Fourier syntheses, Zalkin's FORDAP; least-squares refinement, WOCLS, a version of Ibers' NUCLS; absorption correction, AGNOST, by Cahen and Ibers; Johnson's ORTEP for illustrations; and ORFFE, Busing, Martin and Levy's function and error program.

TABLE 1

CRYSTAL DATA FOR $(PPh_3)_2Pt(PhC{\equiv}CMe)$

$PtP_2C_{45}H_{38}$	$f.w. = 835.8$
Crystal description	Pale yellow prisms
Systematic absences	$0k0$, $k = 2n + 1$
Space group	Monoclinic, $P2_1$ (C_2^2)
Cell constants	$a = 14.840(4)$ Å, $b = 9.558(3)$ Å, $c = 13.553(4)$ Å, $\beta = 102.74(2)°$
Cell volume	1875 $Å^3$
Density (observed)	1.47(2) g cm^{-3}, by flotation in $C_2H_4Br_2/n\text{-}C_5H_{12}$
(calculated)	1.480 g cm^{-3} for $Z = 2$

carefully centred reflection for which $14° < 2\theta < 31°$.

The experimental conditions used for data collection are summarised in Table 2. The standard reflections showed only random fluctuations during the collection period. The scan range, 0.8°, was corrected for dispersion, such that the scan started 0.4° below the $K\alpha_1$ peak, and ended 0.4° above the $K\alpha_2$ peak.

A total of 4771 hkl reflections was collected, with $0° < 2\theta < 55°$. A further 3381 $h\bar{k}l$ reflections were also measured, out to a 2θ maximum of 50°. The data were corrected for background, and values of $\sigma(I)$ calculated, as described elsewhere [1]. The initial value of p was chosen as 0.00, though this value was adjusted as the refinement proceeded in order to achieve an error on an observation of unit weight approaching unity at convergence. After correction for Lorentz and polarization effects, 3509 of the hkl reflections, and 2556 of the $h\bar{k}l$ data had magnitudes $I > 3\sigma(I)$.

Absorption correction trials indicated transmission factors varying from 0.548 to 0.705, so on absorption correction was applied. The Gaussian method was used, with 8 × 12 × 6 grid.

TABLE 2

EXPERIMENTAL CONDITIONS FOR DATA COLLECTION

Radiation	Mo-K_α ($\lambda K_{\alpha_1} = 0.70926$ Å)
Filter	Nb foil (0.07 mm thick) prefilter
Temperature	22°C
Mean 'ω' scan width at half height	0.09°
Reflections centered, in 2θ range	29, $14 < 2\theta < 31°$
Scan range, speed	0.8°, 1° min^{-1}
Stationary background count time	10 sec (20 sec for $2\theta \geq 50°$)
Standards	5; 020, 331, 200, 002, $\bar{2}00$
Take-off angle	1.4°
Intensity obtained for a given reflection	90% of maximum
Crystal-counter distance	32 cm
Aperture size	4 × 4 mm
2θ range	$0 < 2\theta < 55°$
μ(Mo-K_α)	36.6 cm^{-1}
Crystal faces	$\{001\}$, $\{101\}$ and $\{100\}$ $(\bar{1}1\bar{1})$, $(1\bar{2}1)$ and (121)
Crystal dimensions	0.18 × 0.18 × 0.26 mm

Structure solution and refinement

The positions of the Pt and two P atoms were readily located from a three-dimensional Patterson synthesis. Two cycles of full matrix least-squares refinement on F utilizing the hkl reflections with $I > 2\sigma(I)$, refining a scale factor, positional and isotropic thermal parameters and with the origin defined by the Pt at $y = 1/4$, led to residuals $R_1 = 0.199$ and $R_2 = 0.235$ (3745 observations, 12 variables, $p = 0.020$). Agreement factors are defined as $R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$, $R_2 = \Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2$, the weight w is $4F_0^2/\sigma^2(F_0^2)$ and the function minimized is $\Sigma w(|F_0| - |F_c|)^2$. The atomic scattering factors for Pt, P and C atoms were those of Cromer and Waber [25], while those of H were taken from Stewart et al. [26]. Anomalous dispersion contributions [27] to the F_c values were included for the Pt and P atoms and were taken from Cromer and Liberman [28].

A series of difference Fourier syntheses and least-squares refinements resulted in the location of the other 45 non-hydrogen atoms in the molecule. The phenyl rings were refined as rigid groups with D_{6h} symmetry and C—C = 1.392 Å [29]. The molecular geometry obtained showed that m symmetry could not be imposed on the molecule and so refinement was not attempted in $P2_1/m$. Two cycles with all non-group atoms refined anisotropically, and with individual temperature factors refined for the group C atoms led to residuals $R_1 = 0.049$ and $R_2 = 0.064$ (3472 observations, 138 variables).

$P2_1$ is a polar space group and thus there are two possible orientations of the molecule with respect to the 2_1 axis. One model, A, had been arbitrarily chosen up to this point. The second model, B, is the mirror image of model A. Several refinements were now attempted on B in order to determine which model better fitted the observed intensity data. It was not possible to differentiate between A and B on the basis of R_2 values obtained in the refinements, and the molecular geometries observed in each case were virtually indistinguishable. Structure factors were calculated for both A and B, and Bijvoet pairs examined. Again, no conclusive evidence was obtained in support of either model, and it became evident that rejection of one model would have to be accomplished by deciding which had the more chemically credible geometry. It has been shown [30,31] that the choice of the wrong model for the value of $\Delta f''$ applied to the scattering factor will lead to errors in the coordinates of the atoms for which there are anomalous scattering effects. Although the $\Delta f''$ contributions are considerable (8.388e for Pt, 0.095e for P) the plane of the PtP_2 moiety is virtually perpendicular to the y axis, and so the relative positions of these atoms will only slightly be affected by such polar dispersion effects. On the basis of known structural evidence for $(PPh_3)_2Pt$(acetylene) complexes (Table 9) model A was retained.

The conditions for the final cycles of refinement were:

(i) only those reflections with $I > 3\sigma(I)$ out to a 2θ value of 50° were employed.

(ii) the p value was 0.027.

(iii) the origin was defined by the Pt atom at $y = 0.10$.

(iv) phenyl H atom contributions were included in the calculated structure factor. Idealized positions (C—H = 1.00 Å) were assumed. Isotropic thermal

(continued on p. 321)

TABLE 3

ATOMIC POSITIONAL AND THERMAL PARAMETERS [a]

Atom	x	y	z	$U(1,1)$ [b]	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Pt	0.20381(3)	0.10	0.15954(3)	336(2)	319(2)	324(2)	33(8)	60(1)	8(9)
P(1)	0.1304(2)	0.1065(13)	0.2903(2)	398(15)	377(17)	347(13)	145(48)	83(11)	−23(52)
P(2)	0.3356(3)	0.2284(4)	0.2186(3)	440(19)	330(19)	414(19)	−42(16)	39(16)	16(16)
C(1)	0.0301(16)	−0.0585(48)	−0.0008(19)	658(132)	2496(436)	659(129)	−781(217)	82(114)	−431(199)
C(2)	0.1215(13)	0.0081(23)	0.0389(12)	574(100)	862(132)	275(72)	−99(96)	−50(67)	17(83)
C(3)	0.1952(10)	0.0451(18)	0.0120(12)	345(74)	598(89)	446(81)	−57(62)	32(64)	−0(66)

[a] Estimated standard deviations are given in parentheses and correspond to the least significant digits. Values without e.s.d.'s were not refined. [b] The values have been multiplied by 10^4. The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$.

TABLE 4. GROUP PARAMETERS AND DERIVED PHENYL C AND H ATOM POSITIONAL AND THERMAL PARAMETERS

Group	x_g [a]	y_g	z_g	δ	ϵ	η
Ring 1	−0.0773(5)	−0.0140(9)	0.2230(6)	0.419(6)	−2.931(8)	−3.022(8)
Ring 2	0.1053(6)	0.4221(9)	0.3648(7)	−3.026(28)	−1.871(6)	1.583(28)
Ring 3	0.2112(6)	−0.0785(11)	0.4879(7)	−1.650(10)	2.627(7)	1.018(11)
Ring 4	0.4148(6)	0.2578(11)	0.4595(7)	−2.344(10)	2.953(7)	1.844(10)
Ring 5	0.5072(5)	0.1126(20)	0.1355(7)	2.729(16)	−2.932(16)	−2.547(10)
Ring 6	0.3068(6)	0.5524(9)	0.1459(7)	−1.182(9)	−2.508(8)	−2.800(10)
Ring 7	0.2650(7)	0.0462(12)	−0.1681(7)	2.228(12)	2.868(7)	−1.773(11)

Derived phenyl group C atoms					Derived phenyl group H atoms			
Atom	x	y	z	B(A^2)	Atom	x	y	z
Ring 1								
1C1	0.0108(5)	0.0416(11)	0.2563(9)	3.6(3)				
1C2	−0.0664(6)	0.1265(9)	0.2503(8)	4.1(3)	H1C2	−0.058	0.227	0.270
1C3	−0.1546(5)	0.0709(12)	0.2170(10)	5.5(4)	H1C3	−0.210	0.132	0.213
1C4	−0.1655(6)	−0.0696(13)	0.1898(12)	6.5(5)	H1C4	−0.229	−0.109	0.165
1C5	−0.0883(8)	−0.1545(9)	0.1958(12)	6.4(5)	H1C5	−0.096	−0.255	0.176
1C6	−0.0001(7)	−0.0989(10)	0.2290(10)	4.8(3)	H1C6	−0.055	−0.160	0.233
Ring 2								
2C1	0.1147(8)	0.2837(9)	0.3367(8)	3.3(3)				
2C2	0.1128(9)	0.3158(12)	0.4364(7)	5.3(4)	H2C2	0.118	0.240	0.488
2C3	0.1034(11)	0.4542(14)	0.4645(8)	6.1(4)	H2C3	0.101	0.477	0.536
2C4	0.0958(13)	0.5605(10)	0.3929(11)	9.4(8)	H2C4	0.088	0.660	0.413
2C5	0.0977(11)	0.5284(10)	0.2931(10)	5.8(4)	H2C5	0.092	0.605	0.241
2C6	0.1071(9)	0.3900(12)	0.2650(7)	4.7(3)	H2C6	0.109	0.367	0.193
Ring 3								
3C1	0.1751(7)	0.0025(13)	0.4031(8)	3.8(3)				
3C2	0.2654(7)	−0.0467(15)	0.4191(9)	4.8(4)	H3C2	0.304	−0.024	0.370
3C3	0.3016(7)	−0.1278(18)	0.5039(11)	7.5(6)	H3C3	0.366	−0.163	0.515
3C4	0.2474(10)	−0.1596(18)	0.5727(10)	7.7(6)	H3C4	0.273	−0.217	0.634
3C5	0.1570(10)	−0.1104(18)	0.5567(9)	6.3(5)	H3C5	0.118	−0.133	0.606
3C6	0.1209(7)	−0.0293(15)	0.4719(10)	5.2(4)	H3C6	0.056	0.006	0.461
Ring 4								
4C1	0.3843(8)	0.2479(14)	0.3550(7)	4.0(3)				
4C2	0.4582(8)	0.1663(13)	0.4048(9)	4.9(4)	H4C2	0.489	0.099	0.366
4C3	0.4887(9)	0.1762(16)	0.5093(9)	7.4(5)	H4C3	0.541	0.116	0.545
4C4	0.4454(11)	0.2677(19)	0.5640(7)	6.8(5)	H4C4	0.467	0.275	0.639
4C5	0.3715(11)	0.3493(17)	0.5143(9)	7.3(5)	H4C5	0.341	0.416	0.553
4C6	0.3410(8)	0.3394(14)	0.4098(9)	5.5(3)	H4C6	0.289	0.399	0.374
Ring 5								
5C1	0.4387(9)	0.1764(30)	0.1752(12)	5.2(8)				
5C2	0.4403(11)	0.0314(29)	0.1659(14)	5.0(8)	H5C2	0.394	−0.027	0.191
5C3	0.5088(17)	−0.0325(20)	0.1262(21)	7.6(8)	H5C3	0.513	−0.138	0.125
5C4	0.5757(10)	0.0487(23)	0.0957(13)	5.8(5)	H5C4	0.626	0.001	0.070
5C5	0.5741(11)	0.1937(22)	0.1050(15)	9.3(10)	H5C5	0.621	0.251	0.080
5C6	0.5056(16)	0.2576(20)	0.1447(20)	5.9(5)	H5C6	0.502	0.361	0.145
Ring 6								
6C1	0.3235(8)	0.4145(10)	0.1777(9)	3.5(3)				
6C2	0.3773(8)	0.5221(15)	0.2295(9)	7.5(6)	H6C2	0.429	0.500	0.289
6C3	0.3606(10)	0.6600(12)	0.1977(12)	6.4(5)	H6C3	0.400	0.737	0.234
6C4	0.2901(11)	0.6904(10)	0.1141(12)	7.0(5)	H6C4	0.279	0.789	0.091
6C5	0.2363(8)	0.5828(13)	0.0624(8)	5.0(3)	H6C5	0.186	0.605	0.002
6C6	0.2530(7)	0.4449(11)	0.0941(8)	4.5(3)	H6C6	0.215	0.368	0.057

(continued)

TABLE 4 (*continued*)

Derived phenyl group C atoms					Derived phenyl group H atoms			
Atom	*x*	*y*	*z*	$B(A^2)$	Atom	*x*	*y*	*z*
Ring 7								
7C1	0.2330(8)	0.0458(14)	—0.0790(8)	3.9(3)				
7C2	0.1855(10)	—0.0282(16)	—0.1629(11)	6.8(5)	H7C2	0.128	—0.080	—0.160
7C3	0.2175(13)	—0.0279(20)	—0.2521(10)	9.5(8)	H7C3	0.183	—0.080	—0.313
7C4	0.2970(12)	0.0466(21)	—0.2573(8)	7.9(7)	H7C4	0.320	0.047	—0.321
7C5	0.3445(8)	0.1206(19)	—0.1733(9)	6.4(4)	H7C5	0.402	0.173	—0.177
7C6	0.3125(7)	0.1203(16)	—0.0842(8)	4.9(3)	H7C6	0.347	0.173	—0.024

[a] x_g, y_g and z_g are the fractional coordinates of the group center; δ, ϵ and η (in radians) are the group orientation angles [29].

parameters were assigned such that the H atom temperature factor was 1.0 Å^2 greater than that of the C atom to which it was bonded, rounded up to the next higher integral value.

(v) no contribution was included for the methyl H atoms. A difference Fourier plane calculated for the methyl group (C—H 1.00 Å, angle H—C—H 109° 27′) showed only a smearing of electron density and, in view of the pronounced motion of C(1), no satisfactory description of the methyl H atoms was possible.

(vi) 4 reflections, 1 2 0, $\bar{1}$ 2 0, 1 2 3 and 0 3 1 were seriously in error with the model and therefore were assigned zero weight.

(viii) anomalous dispersion contributions for the Pt and the two P atoms were included in the calculated structure factor.

(ix) the seven phenyl rings were refined as rigid groups, with individual isotropic temperature factors assigned to each group atom.

Under these conditions (2843 observations, 138 variables) refinement converged at $R_1 = 0.042$ and $R_2 = 0.055$. In the final cycle no parameter shift exceeded 0.18 of its estimated standard deviation. A final difference Fourier synthesis showed no peaks in excess of 1.0 eÅ^{-3}. The largest peak, 0.84(19) eÅ^{-3}, at (—0.16, 0.19, 0.19) is in the vicinity of phenyl ring 1, in a position of no chemical significance. A statistical examination of $|F_0|$ and $|F_c|$ values in terms of indices, magnitudes, $\lambda^{-1} \sin \theta$, and diffractometer angles (χ and ϕ) showed no abnormal trends. The error on an observation of unit weight is 1.05 electrons.

The final atomic positional and thermal parameters of the six non-group atoms are given in Table 3. Table 4 gives the group parameters and the derived phenyl C and H atom positional and thermal parameters. Table 5 lists the root-

TABLE 5

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (in Å × 10^3)

Atom	Minimum	Median	Maximum
Pt	171(2)	181(2)	191(2)
P(1)	152(14)	187(4)	233(12)
P(2)	178(5)	195(5)	226(5)
C(1)	175(29)	270(28)	530(46)
C(2)	156(22)	250(23)	302(23)
C(3)	179(20)	219(20)	248(18)

mean-square amplitudes of vibrations of the non-group atoms. A listing of observed and calculated structure factors (X 10 in electrons) has been deposited*.

Description of the structure

The structure consists of discrete molecules, the closest intermolecular distance of approach being 2.23 Å between H atoms bonded to 7C5 and 5C3. This distance is shorter than the sum of the Van der Waals H radii, 2.4 Å [33]. The shortest intermolecular contact not involving H atoms is 3.62 Å between 2C3 and 3C6. The principal intramolecular bond lengths and bond angles are given in Table 6. A view of the molecule, together with the atom labelling scheme, is given in Fig. 1. The inner coordination sphere about the Pt atom, together with some selected bond distances and angles is given in Fig. 2. Fig. 3 shows a stereoview of the molecule. Selected weighted least-squares planes appear in Table 7.

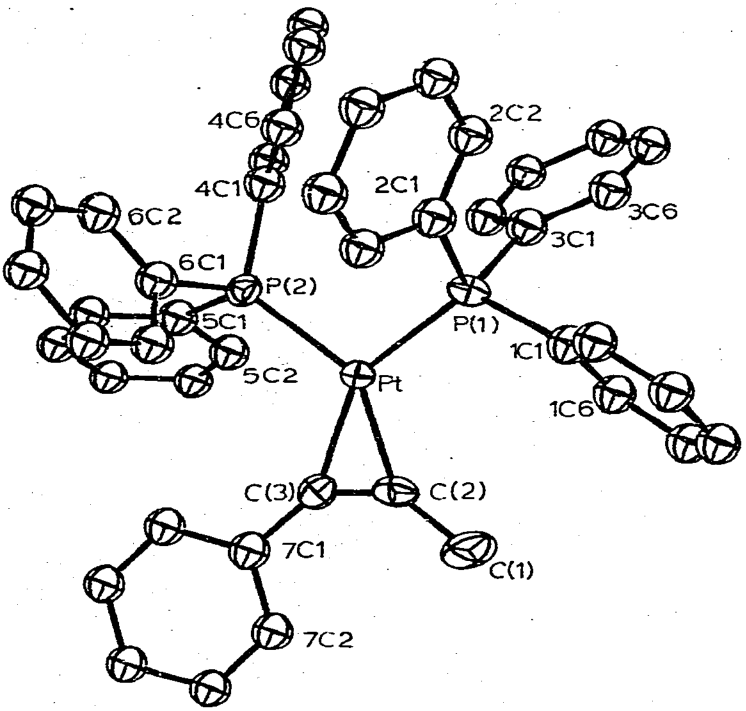

Fig. 1. An ORTEP illustration of the molecule, showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

---

* The table of structure factors has been deposited as NAPS Document No. 02638 (9 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside of the United States and Canada postage is $2.00 for a photocopy or $1.00 for a fiche.

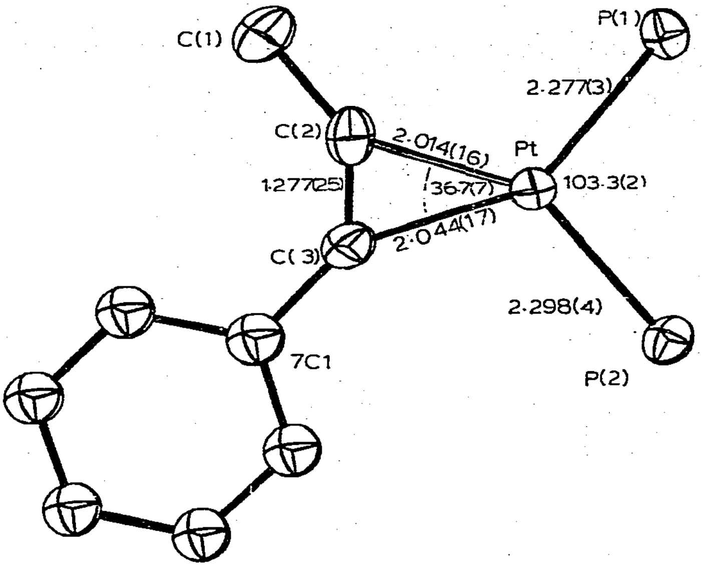

Fig. 2. The inner coordination sphere.

The coordination about the Pt atom is essentially planar, with the acetylene triple bond approximately in the plane of the PtP_2 moiety. The dihedral angle (the angle between the normals to the planes through P(1), Pt, P(2), and C(2), Pt, C(3) is 6.4(7)°. The Pt—P distances are 2.277(3) and 2.298(4) Å, just significantly different values ($\Delta = 4\sigma$). The P(1)—Pt—P(2) angle is 103.2(2)° and the C(2)—Pt—C(3) angle is 36.7(7)°. The Pt—acetylene C atom interactions are 2.014(16) and 2.044(17) Å, not significantly different values. The P(1)—Pt—

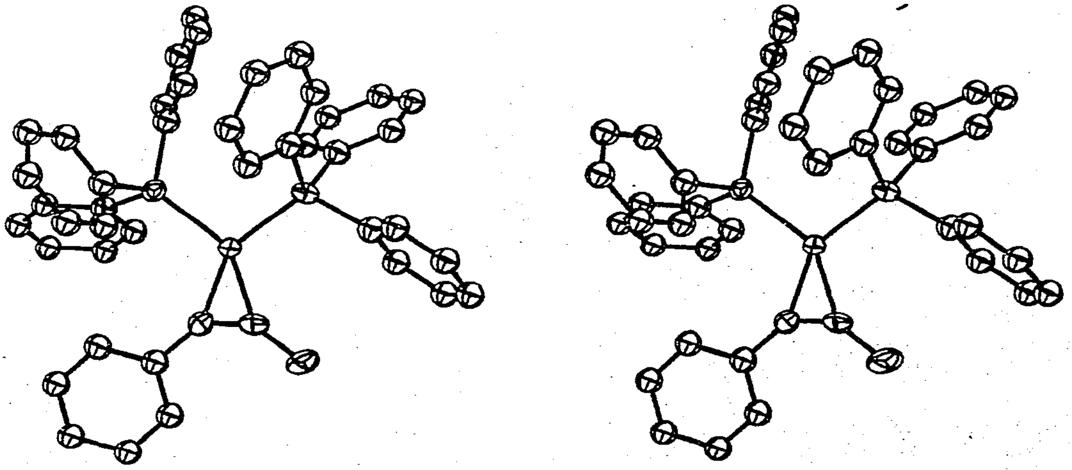

Fig. 3. A stereoview of the molecule.

TABLE 6

SELECTED INTRAMOLECULAR BOND DISTANCES AND ANGLES

Bond	Distance (Å)	Atoms	Angle (°)
(a) Coordination about the Pt atom			
Pt—P(1)	2.277(3)	P(1)—Pt—P(2)	103.3(2)
Pt—P(2)	2.298(4)	P(1)—Pt—C(2)	109.6(6)
Pt—C(2)	2.014(16)	P(2)—Pt—C(3)	110.0(4)
Pt—C(3)	2.044(17)	C(2)—Pt—C(3)	36.7(7)
(b) The triphenylphosphine ligands			
P(1)—1C1	1.839(11)	Pt—P(1)—1C1	113.4(4)
P(1)—2C1	1.839(12)	Pt—P(1)—2C1	114.2(4)
P(1)—3C1	1.822(13)	Pt—P(1)—3C1	119.4(5)
		1C1—P(1)—2C1	102.1(5)
		1C1—P(1)—3C1	100.3(5)
		2C1—P(1)—3C1	105.5(5)
P(2)—4C1	1.839(12)	Pt—P(2)—4C1	121.3(4)
P(2)—5C1	1.825(20)	Pt—P(2)—5C1	116.8(6)
P(2)—6C1	1.860(12)	Pt—P(2)—6C1	112.9(4)
		4C1—P(2)—5C1	100.4(7)
		4C1—P(2)—6C1	101.2(5)
		5C1—P(2)—6C1	101.3(9)
(c) The 1-phenylpropyne ligand			
C(1)—C(2)	1.487(28)	Pt—C(2)—C(1)	145.2(1.5)
C(2)—C(3)	1.277(25)	Pt—C(2)—C(3)	73.0(1.0)
C(3)—7C1	1.463(20)	Pt—C(3)—7C1	150.5(1.2)
		Pt—C(3)—C(2)	70.4(1.0)
		C(1)—C(2)—C(3)	141.8(1.8)
		C(2)—C(3)—7C1	139.0(1.6)
		C(3)—7C1—7C2	117.8(1.2)
		C(3)—7C1—7C6	122.1(1.2)

TABLE 7

SELECTED LEAST-SQUARES PLANES

Plane	Atoms in plane	Departure (Å) from plane
A	P(1)	0.058(10)
	P(2)	0.009(4)
	C(2)	0.19(2)
	C(3)	0.12(2)
	Pt	−0.0001(2)
B	C(1), C(2), C(3)	
C	7C1, 7C3, 7C5	

Dihedral angle between planes B/C = 10.4°

EQUATION OF PLANES

A $-6.191x + 8.000y - 3.435z = -0.101$

B $-5.025x + 8.591y - 2.426z = -0.657$

C $-11.79x + 0.943y + 10.29z = -1.594$

C(2) and P(2)—Pt—C(3) angles are similar, 109.6(6) and 110.0(4)° respectively, in contrast to the situation in $(PPh_3)_2Pt(F_3CC{\equiv}CCF_3)$ [1] where the corresponding values were 114.05(19) and 109.78(18)°. The non-bonded distances P(1)—C(2) and P(2)—C(3) are 3.51 and 3.56 Å respectively.

The P—C distances in the phosphine ligands range from 1.822(13) to 1.860(12) Å, with a mean value of 1.837(7) Å. The mean value in triphenylphosphine is 1.828(5) Å [34]. The mean angle subtended by the bonded C atoms at the P atoms is 102(1)°, while the mean Pt—P—C1 angle is 116(2)°, indicating the usual compression of the phenyl substituents away from the Pt atom.

The geometry of the coordinated 1-phenylpropyne ligand differs considerably from that of the free acetylene. The coordinated triple bond length is 1.277(25) Å, whereas a mean value observed for a triple bond is 1.202(5) Å [35]. The acetylenic substituents are bent back away from the Pt by approximately 40°, the methyl substituent by 38(2)°, and the phenyl substituent by 41(2)°. These values are not significantly different. The C(1)—C(2) distance is 1.487(28) Å and the C(3)—7C1 distance is 1.463(20) Å. The phenyl ring is inclined at an angle of 10.4° with the plane of the acetylene C atoms, C(1), C(2) and C(3).

Discussion

The essentially planar coordination geometry about the Pt atom is consistent with the ^{1}H NMR study [5,6]. The structural results obtained agree well with those results available for X-ray crystallographic studies on $(PPh_3)_2Pt$-(acetylene) complexes (Table 8), and are consistent with the observation that $\Delta\nu(C{\equiv}C)$ is 478 cm^{-1} [6, 36]. It is evident from Table 8 that a wide range of Pt—P, Pt—C(acetylene) distances and P—Pt—P angles exists in these complexes. It does not seem possible to correlate any trends in the Pt—P and Pt—C distances and the P—Pt—P angles with the electron-withdrawing or -releasing behaviour of the acetylene substituents. The value of interpreting small changes in Pt—P or Pt—C distances in terms of bonding trends can only be justified if the values differ markedly from the "mean" values (approximately 2.03 ± 0.02 Å and 2.28 ± 0.02 Å for Pt—C and Pt—P distances respectively).

The perturbations of the coordinated acetylene in the complexes listed in Table 8 are remarkably constant. With the exception of the cyclohexyne complex, all the compounds studied have their acetylenic substituents *cis*-bent away from the Pt atom to a mean extent of 40 ± 1°, and the coordinated triple bond lengths lie in the range 1.26-1.32 Å. The magnitude of the mean bend-back angle in the cyclohexyne complex, 52.7(9)°, [21] is probably affected by the cyclic nature of the ligand. Also noteworthy is the fact that three of the acetylene complexes contain unsymmetrical acetylene ligands, $PhC{\equiv}CMe$, $PhC{\equiv}CCO_2Et$ and $p\text{-}NO_2C_6H_4C{\equiv}CCO_2Et$. When the ligand is $PhC{\equiv}CCO_2Et$ the bend-back angles are equivalent, but the Pt—C(acetylene) distances are not [37]; with $p\text{-}NO_2C_6H_4\text{-}C{\equiv}CCO_2Et$ the bend-back angles are significantly different, but the Pt—C(acetylene) distances are equivalent [37]; and with $PhC{\equiv}CMe$ both the bend-back angles and Pt—C(acetylene) distances are equivalent. Rationalization of these observations is difficult, for a bend-back angle of ~40° is observed regardless of whether the acetylene substituent is considered electron-donating (Me), electron-

TABLE 8

STRUCTURAL DATA FOR $(PPh_3)_2Pt$(acetylene) COMPLEXES

Acetylene	Bond distances (Å)			Bond angles (°)				Reference
	Pt—P	Pt—C	C—C	P—Pt—P	C—Pt—C	dihedral angle	bend-back angle	
1. PhC≡CPh	2.28 2.27	2.01 2.06	1.32(9)	102	39	14	40.41	19
2. NCC≡CCN			1.40			8		20
3. cyclo-C_6H_8	2.264(1) 2.271(1)	2.034(6) 2.044(5)	1.297(8)	109.54(5)	37.1(2)	4.4(3)	41(2)	21
4. cyclo-C_7H_{10}	2.264(1) 2.270(1)	2.035(4) 2.064(4)	1.283(5)	102.58(3)	36.5(1)	7.9(3)	52.7(9)	21
5. PhC≡CCO_2Et	2.269(1) 2.289(1)	2.046(5) 2.014(5) (CO_2Et)	1.286(8)	109.84(5)	36.9(2)	5.2(3)	39.4(4)	37
6. *p*-$NO_2C_6H_4C$≡CCO_2Et	2.278(1) 2.286(1)	2.033(5) 2.015(5) (CO_2Et)	1.313(7)	103.42(4)	37.8(2)	9.1(3)	39.2(1.2)	37
7. F_3CC≡CCF_3	2.277(1) 2.285(1)	2.024(5) 2.031(5)	1.255(9)	100.17(4)	36.1(2)	3.7(4)	39.9(5)	1
8. PhC≡CMe	2.277(3) 2.298(4)	2.014(16) 2.044(17) (Ph)	1.277(25)	103.3(2)	36.7(7)	6.4(7)	39.6(1.4)	This work

withdrawing (CO_2Et), or intermediate (Ph). This apparently "limiting" bend-back angle of approximately 40° suggests that either the mode of bonding in these complexes is relatively insensitive to the nature of the acetylene substituent, or such differences in the bonding in these complexes are too small to be detected by X-ray diffraction studies. A similar "limiting bend-back angle" close to 40° has also been observed for acetylene complexes of other transition metals [38].

The excited state theory described by Orgel [39] and later expanded by Mason [40-42], and the Maitlis molecular orbital continuum of bond types model [6] can both accommodate the bonding in these complexes. In the Maitlis scheme the bonding in these complexes can be presented as being intermediate between A and B, with the Pt—acetylene π^* back donation dominating the acetylene-π—Pt interaction. The *cis*-bent excited state of acetylene was predicted to be *cis*-bent to the extent of 38° in one set of calculations [43], whereas more recent calculations [44] indicate that the state was *cis*-bent to 45.6° with a C≡C bond length of 1.33 Å. This would indicate that the geometry of the coordinated acetylene resembles that of the *cis*-bent excited state.

Acknowledgements

We thank Dr. G.B. Robertson for communicating his results prior to publication. Financial support from the National Research Council of Canada is gratefully acknowledged, and B.W.D. thanks the N.R.C. for the award of a scholarship.

References

1 B.W. Davies and N.C. Payne, Inorg. Chem., 13 (1974) 1848.
2 J. Chatt, G.A. Rowe and A.A. Williams, Proc. Chem. Soc., (1957) 208.
3 J.L. Boston, S.O. Grim and G. Wilkinson, J. Chem. Soc., (1963) 3468.
4 D.A. Harbourne, D.T. Rosever and F.G.A. Stone, Inorg. Nucl. Chem. Lett., 2 (1966) 247.
5 E.O. Greaves, R. Bruce and P.M. Maitlis, Chem. Commun., (1967) 860.
6 E.O. Greaves, C.J.L. Lock and P.M. Maitlis, Canad. J. Chem., 46 (1968) 3879.
7 T.L. Gilchrist, F.J. Graveling and C.W. Rees, Chem. Commun., (1968) 821.
8 C.D. Cook and G.S. Jauhal, J. Amer. Chem. Soc., 90 (1968) 1464.
9 J.H. Nelson, H.B. Jonassen and D.M. Roundhill, Inorg. Chem., 8 (1969) 2591.
10 P.B. Tripathy and D.M. Roundhill, J. Organometal. Chem., 24 (1970) 247.
11 G.L. McLure and W.H. Baddely, J. Organometal. Chem., 25 (1970) 261.
12 J.H. Nelson, J.J.R. Reed and H.B. Jonassen, J. Organometal. Chem., 29 (1971) 163.
13 M.A. Bennett, G.B. Robertson, P.O. Whimp and T. Yoshida, J. Amer. Chem. Soc., 93 (1971) 3797.
14 S. Cenini, R. Ugo and G. La Monica, J. Chem. Soc. A, (1971) 409.
15 P.B. Tripathy, B.W. Renoe, K. Adzamli and D.M. Roundhill, J. Amer. Chem. Soc., 93 (1971) 4406.
16 A. Furlani, P. Carusi and M.V. Russo, J. Organometal. Chem., 67 (1974) 315.
17 W.J. Cherwinski, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1974) 1405.
18 T. Attig and H.C. Clark, personal communication.
19 J.O. Glanville, J.M. Stewart and S.O. Grim, J. Organometal. Chem., 7 (1967) P9.
20 C. Panattoni and R. Graziani, in M. Cais (Ed.), Progress in Coordination Chemistry, Elsevier, London, 1968, p. 310.
21 G.B. Robertson and P.O. Whimp, J. Organometal. Chem., 32 (1972) C69, and J. Amer. Chem. Soc., 97 (1975) 1051.
22 International Tables for X-ray Crystallography, 3rd ed., Kynoch Press, Birmingham, England. Vol. I (1969).
23 W.A. Zachariasen, Acta Crystallogr., 18 (1965) 705.
24 T.C. Furnas, Single Crystal Orienter Instruction Manual. General Electric Company, Milwaukee, Wis., 1957.
25 D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104.

26 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
27 J.A. Ibers and W.C. Hamilton, Acta Crystallogr., 17 (1964) 781.
28 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.
29 R. Eisenberg and J.A. Ibers, Inorg. Chem., 4 (1965) 773.
30 T. Ueki, A. Zalkin and D.H. Templeton, Acta Crystallogr., 20 (1966) 836.
31 D.W.J. Cruickshank and W.S. McDonald, Acta Crystallogr., 23 (1967) 9.
32 A. Zalkin, T.E. Hopkins and D.H. Templeton, Inorg. Chem., 5 (1966) 1769.
33 L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, New York, 1960.
34 J.J. Daly, J. Chem. Soc., (1964) 3799.
35 Interatomic Distances, Special publication No. 18, The Chemical Society, London (1965) p. S16s.
36 M.J. Murray and F.L. Cleveland, J. Amer. Chem. Soc., 61 (1939) 3546.
37 M.A. Bennett, G.B. Robertson, J.M. Rosalky and P.O. Whimp, personal communication.
38 B.W. Davies, Ph. D. Thesis, The University of Western Ontario, London, Ontario, Canada, 1974.
39 L.E. Orgel, Introduction to Transition-Metal Chemistry: Ligand-Field Theory, Wiley, 1960.
40 R. Mason, Nature, 217 (1968) 543.
41 R. McWeeny, R. Mason and A.D.C. Towl, Discuss. Faraday Soc., No. 47, (1969) 20.
42 R. Mason, Chem. Soc. Rev., 1 (1972) 431.
43 H.W. Kroto and D.P. Santry, J. Chem. Phys., 47 (1967) 792.
44 R. Ditchfield, J. Del Bene and J.A. Pople, J. Amer. Chem. Soc., 94 (1972) 4806.