strongly resembles that of the Pt(0) complexes, which are also resistant to nucleophilic attack, that we conclude rather that the reactivity of *trans*-Cl(CH$_3$)(As(CH$_3$)$_3$)$_2$Pt(F$_3$CC≡CCF$_3$) is the observation which requires examination. There are two possible explanations which occur to us. First, whereas the coordination geometry at the Pt atom in both cases is trigonal bipyramidal, the (HB(pz)$_3$)$^-$ ligand is polydentate, occupying three coordination sites. In contrast, in the other five-coordinate complex, there are no chelating ligands, and the possibility of a dissociative mechanism is more readily entertained. We also observe an exceptionally long Pt-Cl bond length in that compound.[2] The second possibility is that the steric constraint imposed by the (HB(pz)$_3$)$^-$ ligand has affected the reactivity of the platinum-acetylene fragment. However, we consider this explanation less likely in the light of the similar geometries of the coordinated acetylene ligand in both compounds (Table VI). The significance of these geometries, and a discussion of the bonding in these compounds, will be given in greater detail in the following paper.[20]

Acknowledgment. We thank the National Research Council of Canada for financial support of this work. B. W. D. is grateful for the award of an NRC scholarship.

Registry No. (CH$_3$)[HB(N$_2$C$_3$H$_3$)$_3$]Pt(F$_3$CC≡CCF$_3$), 50859-75-1.

Supplementary Material Available. Table II, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1843.

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Studies on Metal-Acetylene Complexes. IV. Crystal Structure of Bis(triphenylphosphine)hexafluorobut-2-yneplatinum(0)

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Received October 15, 1973 AIC30753T

The crystal and molecular structure of bis(triphenylphosphine)hexafluorobut-2-yneplatinum(0) has been determined by diffractometric methods. The compound crystallizes in the triclinic space group $P\bar{1}$ (C_i^1). The unit cell constants $a = 11.799$ (2) Å, $b = 16.062$ (3) Å, $c = 9.723$ (1) Å, $\alpha = 99.33$ (1)°, $\beta = 101.47$ (1)°, and $\gamma = 96.75$ (1)° were determined by a least-squares refinement of the diffractometer setting angles of 27 reflections from all regions of reciprocal space in which the data were collected. Full-matrix least-squares refinement on F utilizing 6153 significant ($>3\sigma$) reflections led to residuals $R_1 = 0.037$ and $R_2 = 0.057$. The observed density of 1.65 (2) g cm^{-3} is in good agreement with the calculated density, 1.662 g cm^{-3}, assuming two molecules in the unit cell. The coordination about the platinum atom is essentially trigonal. The C≡C bond of the coordinated hexafluorobut-2-yne ligand makes an angle of 3.6 (4)° with the coordination plane of the platinum atom. The acetylenic triple-bond length has been lengthened on coordination to 1.255 (9) Å in comparison with the average value 1.204 (2) Å observed for a series of uncoordinated acetylenes. The mean departure of the hexafluorobut-2-yne ligand from linearity in the complex is 39.9 (5)°. This value is consistent with the acetylene being considerably perturbed on coordination, in agreement with the observation that $\Delta\nu$(C≡C) is 525 cm^{-1}. The bonding in this and other acetylene complexes is discussed with particular emphasis being paid to the X-ray structural information gained to date.

Introduction

During our recent studies[1,2] of five-coordinate platinum-acetylene complexes we noticed that there was little reliable crystallographic structural information on any platinum(0)-acetylene complex apart from a preliminary communication of the structure of bis(triphenylphosphine)diphenylacetyleneplatinum(0)[3] and a description of the structure of bis(triphenylphosphine)cycloheptyneplatinum(0)[4] which appeared in 1971. In fact, acetylene complexes of transition metals have received scant attention from X-ray crystallographers despite considerable interest in such compounds.[5-8] Until recently, few complexes had been examined, whereas Guggenberger[9] has recently tabulated structural data for 24 metal-olefin complexes.

One notable aspect of the limited data obtained to date is the fairly high standard deviations associated with the parameters determined in most of the metal-acetylene complexes studied. We therefore undertook a single-crystal X-ray diffraction study of bis(triphenylphosphine)hexafluorobut-2-yneplatinum(0) in an attempt to obtain precise structural information for a platinum(0)-acetylene complex.

((C$_6$H$_5$)$_3$P)$_2$(CF$_3$C≡CCF$_3$)Pt^0 was first prepared by Wilkinson, *et al.*, in 1963.[10] Hexafluorobut-2-yne was chosen as the acetylenic ligand to be studied in order that we might compare the ligand perturbation upon coordination with that we observe in the five-coordinate complexes *trans*-Cl(CH$_3$)(As(CH$_3$)$_3$)$_2$(CF$_3$C≡CCF$_3$)Pt^{II} [1] and (CH$_3$)(HB(N$_2$C$_3$H$_3$)$_3$)(CF$_3$C≡CCF$_3$)Pt^{II}.[2]

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Experimental Section

Crystals were supplied by L. E. Manzer and were recrystallized from hot dichloromethane. A preliminary photographic examination of the $(0\text{-}1)kl$, $h(0\text{-}1)l$, and $hk(0\text{-}2)$ zones showed that the crystals belonged to the triclinic system. The reduced cell $a = 11.799$ (2) Å, $b = 16.062$ (3) Å, $c = 9.723$ (1) Å, $\alpha = 99.33$ (1)°, $\beta = 101.47$ (1)°, and $\gamma = 96.75$ (1)° was chosen. The density of the colorless crystals was determined by the flotation method using dichloromethane and dibromoethane. The observed density, 1.65 (2) g cm^{-3}, agrees well with the calculated density, 1.662 g cm^{-3}, assuming two molecular units in the cell. This fact, together with the centrosymmetric habit of the crystals, led us to choose $P\bar{1}$ (C_i^1, No. 2)[11] as the space group. The successful refinement in this space group confirms our choice.

The crystal used for data collection was approximately 0.2 × 0.2 × 0.3 mm in dimensions. Optical goniometry identified faces of the form $\{010\}$, prismatic faces of the form $\{1\bar{1}0\}$, and end faces $(0\bar{1}1)$, $(01\bar{1})$, $(10\bar{1})$, and $(\bar{1}01)$. Prior to data collection the crystal dimensions were accurately measured using a microscope fitted with a filar eyepiece, in preparation for an absorption correction (μ(Cu Kα) = 86.5 cm^{-1}).

Intensity data were collected on a Picker FACS-1 automatic four-circle diffractometer. Cu Kα radiation (λ 1.54056 Å) was used. The crystal was mounted with the diffractometer spindle axis approximately collinear with the long dimension [001] of the crystal. The cell constants and their estimated standard deviations at 21° were determined by a least-squares refinement of the angular setting values for 27 reflections in all regions of reciprocal space in which the data were collected. ω scans of low-angle axial reflections using a takeoff angle of 0.9° and a wide open counter aperture were typically 0.085° width at half-height. This was considered acceptable.[12] For data collection, Cu radiation was prefiltered with a nickel-foil filter 0.07 mm thick. A takeoff angle on the tube of 2.5° provided 83% of the maximum available Bragg intensity. The counter was placed 32 cm from the crystal and the aperture was 4 mm square. All reflections in the hemisphere for which $l \geq 0$ and $2.0 \leq 2\theta \leq 130°$ were collected in four shells. The θ–2θ scan technique was used. The scan width was 1.5°, corrected for dispersion, at a scan rate of 1°/min. Stationary-background counts for 10 sec were taken at the extremes of each scan. The scan width was increased to 1.7° for the high-angle shells, ($2\theta > 60°$). Coincidence losses were minimized for strong reflections by using copper-foil attenuators. Six standard reflections, (200), (020), $(\bar{2}00)$, $(0\bar{2}0)$, (043), and (002) were recorded at intervals throughout the data collection to monitor crystal and generator stability.

A total of 6702 reflections were measured and the recorded intensities corrected for background, polarization, and Lorentz effects. All six standards remained steady throughout data collection. A standard deviation (σ) was assigned to each intensity (I) such that

$$(\sigma(I))^2 = \text{count} + {}^1\!/_4(t_c/t_b)^2(b_1 + b_2) + (pI)^2$$

where $I = \text{count} - {}^1\!/_2(b_1 + b_2)t_c/t_b$, count = total count measured in time t_c, and b_1 and b_2 are background counts each measured in time t_b. The constant p was chosen as 0.04. A total of 6153 reflections were regarded as observed ($I > 3\sigma(I)$) and were used in the subsequent structure solution and refinement.

Structure Solution and Refinement

The positions of the Pt atom and the two P atoms were located from a three-dimensional Patterson synthesis. One cycle of full-matrix least-squares refinement on F, varying positional parameters and isotropic temperature factors, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, led to the agreement factors

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.236$$

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)^{1/2} = 0.321$$

The weight w is defined as $4F_o{}^2/\sigma^2(F_o{}^2)$. The atomic scattering factors for neutral Pt, P, F, and C atoms were those of Cromer and Waber,[13] while that of H was taken from Stewart, *et al.*[14] Anomalous dispersion contributions to the scattering factor were included for Pt, P, and F atoms and were taken from Cromer and Liberman.[15]

A difference-Fourier synthesis at this stage located the remaining 46 nonhydrogen atoms in the molecule. A series of least-squares refinements in which the Pt atom, the two P atoms, and six F atoms were refined anisotropically, the acetylenic C atoms isotropically, and the phenyl rings as rigid groups with D_{6h} symmetry and a C-C bond length of 1.392 Å led to residuals $R_1 = 0.056$ and $R_2 = 0.081$. The molecular geometry at this stage was satisfactory.

An absorption correction was then applied; trials showed transmission factors varying from 0.209 to 0.318. The analytical method was used.[16] The final cycles of refinement were performed under the following conditions. (i) The 13 nongroup atoms in the molecule were allowed to vibrate anisotropically. (ii) The six phenyl rings were constrained as groups. (iii) Isotropic factors were refined for each ring C atom. (iv) The contributions of the 30 phenyl H atoms were included. Calculated positions ($d_{\text{C-H}} = 1.00$ Å) were assumed. All 30 calculated positions corresponded to regions of positive electron density (0.4–0.6 e Å^{-3}) in a difference Fourier synthesis calculated at $R_1 = 0.056$. (v) As F_o was consistently less than F_c for intense, low-angle reflections, an extinction parameter was refined. The final value of the extinction coefficient was 1.15 (6) × 10^{-5}. Under these conditions, with 6153 observations and 191 variables, an observations to variables ratio of 32.2 to 1, the refinement converged at $R_1 = 0.037$ and $R_2 = 0.057$. No positional parameter shift exceeded one-third of its estimated standard deviation in the final cycle of refinement. A statistical examination of the R_2 values of all reflections showed no unusual trends with $|F_o|$, indices, $\lambda^{-1} \sin\theta$, or the diffractometer setting angles χ and ϕ. The standard deviation on an observation of unit weight is 2.54 electrons. A final difference-Fourier synthesis showed five peaks of intensity greater than 1.0 e Å^{-3}, the largest of which, 1.36 (13) e Å^{-3}, is at (0.20, 0.30, 0.24) in the vicinity of P(2).

The final positional and thermal parameters of the nongroup atoms are given in Table I. The group parameters and the derived atom positional and isotropic thermal parameters for the C atoms in the six phenyl rings are given in Table II, along with the phenyl H atom parameters. The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table III.[17]

Description of the Structure

The structure consists of discrete molecular units, the closest intermolecular distance of approach being 2.66 Å between phenyl ring H atoms bonded to 6C2 and 5C3. The principal intramolecular bond lengths and bond angles are given in Table IV. The inner coordination sphere of the Pt atom, together with the atom-labeling scheme and selected bond distances, is shown in Figure 1. Figure 2 shows a stereoview of the molecule. Table V lists the root-mean-square amplitudes of vibration (in Å × 10^3). Selected least-squares planes are tabulated in Table VI.

The coordination about the Pt atom is essentially planar. A weighted least-squares plane through the Pt, P(1), P(2), C(2), and C(3) atoms is included in Table VI. The bond between the acetylenic C atoms C(2) and C(3) makes an angle of 3.6 (4)° with the plane of the Pt and the two P atoms. The Pt–P distances are 2.277 (1) and 2.285 (1) Å. Although statistically inequivalent due to the low errors associated with these bond lengths, the two P atoms are in chemically equivalent environments and no significance is attached to this difference (0.008 Å = 6σ). Comparable values of 2.292 (7)

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[17] See paragraph at end of paper regarding supplementary material.

Table I. Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.156106 (14)	0.216122 (11)	0.201626 (18)	341 (1)	447 (2)	332 (1)	34 (1)	94 (1)	84 (1)
P(2)	0.22725 (10)	0.33254 (7)	0.11948 (13)	388 (6)	429 (6)	349 (6)	45 (5)	74 (5)	82 (5)
P(1)	0.31993 (10)	0.15358 (8)	0.24335 (13)	390 (6)	439 (6)	382 (6)	55 (5)	105 (5)	95 (5)
F(1)	−0.0533 (5)	0.0054 (3)	0.2016 (7)	1448 (48)	774 (28)	1468 (52)	−393 (31)	332 (41)	68 (32)
F(2)	−0.1309 (7)	0.0850 (5)	0.3378 (12)	1574 (58)	1632 (59)	3755 (128)	488 (46)	1972 (79)	1340 (73)
F(3)	0.0373 (6)	0.0599 (4)	0.4099 (7)	1751 (60)	1379 (48)	1244 (47)	−65 (42)	491 (44)	789 (41)
F(4)	−0.2130 (4)	0.2205 (4)	0.1848 (11)	439 (24)	1596 (56)	3106 (114)	122 (29)	204 (42)	370 (67)
F(5)	−0.1017 (6)	0.3294 (5)	0.3018 (9)	1003 (41)	1922 (66)	2025 (81)	760 (45)	−103 (42)	−969 (60)
F(6)	−0.1290 (6)	0.3025 (6)	0.0869 (9)	1552 (58)	2630 (90)	1870 (73)	1425 (63)	747 (53)	1335 (70)
C(1)	−0.0347 (8)	0.0768 (5)	0.2980 (11)	924 (55)	786 (47)	1040 (65)	−200 (41)	526 (52)	197 (46)
C(2)	0.0142 (5)	0.1519 (4)	0.2471 (6)	488 (29)	685 (35)	467 (30)	−77 (26)	163 (25)	49 (26)
C(3)	−0.0140 (5)	0.2193 (4)	0.2101 (6)	425 (27)	695 (34)	459 (29)	19 (24)	148 (23)	34 (26)
C(4)	−0.1136 (5)	0.2654 (5)	0.1966 (8)	473 (33)	907 (46)	743 (45)	129 (31)	128 (31)	14 (38)

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. [b] $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$ (Å). The values have been multiplied by 10^4. The thermal ellipsoid expression is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Group Parameters

Group	x_g[a]	y_g	z_g	δ	ϵ	η
Ring 1	0.4350 (2)	0.1118 (2)	−0.0284 (3)	−1.858 (3)	−2.736 (2)	−1.577 (3)
Ring 2	0.2756 (3)	−0.0352 (2)	0.3155 (3)	−1.483 (3)	−2.250 (3)	0.335 (4)
Ring 3	0.5022 (2)	0.2708 (2)	0.5162 (3)	1.755 (4)	−2.372 (2)	1.295 (4)
Ring 4	0.1352 (2)	0.4996 (2)	0.2612 (3)	−2.987 (5)	−2.141 (2)	1.389 (5)
Ring 5	0.5061 (2)	0.3979 (2)	0.1798 (3)	0.107 (3)	−2.162 (2)	−0.054 (4)
Ring 6	0.1453 (2)	0.3015 (1)	−0.2238 (3)	−0.726 (2)	2.958 (2)	−1.782 (2)

Derived phenyl group C atoms					Derived phenyl group H atoms[b]			
Atom	x	y	z	B, Å^2	Atom	x	y	z
Ring 1								
1C1	0.3887 (3)	0.1288 (2)	0.0923 (3)	3.70 (9)				
1C2	0.5048 (3)	0.1161 (3)	0.1069 (3)	4.49 (10)	H2	0.5545	0.1193	0.2038
1C3	0.5512 (3)	0.0991 (3)	−0.0138 (5)	5.60 (13)	H3	0.6344	0.0909	−0.0037
1C4	0.4814 (4)	0.0948 (3)	−0.1490 (4)	6.15 (15)	H4	0.5144	0.0838	−0.2358
1C5	0.3652 (3)	0.1075 (3)	−0.1636 (3)	5.66 (13)	H5	0.3147	0.1050	−0.2606
1C6	0.3188 (2)	0.1245 (3)	−0.0429 (4)	4.42 (10)	H6	0.2348	0.1333	−0.0532
Ring 2								
2C1	0.2965 (3)	0.0477 (2)	0.2912 (4)	3.66 (9)				
2C2	0.3522 (3)	0.0274 (2)	0.4191 (4)	5.21 (12)	H2	0.4086	0.0721	0.4925
2C3	0.3313 (4)	−0.0555 (3)	0.4434 (4)	6.17 (15)	H3	0.3722	−0.0702	0.5347
2C4	0.2547 (4)	−0.1181 (2)	0.3398 (5)	6.38 (15)	H4	0.2391	−0.1775	0.3581
2C5	0.1991 (4)	−0.0979 (2)	0.2120 (5)	6.24 (15)	H5	0.1424	−0.1425	0.1393
2C6	0.2200 (2)	0.0150 (2)	0.1877 (3)	4.65 (11)	H6	0.1787	−0.0002	0.0971
Ring 3								
3C1	0.4281 (3)	0.2187 (2)	0.3958 (4)	3.57 (8)				
3C2	0.3906 (3)	0.2350 (3)	0.5232 (4)	5.42 (13)	H2	0.3104	0.2089	0.5275
3C3	0.4647 (4)	0.2871 (3)	0.6436 (4)	6.50 (16)	H3	0.4377	0.2980	0.7347
3C4	0.5763 (4)	0.3228 (3)	0.6366 (4)	6.14 (15)	H4	0.6292	0.3599	0.7228
3C5	0.6138 (3)	0.3065 (3)	0.5092 (5)	5.60 (13)	H5	0.6934	0.3325	0.5037
3C6	0.5397 (3)	0.2545 (2)	0.3888 (4)	4.70 (11)	H6	0.5661	0.2434	0.2965
Ring 4								
4C1	0.1725 (3)	0.4278 (2)	0.1944 (4)	3.74 (9)				
4C2	0.1626 (4)	0.4351 (2)	0.3360 (4)	4.82 (11)	H2	0.1840	0.3890	0.3905
4C3	0.1253 (4)	0.5069 (3)	0.4028 (4)	6.06 (14)	H3	0.1199	0.5122	0.5063
4C4	0.0978 (4)	0.5714 (2)	0.3280 (5)	6.50 (16)	H4	0.0712	0.6230	0.3783
4C5	0.1077 (4)	0.5642 (2)	0.1864 (5)	6.91 (17)	H5	0.0866	0.6106	0.1345
4C6	0.1451 (4)	0.4923 (3)	0.1196 (4)	5.69 (13)	H6	0.1507	0.4874	0.0187
Ring 5								
5C1	0.3857 (2)	0.3716 (2)	0.1514 (4)	3.39 (8)				
5C2	0.4396 (3)	0.4359 (2)	0.2683 (4)	4.17 (10)	H2	0.3924	0.4641	0.3302
5C3	0.5600 (3)	0.4622 (2)	0.2966 (4)	5.63 (13)	H3	0.5992	0.5097	0.3785
5C4	0.6265 (2)	0.4242 (3)	0.2082 (5)	5.21 (12)	H4	0.7137	0.4439	0.2277
5C5	0.5726 (3)	0.3599 (2)	0.0913 (4)	4.72 (11)	H5	0.6216	0.3323	0.0286
5C6	0.4522 (3)	0.3336 (2)	0.0629 (3)	4.16 (10)	H6	0.4148	0.2867	−0.0197
Ring 6								
6C1	0.1788 (3)	0.3185 (2)	−0.0752 (3)	3.53 (8)				
6C2	0.2309 (3)	0.3707 (2)	−0.1537 (4)	4.28 (10)	H2	0.2919	0.4209	−0.1030
6C3	0.1974 (3)	0.3537 (2)	−0.3023 (4)	4.73 (11)	H3	0.2341	0.3917	−0.3583
6C4	0.1117 (3)	0.2845 (2)	−0.3724 (3)	4.98 (12)	H4	0.0873	0.2726	−0.4786
6C5	0.0596 (3)	0.2323 (2)	−0.2938 (4)	4.64 (11)	H5	−0.0017	0.1827	−0.3436
6C6	0.0931 (3)	0.2493 (2)	−0.1452 (3)	4.02 (9)	H6	0.0561	0.2119	−0.0883

[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: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965). [b] Hydrogen atoms were assigned isotropic thermal parameters, $B = 4.0$ Å^2.

Table IV. Selected Bond Distances and Angles

Bond	Distance, Å	Bond	Distance, Å
Pt-P(1)	2.277 (1)	C(1)-F(1)	1.324 (10)
Pt-P(2)	2.285 (1)	C(1)-F(2)	1.284 (9)
Pt-C(2)	2.024 (5)	C(1)-F(3)	1.328 (11)
Pt-C(3)	2.031 (5)	C(4)-F(4)	1.276 (9)
P(1)-1C1	1.825 (4)	C(4)-F(5)	1.297 (10)
P(1)-2C1	1.839 (4)	C(4)-F(6)	1.301 (9)
P(1)-3C1	1.831 (4)	C(1)-C(2)	1.475 (9)
P(2)-4C1	1.829 (4)	C(2)-C(3)	1.255 (9)
P(2)-5C1	1.848 (4)	C(3)-C(4)	1.457 (9)
P(2)-6C1	1.833 (4)		

Atoms	Angle, deg	Atoms	Angle, deg
P(1)-Pt-P(2)	100.17 (4)	C(2)-C(1)-F(1)	112.90 (69)
P(1)-Pt-C(2)	114.05 (19)	C(2)-C(1)-F(2)	113.56 (76)
P(2)-Pt-C(3)	109.78 (18)	C(2)-C(1)-F(3)	112.65 (68)
C(2)-Pt-C(3)	36.05 (24)	F(1)-C(1)-F(2)	107.70 (76)
Pt-P(1)-1C1	116.32 (13)	F(1)-C(1)-F(3)	103.86 (79)
Pt-P(1)-2C1	114.66 (12)	F(2)-C(1)-F(3)	105.43 (83)
Pt-P(1)-3C1	110.07 (12)	C(3)-C(4)-F(4)	115.65 (68)
1C1-P(1)-2C1	100.51 (17)	C(3)-C(4)-F(5)	112.74 (60)
1C1-P(1)-3C1	109.56 (17)	C(3)-C(4)-F(6)	114.41 (61)
2C1-P(1)-3C1	104.81 (17)	F(4)-C(4)-F(5)	107.11 (76)
Pt-P(2)-4C1	110.75 (13)	F(4)-C(4)-F(6)	103.79 (76)
Pt-P(2)-5C1	122.29 (12)	F(5)-C(4)-F(6)	101.82 (81)
Pt-P(2)-6C1	111.30 (11)	Pt-C(2)-C(1)	72.25 (35)
4C1-P(2)-5C1	101.78 (16)	Pt-C(2)-C(3)	147.06 (56)
4C1-P(2)-6C1	106.16 (16)	Pt-C(3)-C(4)	148.62 (50)
5C1-P(2)-6C1	103.02 (15)	Pt-C(3)-C(2)	71.71 (35)
		C(1)-C(2)-C(3)	140.62 (63)
		C(4)-C(3)-C(2)	139.55 (59)

Table V. Root-Mean-Square Amplitudes of Vibration (in Å × 10^3)

Atom	Min	Med	Max
Pt[a]	1744 (4)	1877 (4)	2143 (4)
P(1)	188 (2)	200 (1)	211 (1)
P(2)	186 (2)	196 (1)	210 (1)
F(1)	229 (5)	382 (7)	435 (7)
F(2)	202 (6)	372 (7)	651 (11)
F(3)	224 (6)	407 (7)	451 (7)
F(4)	208 (6)	401 (7)	567 (10)
F(5)	231 (6)	318 (7)	626 (11)
F(6)	246 (6)	363 (7)	582 (10)
C(1)	188 (8)	307 (9)	374 (11)
C(2)	194 (7)	217 (7)	289 (7)
C(3)	194 (7)	216 (7)	276 (7)
C(4)	215 (8)	262 (8)	320 (8)

[a] Å × 10^4.

Table VI. Weighted Least-Squares Planes

Plane 1		Plane 2	
Atoms	Distance from plane, Å	Atoms	Distance from plane, Å
Pt	−0.0001 (2)	C(1)	−0.0026 (98)
P(1)	0.0025 (12)	C(2)	0.0025 (56)
P(2)	0.0013 (12)	C(3)	−0.0024 (55)
C(2)	−0.0107 (56)	C(4)	0.0015 (74)
C(3)	0.0672 (55)		

Equation of plane

Plane 1: $0.1129x + 5.645y + 8.081z - 2.867 = 0$

Plane 2: $1.094x + 4.832y + 8.089z - 2.747 = 0$

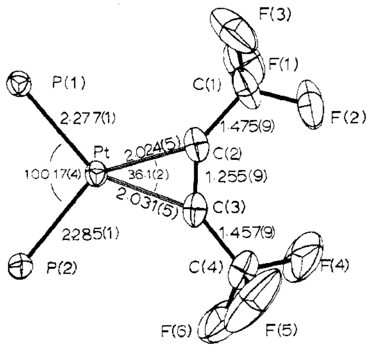

Figure 1. The inner coordination sphere about the Pt atom showing the labeling scheme and selected bond distances and angles.

and 2.278 (8) Å are observed in $((C_6H_5)_3P)_2Pt(Cl_2C{=}CCl_2)$,[18] 2.291 (9) and 2.288 (8) Å in $((C_6H_5)_3P)_2Pt((NC)_2C{=}C(CN)_2)$,[19] and 2.265 (2) and 2.270 (2) Å in $((C_6H_5)_3P)_2Pt(H_2C{=}CH_2)$.[20] The two P atoms of the triphenylphosphine ligands subtend an angle of 100.17 (4)° at the Pt atom. Comparable values of 111.6 (1), 101.4 (3), and 100.6 (2)° are observed in $((C_6H_5)_3P)_2Pt(H_2C{=}CH_2)$, $((C_6H_5)_3P)_2Pt((NC)_2C{=}C(CN)_2)$, and $((C_6H_5)_3P)_2Pt(Cl_2C{=}CCl_2)$, respectively. The observed dimensions are consistent with a trigonal-planar geometry about the Pt atom, if the acetylene is viewed as a monodentate ligand. Table VII shows some comparative data on the systems $((C_6H_5)_3P)_2Pt(un)$ where un is an olefin or an acetylene ligand.

The mean P-C distance in the triphenylphosphine ligands is 1.837 (5) Å. The mean angle subtended by the phenyl ring C1 atoms at the P atoms is 104.3 (1.5)°. The acetylene has been perturbed considerably on coordination. The acetylenic triple-bond length of 1.255 (9) Å is larger than an average value for uncoordinated acetylenes of 1.204 (2) Å. The mean acetylenic bend-back angle is 39.9 (5)°. Geometrical data on the previously determined metal-acetylene structures are summarized in Table VIII. In $(CH_3)(HB(N_2C_3H_3)_3)(F_3CC{\equiv}CCF_3)Pt^{II}$ [2] the bend back-angle is 34.4 (3)° and the acetylenic bond length is 1.292 (12) Å. Thus it would appear that the acetylenic triple bond in $((C_6H_5)_3P)_2Pt(F_3CC{\equiv}CCF_3)$ is shorter than might have been expected. A least-squares plane through the acetylenic C atoms is given in Table VI. The acetylenic C atoms C(2) and C(3) subtend an angle of 36.0 (2)° at the Pt atom. The dihedral angle between the P(1)-Pt-P(2) plane and the C(2)-Pt-C(3) plane is 3.7 (4)°. The Pt-C distances to C(2) and C(3) are 2.024 (5) and 2.031 (5) Å, respectively, shorter than the values observed in the corresponding olefin complexes. The mean C-F distance in the two CF_3 groups is 1.301 (8) Å and the mean F-C-F angle is 104.9 (9)°. Comparable mean values of 1.306 (11) Å and 105.9 (5)° are observed in $(CH_3)(HB(N_2C_3H_3)_3)Pt(F_3CC{\equiv}CCF_3)$.[2] The mean C-$CF_3$ distance is 1.466 (9) Å, comparable to the value of 1.463 (9) Å we observed in the polylpyrazolylborate complex.

Discussion

Pertinent data on the previously determined structures of metal-acetylene complexes in which the acetylene is sideways bonded to one metal atom are presented in Table VIII. The high standard deviations associated with these observations limit the significant comparisons to be made. Clearly, there is a need for further precise X-ray structural information on metal-acetylene complexes. However, some comments can be made. There appears to be a general trend such that as the acetylenic triple bond is lengthened upon coordination, so the bend-back angle increases. This is only qualitative as the graphical representation (Figure 3) illustrates.

The acetylenic triple-bond length observed in this study, 1.255 (9) Å, is shorter than might have been expected for an

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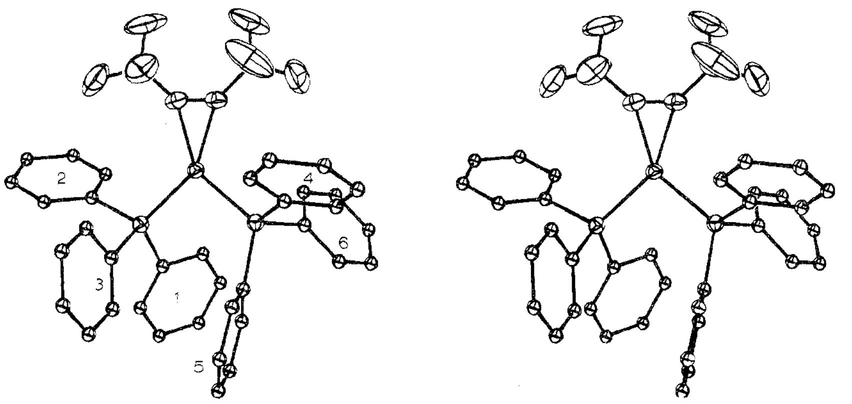

Figure 2. A stereoview of the molecule. Thermal ellipsoids are drawn at the 30% probability level. For clarity, the phenyl ring C atoms are assigned isotropic thermal parameters of 2.0 Å^2.

Table VII. Structural Data for $((C_6H_5)_3P)_2Pt(un)$ (un = olefin or acetylene)

un	Bond distances, Å			Angles, deg			Ref
	Pt-P	Pt-C	C-C	P-Pt-P	C-Pt-C	Dihedral[a]	
C_2H_4	2.265 (2) 2.270 (2)	2.106 (8) 2.116 (8)	1.434 (13)	111.6 (1)	39.7 (4)	1.6	20
C_2Cl_4	2.278 (8) 2.292 (7)	2.02 (3) 2.05 (3)	1.62 (3)	100.6 (2)	47.1 (1.0)	12.3 (1.5)	18
$C_2(CN)_4$	2.288 (8) 2.291 (9)	2.10 (3) 2.12 (3)	1.49 (5)	101.4 (3)	41.5 (1.3)	8.3	19
$C_6H_5C{\equiv}CC_6H_5$	2.28 2.27	2.01 2.06	1.32 (9)	102	39		3
$F_3CC{\equiv}CCF_3$	2.277 (1) 2.285 (1)	2.024 (5) 2.031 (5)	1.255 (9)	100.17 (4)	36.05 (24)	3.7 (4)	This work
c-C_7H_{10}	2.272 (2) 2.264 (2)	2.04 (1) 2.07 (1)	1.294 (17)	102.5	36.7	8.3	4

[a] The dihedral angle is the angle between the normals to the P-Pt-P and the C-Pt-C planes.

Table VIII. Structural Data for Transition Metal-Acetylene Complexes

No.	Compd	C≡C, Å	Bend-back angle, deg	Δν(C≡C),[n] cm^{-1}	Ref
1	$((C_6H_5)_3P)_2Pt(C_6H_5C{\equiv}CC_6H_5)$	1.32 (9)	40	468[a]	3
2	$((CH_3)_3CN{\equiv}C)_2Ni(C_6H_5C{\equiv}CC_6H_5)$	1.28 (2)	31 (1)	412[b]	*c*
3	$((C_6H_5)_3P)_2Pt(F_3CC{\equiv}CCF_3)$	1.255 (9)	39.9 (5)	525[a]	This work
4	$(\pi\text{-}C_5H_5)(CO)Nb(C_6H_5C{\equiv}CC_6H_5)_2$	1.35 (2)	42 (1)	493	*d*
5	$(\pi\text{-}C_5H_5)(CO)(\pi\text{-}C_4(C_6H_5)_4)Nb(C_6H_5C{\equiv}CC_6H_5)$	1.26 (4)	39 (3)	442	*e*
6	$(CO)W(C_6H_5C{\equiv}CC_6H_5)_3$	1.30	40	542[f]	*g*
7	*trans*-$(H_3CC_6H_4NH_2)Cl_2Pt((CH_3)_3CC{\equiv}CC(CH_3)_3)$	1.24 (2)	18, 15 (1)		*h*
8	*trans*-$[(CH_3)((CH_3)_2C_6H_5)P)_2Pt(H_3CC{\equiv}CCH_3)]PF_6$	1.22 (3)	8, 16 (3)	156	*i*
9	$K[Cl_3Pt((C_2H_5)_2C(OH)C{\equiv}CC(OH)(C_2H_5)_2)]$	1.18 (3)	19, 21 (2)		*j*
10	*trans*-$Cl(CH_3)((CH_3)_3As)_2Pt(F_3CC{\equiv}CCF_3)$	1.32 (4)	30, 45 (4)	462	1
11	$(CO)((C_6H_5)_3P)_2Ir(\text{-}C(CN){=}CHCN)(NCC{\equiv}CCN)$	1.29 (2)	40 (1)	521[k]	*l*
12	$(CH_3)(HB(N_2C_3H_3)_3)Pt(F_3CC{\equiv}CCF_3)$	1.292 (12)	34.4 (4)	457	2
13	$((C_6H_5)_3P)_2Pt(c\text{-}C_7H_{10})$	1.294 (17)	39, 43		3
14	$(\pi\text{-}C_5H_5)(C_6H_5)(C_6H_5C{\equiv}CC_6H_5)OW$	1.29 (3)	35, 38 (4)	474	*m*

[a] E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968). [b] S. Otsuka, T. Yoshida, and Y. Tatsumo, *J. Chem. Soc. D*, 67 (1967). [c] R. S. Dickson and J. A. Ibers, *J. Organometal. Chem.*, **36**, 191 (1972). [d] A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 294 (1969). [e] A. I. Gusev and Yu. T. Struchkov, *ibid.*, **10**, 515 (1969). [f] D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasseli, *J. Amer. Chem. Soc.*, **86**, 3261 (1964). [g] R. M. Laine, R. E. Moriarty, and R. Bau, *ibid.*, **94**, 1402 (1972). [h] G. R. Davies, W. Hewertson, R. H. B. Mais, P. G. Owston, and C. G. Patel, *J. Chem. Soc. A*, 1873 (1970). [i] B. W. Davies and N. C. Payne, *Can. J. Chem.*, **51**, 3477 (1973). [j] A. I. Beauchamp, F. D. Rochon, and T. Theophanides, *ibid.*, **51**, 126 (1973). [k] G. L. McLure and W. H. Baddely, *J. Organometal. Chem.*, **27**, 155 (1971). [l] R. M. Kirchner and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 1095 (1973). [m] N. G. Bokiy, Yu. V. Gatilov, Yu. T. Struchkov, and N. A. Ustynyuk, *J. Organometal. Chem.*, **54**, 213 (1973). [n] Δν(C≡C) = [ν(C≡C)(acetylene)] − [ν(C≡C)(complex)].

acetylene that has been perturbed from linearity to the extent of 40°. However, this bond length has the lowest standard deviation of all the complexes listed in Table VIII. We noted earlier that the two Pt-P distances differed by 0.008 Å, a difference of 6σ, although the two P atoms are in chemically equivalent environments in the molecule. We therefore recognize that there exists the possibility that the standard deviations have been underestimated. More precise data on related complexes are needed before any theoretical significance can be attached to this apparently "short" bond.

However, the acetylenic bend-back angles, which measure the departure of the acetylene ligand from linearity, provide a more useful criterion for evaluating the perturbation of the acetylene on coordination. Another criterion for evaluating this perturbation is Δν(C≡C), the reduction in frequency of the symmetric stretching mode of the acetylenic triple bond resulting from coordination. Figure 4 shows that, for those complexes for which there are infrared data available, there is a reasonable straight-line relationship between the mean acetylenic bend-back angle determined by crystallographic studies and Δν(C≡C).

The bonding in metal-acetylene complexes has received

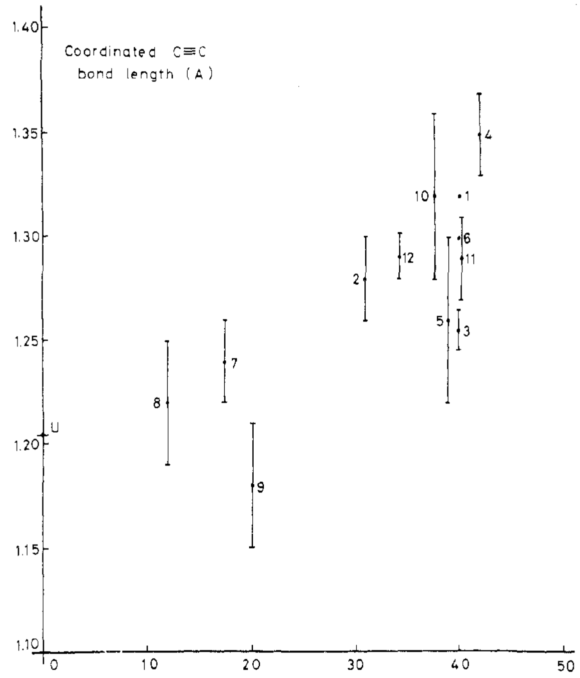

Figure 3. A plot of acetylenic triple bond lengths $d(\mathrm{C{\equiv}C})$ *vs.* mean bend-back angles observed in metal-acetylene complexes. Error bars are $\pm\sigma$ on $d(\mathrm{C{\equiv}C})$. *U* indicates the average triple-bond length of free acetylenes. Points on the graphs in Figures 3 and 4 are labeled to correspond to the compound numbers in Table VIII.

much theoretical attention. A modified Dewar-Chatt-Duncanson scheme,[21] a scheme based on contributions from the excited state of the coordinated acetylene,[22] and the molecular orbital continuum of bond types[23] have all been used. All theories seem to suggest that the stronger the metal-acetylene interaction, the longer the acetylenic triple bond becomes and the greater is the departure of the coordinated acetylene from linearity. CNDO calculations showed that metal→acetylene π^* back-bonding is essential for the acetylene to become bent on coordination.[24] The cis-bent excited state of acetylene (bend-back angle = 38°, C≡C = 1.38 Å[25]) was shown to be preferred to the trans-bent excited state, the first excited state of the free acetylene.[24]

The crystallographic results obtained to date can be summarized thus as follows: (a) all metal-acetylene complexes investigated have a cis-bent acetylene moiety; (b) there is yet no clear correlation between bend-back angle and acetylenic bond length. If we accept the general theoretical agreement about the metal-acetylene bond, three distinct classes of complex emerge from the structural studies to date.

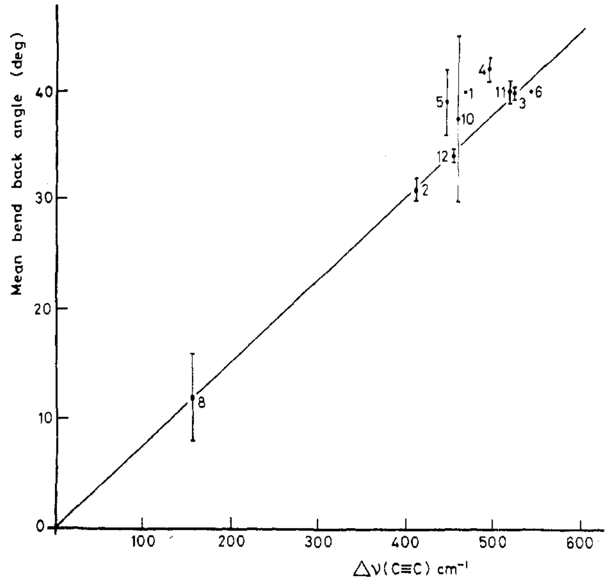

Figure 4. A plot of mean bend-back angles ($\pm\sigma$) *vs.* $\Delta\nu(\mathrm{C{\equiv}C})$. σ values are calculated from $\sigma = [\Sigma_{i=1}{}^{i=n}(x_i - \bar{x})^2/n(n-1)]^{1/2}$.

(a) **Complexes with "Electron-Rich" Metal Atoms (*e.g.*, Compounds 1-6 and 13-14 in Table VIII).** These complexes have some donation from the acetylene π orbitals to empty metal d or dp hybrids, but the principal component of the bonding is back-donation from filled metal orbitals to empty π^* orbitals of the acetylene ligand. The largest $\Delta\nu(\mathrm{C{\equiv}C})$ values and the biggest departures of the ligand from linearity upon coordination are observed here.

(b) **Complexes with "Electron-Deficient" Metal Atoms (*e.g.*, Compounds 7-9 in Table VIII, the Methylplatinum Cations and the Acetylene Analogs of Zeise's Salt).** These complexes have a small (~200 cm^{-1}) reduction in $\Delta\nu(\mathrm{C{\equiv}C})$ on coordination, and the acetylene is bonded perpendicular to the coordination plane of the Pt atom. Crystallographic results indicate only small ligand perturbations (bend-back angles ~20°). Acetylene to metal σ bonding is dominant, though there is some metal to acetylene π back-bonding, as evidenced by the bend-back angles.

(c) **Five-Coordinate Complexes—an Intermediate Situation (*e.g.*, Compounds 10-12 in Table VIII).** The complexes have appreciable $\Delta\nu(\mathrm{C{\equiv}C})$ values on coordination and fairly large bend-back angles in the range 30-40°. Both σ and π contributions are important in the bonding. The large bend-back angles suggest that metal→acetylene π^* back-bonding may be dominant and that these complexes more closely resemble class (a) rather than class (b) complexes.

Acknowledgments. We thank the National Research Council of Canada for financial support. B. W. D. gratefully acknowledges the award of an NRC scholarship.

Registry No. $((\mathrm{C_6H_5})_3\mathrm{P})_2(\mathrm{CF_3C{\equiv}CCF_3})\mathrm{Pt}^0$, 23626-16-6.

Supplementary Material Available. Table III, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1848.

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