Drs. H. L. Carrell and C.-C. Tsai for helpful suggestions during the course of this investigation. The figures were prepared by the late Mrs. Maryellin Reinecke.

Registry No. $Ni_2[(CF_3)_2PSP(CF_3)_2]_2(CO)_3$, 51391-40-3.

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-74-1839.

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Studies on Metal-Acetylene Complexes. III. Crystal and Molecular Structure of Methyl(hydrotris(1-pyrazolyl)borato)hexafluorobut-2-yneplatinum(II)

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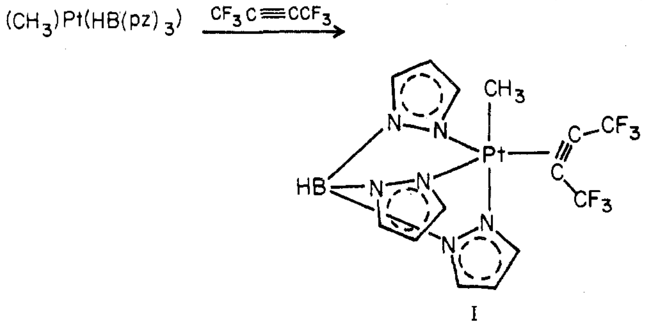
The crystal and molecular structure of methyl(hydrotris(1-pyrazolyl)borato)hexafluorobut-2-yneplatinum(II), $(CH_3)(HB(N_2C_3H_3)_3)(F_3CC{\equiv}CCF_3)Pt^{II}$, has been determined by X-ray diffractometric methods. Crystals are orthorhombic with $a = 18.424$ (5), $b = 13.385$ (3), and $c = 7.568$ (2) Å. Refinement has been achieved in the centric space group *Pnma*. A crystallographic mirror plane is imposed on the molecule such that the platinum atom, the methyl carbon atom, the boron atom, and one pyrazole ring lie on the mirror plane. Full-matrix least-squares refinement on F utilizing 1917 observations for which $I > 3\sigma(I)$ has led to residuals $R_1 = 0.035$ and $R_2 = 0.050$. The coordination about the platinum atom is essentially trigonal bipyramidal, with the acetylene considered to be a monodentate ligand. The acetylenic triple bond is lengthened on coordination to 1.292 (12) Å. The acetylene bend-back angle is 34.4 (4)°, consistent with a reasonably perturbed acetylene, $\Delta\nu(C{\equiv}C)$ being 457 cm^{-1}. The polypyrazolylborate ligand has essentially C_{3v} symmetry, the mean angle between the pyrazolyl rings being 120.1 (2)°. Two equatorial and one axial sites of the trigonal bipyramid about the Pt atom are occupied by the tridentate ligand.

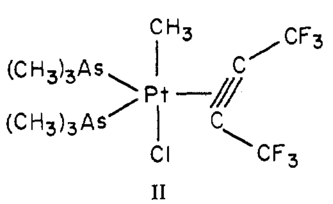
Introduction

Recently Clark and Manzer prepared a series of Pt(II) complexes containing polypyrazolylborate ligands.[1] The complexes were prepared by cleavage of the polymeric complex $(CH_3)Pt[HB(pz)_3]$ with a variety of olefins, acetylenes, and allenes, where $(HB(pz)_3)^-$ is the hydrotris(1-pyrazolyl)borate anion. Thus with hexafluorobut-2-yne



I

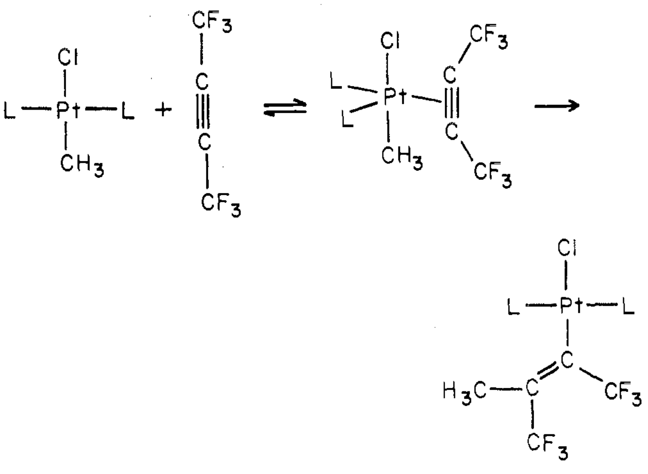
Nmr evidence suggested that the product was best formulated as I. This formulation is similar to that of *trans*-chloromethylbis(trimethylarsine)hexafluorobut-2-yneplatinum(II), $Cl(CH_3)((CH_3)_3As)_2(C_4F_6)Pt$, II, the structure of which has



II

been determined in this laboratory.[2]

Of particular interest to us is the difference in reactivities of I and II toward "insertion" reactions. Thus, II was postulated as a possible intermediate in the reaction



(where L = $As(CH_3)_3$) which occurs readily under mild conditions.[3]

In direct contrast, I does not "insert" and is remarkably unreactive. It is stable in solution up to 100° and the acetylene is resistant to nucleophilic attack.[1] Both complexes have similar reductions in C≡C stretching frequencies upon coordination, $\Delta\nu(C{\equiv}C)$ being 457 cm^{-1} for I and 462 cm^{-1} for II. We investigated the structure of I as part of our continuing studies of metal-acetylene complexes and for the purpose of seeing whether any structural feature could explain

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(1) L. E. Manzer and H. C. Clark, *J. Amer. Chem. Soc.*, 95, 3812 (1973); *Inorg. Chem.*, 13, 1291, 1996 (1974).

(2) Part I: B. W. Davies, R. J. Puddephat, and N. C. Payne, *Can. J. Chem.*, 50, 2276 (1972); part II: B. W. Davies and N. C. Payne, *ibid.*, 51, 3477 (1973).

(3) R. J. Puddephat and H. C. Clark, *Inorg. Chem.*, 10, 18 (1971).

this difference in chemical reactivity between I and II.

Experimental Section

Crystals were kindly supplied by L. E. Manzer. Weissenberg and precession photographs of the zones (0–2)*kl*, *h*(0–2)*l*, and *hk*(0–2) showed that the crystals belonged to the orthorhombic system. Systematic absences of *hk*0, $h \neq 2n$, were observed, consistent with the following space groups: $Pm2a$, alternate setting of $Pma2$ (C_{2v}^4, No. 28), $P2_1ma$, alternate setting of $Pmc2_1$ (C_{2v}^2, No. 26), and $Pmma$ (D_{2h}^5, No. 51).[4]

However, a photograph of the 0*kl* net using Cu Kα radiation and a large crystal showed a series of very weak reflections, which if *absent* would introduce the further condition for absences of 0*kl*, $k + l \neq 2n$, consistent with the space groups $Pnma$ (D_{2h}^{16}, No. 62) and $Pn2_1a$, alternate setting of $Pna2_1$ (C_{2v}^9, No. 33).

The structure was eventually solved in $Pnma$. A further discussion of the space group problem appears in the structure solution and refinement section. The density was measured by flotation in a dibromoethane–*n*-pentane mixture. The observed density of 2.05 (2) g cm^{-3} agrees well with the calculated density of 2.062 g cm^{-3}, assuming four molecular units in the unit cell.

The unit cell dimensions, $a = 18.424$ (5), $b = 13.385$ (3), and $c = 7.568$ (2) Å, were determined by a least-squares refinement[5] of the angular settings of 17 reflections with $35° < 2\theta < 55°$, measured on a Picker automatic diffractometer with Cu Kα radiation (λ 1.54056 Å) at a temperature of 21°.

For data collection, a centric prismatic crystal of approximate dimensions 0.25 mm × 0.25 mm × 0.36 mm was mounted with the long dimension [010] approximately parallel to the diffractometer spindle axis. The crystal was accurately measured prior to data collection with a microscope fitted with a filar eyepiece, in preparation for an absorption correction. Optical goniometry identified prismatic faces of the forms {101}, {10$\bar{1}$}, and {100}. The two end faces were best approximated as being of the form {010}. ω scans of a number of intense axial reflections showed an average width at half-height of 0.11°, which was considered acceptable.[6]

Intensities were measured on a Picker FACS-1 automatic four-circle diffractometer, using prefiltered (Ni foil, 0.07 mm) Cu radiation. The takeoff angle of 2.5° gave 85% of the maximum Bragg intensity available for a given reflection. The crystal to counter distance was 32.0 cm and the aperture was 4 mm square. All reflections in the range $2.5 \leqslant 2\theta \leqslant 125°$ in the octant *hkl* were collected, together with some additional symmetry-related reflections, to assist in resolving the space group ambiguity. The Miller index ranges were $-1 \leqslant h \leqslant 20$, $-1 \leqslant k \leqslant 15$, and $-1 \leqslant l \leqslant 8$.

The θ–2θ scan technique was used, with a scan range of 1.5°, corrected for dispersion, at a rate of 1.0° min^{-1}. Background counts were made for 10 sec with a stationary crystal and counter at the ends of each scan. Coincidence losses were minimized for strong reflections by employing copper foil attenuators. Five standard reflections, (020), ($\bar{8}$00), (00$\bar{2}$), (002), and (800), were remeasured every 150 reflections throughout the collection of data, as a check of machine and crystal stability. A small linear decay in intensity was observed (~5% of the original intensity was lost after completion of the data collection) and a correction was made.

A total of 2594 reflections were measured and the recorded intensities were corrected for background, Lorentz, and polarization effects.[5] A standard deviation was assigned to each reflection according to the formula

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

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 the background counts each measured in time t_b. The constant p was selected as 0.04. A total of 1962 reflections were regarded as "observed," *i.e.* with $I \geqslant 3\sigma(I)$. Absorption correction trials using $\mu = 138.0$ cm^{-1} for Cu Kα radiation[7] showed transmission factors ranging from 0.123 to 0.186, and a gaussian absorption correction was subsequently applied[8] to all reflections for which $I > 2\sigma(I)$.

Structure Solution and Refinement

A three-dimensional Patterson map could not be solved in the "observed" space groups $Pmma$, $Pm2a$, or $P2_1ma$. The solution was readily effected, however, in space group $Pn2_1a$. Two cycles of least-squares refinement on F, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ and varying the Pt positional parameters, led to agreement factors

$$R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.253$$

$$R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^{\,2})^{1/2} = 0.364$$

where the weight w is $4F_o^{\,2}/\sigma^2(F_o)^2$ and the atomic scattering factors for neutral Pt, F, N, C, and B atoms were those of Cromer and Waber,[9] while that of H was taken from Stewart, *et al.*[10] Anomalous dispersion contributions to the real and imaginary parts of the structure factor were included for Pt, F, and N atoms and were taken from Cromer and Liberman.[7]

A difference Fourier at this stage located the other 26 nonhydrogen atoms in the structure. A mirror plane was observed in the molecule. Subsequent refinement was therefore carried out in space group $Pnma$ (D_{2h}^{16}, No. 62) in which the molecule is constrained to have a mirror plane at $y = {}^1/_4$. Refinement in this space group imposes the condition for the zone 0*kl* that, for a reflection to be observed, $k + l = 2n$. Thus approximately 30 weak reflections, for which $k + l = 2n + 1$, violate this condition. These reflections were assigned zero weight. The successful refinement of the structure and the fact that we could locate and refine the H atoms led us to believe that there was nothing seriously amiss with this solution. Further refinement in $Pnma$ with all atoms given anisotropic temperature factors (139 variables and 1922 observations) led to agreement factors $R_1 = 0.044$ and $R_2 = 0.061$. An examination of the data at this stage showed five reflections to be seriously in error compared to the values predicted by the model. All were discarded on the grounds of unreliable counting statistics. Thus two, (210) and (2$\bar{1}$0), drew five attenuators during data collection, giving an attenuator factor of 137! The remaining three, (020), (040), and (060), were intense axial reflections, with noticeable background streaking.

There are thirteen H atoms in the molecule, three associated with the methyl group, and ten with the $(HB(pz)_3)^-$ ligand. Since the molecule lies on a mirror plane, this number is reduced to nine crystallographically independent atoms. A difference Fourier synthesis at this state located all these atoms. These peaks remained if the five intense reflections were reincluded. The presence of an annular ring of electron density at the methyl C atom led us to assume an ideal methyl group geometry (C–H = 1.05 Å; H–C–H = 109.47°) and to include these atoms as a spinning rotor according to the method of Bijvoet and Ketelaar.[11] The remaining H atoms associated with the ligand were all observed in chemically and structurally reasonable positions. As a test of the data, and of our choice of space group, we decided to attempt the refinement of these H atoms. Both positional and thermal parameters were varied. Under these conditions (all other atoms assigned anisotropic thermal parameters) refinement reached $R_1 = 0.037$ and $R_2 = 0.053$. An examination of $|F_o|$ and $|F_c|$ values showed evidence for secondary extinction, $|F_o|$ being consistently less than $|F_c|$. The extinction parameter was varied in the final three cycles of refinement, yielding a final value of 7.9 (7) × 10^{-6}. Under these conditions refinement converged at $R_1 = 0.035$ and $R_2 = 0.050$. The resulting H atom parameters and the entirely acceptable molecular geometry confirmed our earlier decisions.

In order to eliminate the acentric space group, $Pn2_1a$, we carried out parallel refinements in both "hands" of the polar space group. In each case, a chemically infeasible model was obtained. An examination of the observed and calculated structure factors in terms of magnitude, $\lambda^{-1} \sin\theta$, indices, and diffractometer angles (χ and φ) showed no abnormal trends. A final difference Fourier synthesis

(4) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962.

(5) PICKTT, using the logic of Hamilton's MODE1, was used on the PDP-10 to determine the cell constants and orientation matrix. Other programs modified by NCP for the CYBER 73/14 at the University of Western Ontario were WOCLS, a local version of Ibers' NUCLS, for least-squares refinement, Zalkin's FORDAP for Patterson and Fourier calculations, Johnson's ORTEP for illustrations, and the Busing–Martin–Levy errors program, ORFFE.

(6) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(7) Values for μ/ρ were taken from D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(8) The absorption correction was performed using the gaussian option in AGNOST: D. Cahen and J. A. Ibers, *J. Appl. Crystallogr.*, **5**, 298 (1972).

(9) D. T. Cromer and J. H. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(11) J. M. Bijvoet and J. A. A. Ketelaar, *J. Amer. Chem. Soc.*, **54**, 625 (1932).

Table I. Atomic Positional and Thermal Parameters

Atom	*x*	*y*	*z*	U_{11}[b] or *B*	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.117732 (18)[a]	$^1/_4$	0.076289 (41)	536 (3)	472 (3)	480 (3)	0	−11 (2)	0
N(11)	0.0217 (3)	$^1/_4$	0.2378 (8)	531 (32)	405 (32)	471 (34)	0	−142 (32)	0
N(15)	−0.0452 (4)	$^1/_4$	0.1561 (9)	623 (40)	455 (35)	511 (35)	0	−70 (35)	0
N(21)	0.0630 (3)	0.3550 (4)	−0.0854 (6)	795 (35)	483 (27)	551 (27)	−108 (26)	−42 (24)	48 (22)
N(25)	−0.0079 (3)	0.3434 (4)	−0.1174 (6)	768 (31)	424 (25)	487 (23)	66 (24)	−41 (23)	−38 (22)
F(1)	0.2596 (3)	0.3699 (4)	0.4826 (8)	1193 (38)	959 (37)	1478 (40)	72 (30)	−754 (36)	−284 (37)
F(2)	0.1603 (3)	0.4413 (4)	0.4365 (9)	1046 (41)	1029 (39)	1848 (67)	212 (32)	−185 (39)	−651 (39)
F(3)	0.2424 (4)	0.4465 (5)	0.2476 (8)	2096 (64)	1329 (49)	1269 (46)	−1024 (47)	−76 (49)	181 (42)
C(3)	0.2084 (6)	$^1/_4$	−0.0851 (14)	650 (62)	1048 (92)	883 (77)	0	−116 (55)	0
B	−0.0484 (7)	$^1/_4$	−0.0496 (13)	775 (72)	521 (57)	466 (50)	0	−103 (49)	0
C(14)	−0.0973 (5)	$^1/_4$	0.2764 (13)	515 (42)	659 (53)	610 (49)	0	−77 (45)	0
C(13)	−0.0662 (6)	$^1/_4$	0.4423 (12)	725 (63)	666 (58)	471 (47)	0	89 (46)	0
C(12)	0.0072 (5)	$^1/_4$	0.4155 (10)	661 (57)	532 (48)	389 (39)	0	−9 (38)	0
C(22)	0.0835 (5)	0.4402 (5)	−0.1640 (9)	1155 (60)	437 (33)	579 (37)	−170 (39)	24 (44)	43 (31)
C(23)	0.0245 (5)	0.4835 (6)	−0.2435 (10)	1419 (73)	397 (33)	638 (45)	−37 (43)	−135 (49)	126 (33)
C(24)	−0.0319 (5)	0.4198 (5)	−0.2132 (9)	1077 (54)	498 (35)	516 (33)	189 (37)	−112 (39)	89 (31)
C(1)	0.2105 (4)	0.3885 (5)	0.3589 (10)	629 (36)	614 (38)	825 (41)	−15 (32)	−78 (38)	−8 (39)
C(2)	0.1813 (3)	0.2983 (4)	0.2760 (8)	513 (28)	568 (30)	703 (34)	−32 (24)	−24 (30)	−32 (31)
HB	−0.1182 (78)	$^1/_4$	−0.1024 (240)	14.5 (77)					
HC(12)	0.0584 (51)	$^1/_4$	0.4427 (99)	4.1 (20)					
HC(13)	−0.1001 (55)	$^1/_4$	0.5173 (157)	5.2 (25)					
HC(14)	−0.1541 (69)	$^1/_4$	0.2302 (161)	9.5 (33)					
HC(22)	0.1366 (37)	0.4666 (61)	−0.1560 (109)	6.0 (17)					
HC(23)	0.0223 (32)	0.5301 (51)	−0.3021 (81)	3.7 (13)					
HC(24)	−0.0784 (33)	0.4382 (43)	−0.2338 (83)	4.2 (13)					

[a] Errors in this and other tables are given in parentheses and correspond to the least significant digits. Values without errors were constrained in the refinement. [b] The form of the thermal ellipsoid expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$ (Å). The values have been multiplied by 10^4.

showed three peaks in excess of 1.0 e Å^{-3}, the largest of these, 1.8 (2) e Å^{-3}, at (0.12, 0.33, 0.08) in the vicinity of the Pt atom. The standard deviation of an observation of unit weight is 2.13 electrons.

The final positional and thermal parameters of the nongroup atoms are given in Table I. The final values of $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections employed in the refinement are given in Table II.[12] Table III lists the root-mean-square amplitudes of vibration of the nonhydrogen atoms.

Choice of Space Group

An alternative solution was suggested by a referee. The observed absences restrict the choice of space group to *P*2$_1$*ma*, *Pmma*, or *Pm*2*a*. Whichever is chosen, the atomic arrangement must be close to that in *Pnma*. A solution consistent with the Patterson map may be achieved in *P*2$_1$*ma* by placing a molecule in each of the special positions, both of which have multiplicity 2 and site symmetry *m*. Such a placement retains the observed *m* point symmetry of the molecule, and refinement of both molecules could account for the weak reflections. A similar procedure in *Pmma* requires point symmetry 2/*m* or *mm*, while a twofold axis is imposed upon the molecule in *Pm*2*a*. The molecule does not possess these symmetries.

To test this hypothesis, the molecule was transposed into *P*2$_1$*ma*. For every atom in the asymmetric unit in *Pmma* at (*x*, *y*, *z*), there are two atoms in *P*2$_1$*ma* at (*x*, *y* − $^1/_4$, *z* − $^1/_4$) and ($^1/_2$ − *x*, $^1/_4$ + *y*, $^1/_4$ + *z*), forming an asymmetric unit comprised of two molecules. Thus to refine this model would involve almost twice as many variables, with an increase of only 23 in the number of significant observations. Structure factors calculated for this model gave agreement factors $R_1 = 0.047$ and $R_2 = 0.087$, suggesting that this was indeed a viable alternative. A difference-Fourier synthesis including the weak reflections contained several peaks, the greatest of which were 2.0 (2) and 1.8 (2) e Å^{-3} at (0.118, 0.086, −0.179) and (0.381, 0.417, 0.325), respectively, coincident with the two Pt atoms. The remaining peaks were of no chemical significance. Refinement of this model caused shifts in the atomic parameters such that the "weak" reflections now calculated nonzero as required. The thermal parameters of the atoms related by symmetry in *Pnma* were highly correlated. In addition, the resulting molecular geometry was not chemically credible. The most successful refinement assigned anisotropic thermal parameters to the Pt and F atoms and isotropic parameters to the remaining atoms. The thermal parameters of atoms related by symmetry in *Pnma* were constrained to be equal. The H atoms were included but not refined. With 1940 observations and 128 variables the refinement gave values of $R_1 = 0.049$ and $R_2 = 0.071$.

Table III. Root-Mean-Square Components of Vibration (×10^3 Å)

Atom	Min	Med	Max
Pt	217 (1)	219 (1)	232 (1)
F(1)	230 (6)	307 (6)	465 (6)
F(2)	254 (6)	319 (6)	476 (8)
F(3)	245 (6)	356 (7)	531 (8)
N(11)	189 (9)	201 (8)	254 (8)
N(15)	213 (8)	219 (8)	256 (9)
N(21)	209 (6)	235 (6)	290 (6)
N(25)	200 (6)	222 (6)	281 (6)
C(12)	197 (10)	231 (10)	257 (11)
C(13)	210 (11)	258 (11)	275 (12)
C(14)	217 (11)	256 (11)	257 (10)
C(22)	197 (8)	243 (8)	346 (9)
C(23)	185 (9)	258 (9)	380 (10)
C(24)	188 (9)	244 (8)	338 (8)
C(1)	243 (8)	250 (8)	292 (8)
C(2)	222 (7)	241 (6)	267 (6)
C(3)	245 (13)	305 (13)	324 (14)
B	208 (12)	228 (13)	284 (13)

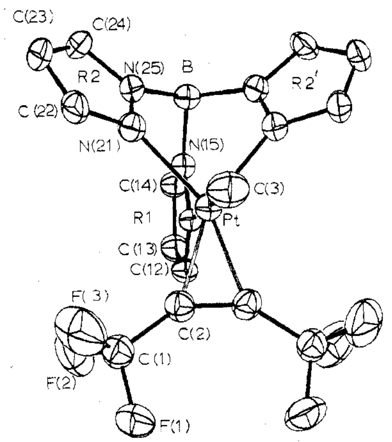

Figure 1. A view of the molecule illustrating the labeling scheme and the crystallographic mirror plane imposed on the molecule. Atoms in the pyrazolyl rings are numbered as follows. N(*n*1) is the N atom of ring *n* bonded to the Pt atom. The ring atoms are then numbered sequentially such that N(*n*5) is bonded to both the B and N(*n*1) atoms.

(12) See paragraph at end of paper regarding supplementary material.

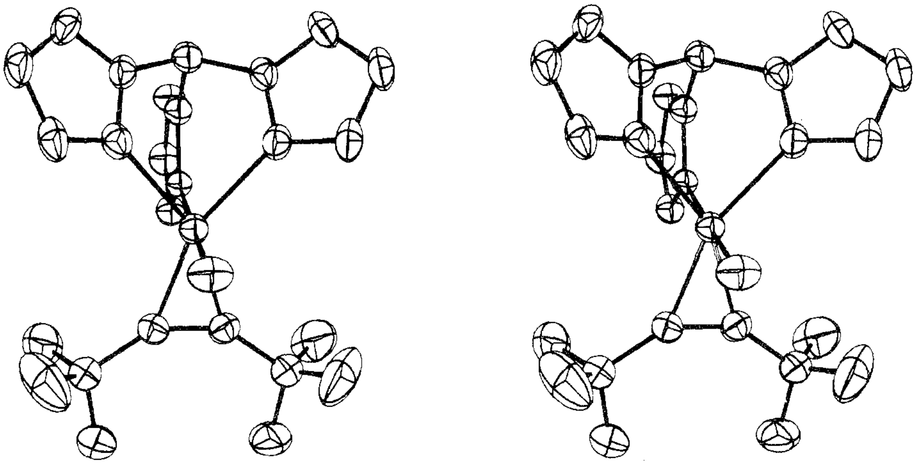

Figure 2. A stereoview of the molecule. Thermal ellipsoids are shown at the 30% probability level.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg)

Atoms	Distance	Atoms	Angle
Pt-C(3)	2.069 (12)	C(3)-Pt-N(11)	178.5 (3)
Pt-N(11)	2.151 (6)	C(3)-Pt-N(21)	92.5 (3)
Pt-N(21)	2.119 (5)	C(3)-Pt-C(2)	88.5 (3)
Pt-C(2)	2.018 (6)	N(21)-Pt-N(21)′	83.1 (3)
		N(21)-Pt-C(2)	119.8 (2)
		C(2)-Pt-C(2)′	37.3 (3)
		N(11)-Pt-C(2)	93.0 (2)
Ring 1		N(11)-Pt-N(21)	86.4 (2)
N(11)-C(12)	1.371 (10)	N(11)-C(12)-C(13)	109.8 (8)
C(12)-C(13)	1.366 (14)	C(12)-C(13)-C(14)	106.0 (8)
C(13)-C(14)	1.380 (12)	C(13)-C(14)-N(15)	108.9 (8)
C(14)-N(15)	1.323 (12)	C(14)-N(15)-N(11)	109.9 (7)
N(15)-N(11)	1.378 (8)	N(15)-N(11)-C(12)	105.4 (7)
		Pt-N(11)-N(15)	118.7 (5)
Ring 2			
N(21)-C(22)	1.340 (8)	N(21)-C(22)-C(23)	109.3 (7)
C(22)-C(23)	1.372 (11)	C(22)-C(23)-C(24)	105.4 (7)
C(23)-C(24)	1.364 (11)	C(23)-C(24)-N(25)	108.6 (7)
C(24)-N(25)	1.329 (7)	C(24)-N(25)-N(21)	109.5 (6)
N(25)-N(21)	1.337 (7)	N(25)-N(21)-C(22)	107.1 (6)
		Pt-N(21)-N(25)	119.5 (4)
C(1)-C(2)	1.463 (9)	C(2)-C(1)-F(1)	113.5 (6)
C(1)-F(1)	1.326 (8)	C(2)-C(1)-F(2)	112.4 (6)
C(1)-F(2)	1.304 (8)	C(2)-C(1)-F(3)	112.6 (6)
C(1)-F(3)	1.288 (8)	F(1)-C(1)-F(2)	105.5 (6)
		F(1)-C(1)-F(3)	105.3 (6)
C(2)-C(2)′	1.292 (12)	F(2)-C(1)-F(3)	106.9 (7)
		C(1)-C(2)-C(2)′	145.6 (4)
B-N(15)	1.558 (12)	N(15)-B-N(25)	108.3 (5)
B-N(25)	1.544 (8)	N(25)-B-N(25)′	108.1 (8)
B-HB	1.35 (15)	HB-B-N(25)	111 (4)
Ring 1		HB-B-N(15)	109 (8)
C(12)-HC(12)	0.97 (9)	N(11)-C(12)-HC(12)	91 (5)
C(13)-HC(13)	0.85 (11)	C(14)-C(13)-HC(13)	108 (7)
C(14)-HC(14)	1.10 (14)	C(13)-C(14)-HC(14)	133 (6)
Ring 2			
C(22)-HC(22)	1.04 (7)	N(21)-C(22)-HC(22)	122 (5)
C(23)-HC(23)	0.77 (7)	C(23)-C(22)-HC(22)	129 (4)
C(24)-HC(24)	0.90 (6)	C(22)-C(23)-HC(23)	130 (5)
		C(24)-C(23)-HC(23)	124 (5)
		C(23)-C(24)-HC(24)	121 (4)
		N(25)-C(24)-HC(24)	128 (4)

However, chemically equivalent distances in the two molecules differed significantly. For example, the Pt-CH_3 distances varied from 1.95 to 2.24 Å, and the C(13)-C(14) distances, from 1.21 to 1.60 Å.

It is apparent that the difference between the two molecules that reduces the symmetry of the *n* glide to a 2_1 axis is too small to be defined satisfactorily by the 23 "weak" reflections. We conclude that the refinement in *Pnma* provides a better description of the molecular geometry and accordingly present the results of this refinement.

Table V. Selected Least-Squares Planes by the Hamilton Method

Plane 1		Plane 2	
Atoms	Departure from plane, Å	Atoms	Departure from plane, Å
Pt	0.0000 (3)	N(21)	−0.003 (5)
N(21)	−0.005 (5)	C(22)	0.008 (7)
C(1)	0.022 (7)	C(23)	−0.009 (8)
C(2)	−0.022 (6)	C(24)	0.004 (7)
		N(25)	0.000 (5)

Equation of Planes: $Ax + By + Cz - D = 0$

Plane	*A*	*B*	*C*	*D*
1	1.438	0.177	−4.728	1.377
2	3.922	−6.689	−6.354	−1.582

Table VI. X-Ray Structural Data for Hexafluorobut-2-yne Complexes

Compd	Mean Pt-C, Å	Mean C≡C, Å	Mean bend-back angle, deg	Ref
trans-Cl(CH_3)(As(CH_3)$_3$)$_2$-Pt($F_3CC{\equiv}CCF_3$)	2.07 (4)	1.32 (4)	37 (7)	*a*
((C_6H_5)$_3$P)$_2$Pt($F_3CC{\equiv}CCF_3$)	2.027 (4)	1.255 (9)	39.9 (5)	*b*
(CH_3)(HB($N_2C_3H_3$)$_3$)Pt-($F_3CC{\equiv}CCF_3$)	2.018 (6)	1.292 (12)	34.4 (4)	*c*

[a] Reference 2. [b] B. W. Davies and N. C. Payne, *Inorg. Chem.*, **13**, 1848 (1974). [c] This work.

Description of the Structure

The structure is monomeric, the closest intermolecular approach being 2.77 Å between F(1) and the hydrogen atoms bonded to C(14). The mirror plane imposed on the molecule, with the atom-numbering scheme, is shown in Figure 1. Ring 1 lies on the mirror plane at $y = 1/4$, as do the Pt, the methyl carbon C(3), and the B atoms. Ring 2 is reflected through the mirror plane to ring 2′. The mirror plane bisects the symmetrical acetylene ligand; *i.e.*, C(1), C(2), F(1), F(2), and F(3) are reflected into C(1)′, C(2)′, F(1)′, F(2)′, and F(3)′. Figure 2 shows a stereoview of the molecule. Selected intramolecular bond distances and angles are given in Table IV. Some weighted least-squares planes are shown in Table V. Table VI summarizes other crystallographic data on hexafluorobut-2-yne complexes of Pt and Table VII summarizes crystallographic data on polypyrazolylborate complexes.

The coordination geometry about the Pt atom is best described as trigonal bipyramidal. A wide range of values has been observed in five-coordinate complexes for the

Table VII. Comparison of Structural Data for Hydrotris(1-pyrazolyl)borato Complexes

Atoms	$(CH_3)(HB(pz)_3)Pt-(F_3CC{\equiv}CCF_3)$[a]	$(HB(pz)_3)_2Co$[b]	$(HB(pz)_3)Mo-(CO)_2N_2C_6H_5$[c]	$(HB(pz)_3)(COCH_3)-Fe(CO)_2$[d]
		Distances, Å		
N(11)-N(15)	1.354 (17)	1.364 (3)	1.361 (12)	1.359 (1)
N(15)-C(14)	1.326 (3)	1.339 (15)	1.348 (1)	1.350 (3)
N(11)-C(12)	1.356 (15)	1.330 (15)	1.336 (6)	1.340 (5)
C(14)-C(13)	1.372 (6)	1.379 (25)	1.380 (3)	1.364 (5)
C(13)-C(12)	1.369 (3)	1.393 (23)	1.403 (5)	1.383 (8)
		Angles, Deg		
N(11)-N(15)-C(14)	109.7 (2)	109.9 (11)	109.5 (1)	109.3 (1)
N(15)-N(11)-C(12)	106.3 (11)	106.0 (9)	107.3 (3)	106.3 (3)
N(15)-C(14)-C(13)	108.8 (2)	109.0 (13)	108.4 (1)	108.7 (2)
N(11)-C(12)-C(13)	109.6 (2)	111.2 (10)	109.3 (2)	110.5 (3)
C(14)-C(13)-C(12)	105.7 (2)	104.1 (8)	105.1 (1)	105.2 (3)
N-M-N	84.7 (17)	85.5 (2)	81.8 (2)	86.8 (17)

[a] This work. [b] M. R. Churchill, K. Gold, and C. E. Maw, Jr., *Inorg. Chem.*, 9, 1597 (1970). [c] G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B*, 27, 725 (1971). [d] F. A. Cotton, B. A. Frenz, and A. Shaver, *Inorg. Chim. Acta*, 7, 161 (1973).

angle subtended at the metal atom by the ligand atoms in the equatorial plane. Thus, the steric requirements of the $(HB(pz)_3)^-$ ligand result in the "bite" (*i.e.*, the angle subtended by the donor N atoms) being 83.1 (3)°, smaller than the values observed in other five-coordinate acetylene complexes which do not possess a chelating ligand; the As-Pt-As angle in *trans*-$Cl(CH_3)(As(CH_3)_3)_2Pt(F_3CC{\equiv}CCF_3)$ is 104.2 (2)°,[2] and the (CO)-Ir-C(vinyl) angle in $(CO)((C_6H_5)_3P)_2$-Ir(-C(CN)=CHCN)(NCC≡CCN)[13] is 101.2 (6)°. The mean angle subtended by the donor N atoms at the central metal atom in $[HB(N_2C_3H_3)_3]_2Co$ is 85.5 (2)°,[14] in $[HB(N_2C_3H_3)_3]Mo(CO)_2(N_2C_6H_5)$ is 81.8 (2)°,[15] and in $(HB(N_2C_3H_3)_3)(COCH_3)Fe(CO)_2$ is 87 (2)°.[16] We observe an axial-equatorial angle subtended by the N atoms of the $(HB(pz)_3)^-$ ligand of 86.4 (2)°.

The values of the Pt-N bond lengths observed, Pt-N(21) = 2.119 (5) Å and Pt-N(11) = 2.151 (6) Å, are also probably governed by the steric requirements of the ligand. For example, in the bidentate ligand complex $[H_2B(N_2C_3H_3)_2]_2$-Co the mean Co-N distance is 1.967 (12) Å[17] while in the tridentate ligand complex $[HB(N_2C_3H_3)_3]_2Co$ the mean Co-N distance is 2.129 (7) Å.[14] In contrast, in the Mo compounds containing bidentate[18] and tridentate[15] polypyrazolyl ligands, similar values of 2.214 (37) and 2.218 (7) Å were found. Whereas the methyl group was considered to exert a strong trans influence in *trans*-$Cl(CH_3)(As(CH_3)_3)_2Pt(F_3CC{\equiv}CCF_3)$,[2] we are not prepared to make any estimates of its trans influence in complexes containing sterically demanding ligands such as $(HB(pz)_3)^-$.

The Pt-C(methyl) distance of 2.069 (12) Å lies in the expected range for a Pt-C(sp^3) bond, the sum of the covalent radii being 2.09 Å.[19]

The mean angle between the pyrazolyl rings of the $(HB(pz)_3)^-$ ligand is 120.1 (2)°, illustrating the C_{3v} symmetry of the ligand. The bond distances and bond angles within the pyrazolyl rings (Figure 3) are comparable to those previously determined and listed in Table VII. The mean B-N distance of 1.551 (7) Å agrees well with values obtained by other workers. The four independent angles at the B atom average to a value 109 (1)°, as expected for a tetrahedral B atom.

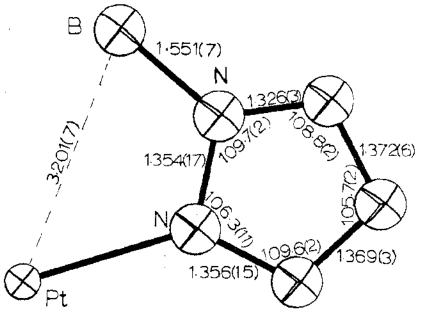

Figure 3. Schematic representation of the mean geometry of the pyrazolyl rings. Bond distances are in angstroms; bond angles in degrees.

The Pt-C(acetylene) distance of 2.018 (6) Å is equivalent to the mean value of 2.027 (4) Å observed in $((C_6H_5)_3P)_2$-$Pt(F_3CC{\equiv}CCF_3)$[20] (Table VII). The acetylenic triple bond has been lengthened on coordination to 1.292 (12) Å and the acetylene adopts the cis-bent configuration, the bend-back angle being 34.4 (4)°. The acetylene subtends an angle of 37.3 (4)° at the Pt atom and occupies the equatorial plane of the trigonal bipyramid, for the dihedral angle between the normals to the planes formed by N(21), Pt, N(21)' and C(2), Pt, C(2)' is 1.8 (2)°.

The mean C-F distance in the CF_3 moiety is 1.306 (11) Å and the mean angle subtended by the F atoms at C(1) is 105.9 (5)°. Comparable values of 1.301 (8) Å and 104.9 (9)° are observed in $((C_6H_5)_3P)_2Pt(F_3CC{\equiv}CCF_3)$.[20] The C(1)-C(2) distance is 1.463 (9) Å, compared to the mean value of 1.466 (9) Å observed in $((C_6H_5)_3P)_2Pt(F_3CC{\equiv}CCF_3)$.

Conclusion

The five-coordinate platinum(II)-acetylene complexes we have studied structurally resemble the trigonal Pt(0) complexes much more than they do the square-planar Pt(II) complexes. The crystallographic results indicate a strong platinum-acetylene bond and a reasonably perturbed acetylene. We cannot identify any abnormal structural parameters to which we can attribute the lack of reactivity. Indeed, the overall geometry of the platinum-acetylene fragment so

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(13) R. M. Kirchner and J. A. Ibers, *J. Amer. Chem. Soc.*, 95, 1095 (1973).

(14) M. R. Churchill, K. Gold, and C. E. Maw, Jr., *Inorg. Chem.*, 9, 1597 (1970).

(15) G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr., Sect. B*, 27, 725 (1971).

(16) F. A. Cotton, B. A. Frenz, and A. Shaver, *Inorg. Chim. Acta*, 7, 161 (1973).

(17) L. J. Guggenberger, C. T. Prewitt, P. Meakin, S. Trofimenko, and J. P. Jesson, *Inorg. Chem.*, 12, 508 (1973).

(18) F. A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, 6, 543 (1972).

(19) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1968.

(20) B. W. Davies and N. C. Payne, *Inorg. Chem.*, 13, 1848 (1974).

strongly resembles that of the Pt(0) complexes, which are also resistant to nucleophilic attack, that we conclude rather that the reactivity of *trans*-$Cl(CH_3)(As(CH_3)_3)_2Pt(F_3CC\equiv CCF_3)$ 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]

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Registry No. $(CH_3)[HB(N_2C_3H_3)_3]Pt(F_3CC\equiv CCF_3)$, 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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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 $\Delta\nu(C\equiv C)$ 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.

$((C_6H_5)_3P)_2(CF_3C\equiv CCF_3)Pt^0$ 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*-$Cl(CH_3)(As(CH_3)_3)_2(CF_3C\equiv CCF_3)Pt^{II}$ [1] and $(CH_3)(HB(N_2C_3H_3)_3)(CF_3C\equiv CCF_3)Pt^{II}$.[2]

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(1) B. W. Davies, R. J. Puddephat, and N. C. Payne, *Can. J. Chem.*, 50, 2276 (1972).

(2) B. W. Davies and N. C. Payne, *Inorg. Chem.*, 13, 1843 (1974).

(3) J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, 7, P9 (1967).

(4) M. A. Bennet, G. B. Robertson, P. O. Whimp, and T. Yoshida, *J. Amer. Chem. Soc.*, 93, 3797 (1971).

(5) J. H. Nelson and H. B. Jonassen, *Coord. Chem. Rev.*, 6, 27 (1971).

(6) F. R. Hartley, *Chem. Rev.*, 69, 799 (1969).

(7) L. D. Pettit and D. S. Barnes, *Fortschr. Chem. Forsch.*, 28, 85 (1972).

(8) F. R. Hartley, *Angew. Chem., Int. Ed. Engl.*, 11, 596 (1972).

(9) L. J. Guggenberger, *Inorg. Chem.*, 12, 499 (1973).

(10) J. L. Boston, S. O. Grim, and G. Wilkinson, *J. Chem. Soc.*, 3468 (1963).