

*Journal of Organometallic Chemistry*, 102 (1975) 245–257  
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

## STUDIES ON METAL—ACETYLENE COMPLEXES

### VI\*. CRYSTAL AND MOLECULAR STRUCTURE OF [DIETHYLBIS(1-PYRAZOLYL)BORATO] METHYL(1-PHENYLPROPYLENE)- PLATINUM(II), $[(C_2H_5)_2B(N_2C_3H_3)_2](CH_3)Pt(C_6H_5C\equiv CCH_3)$

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

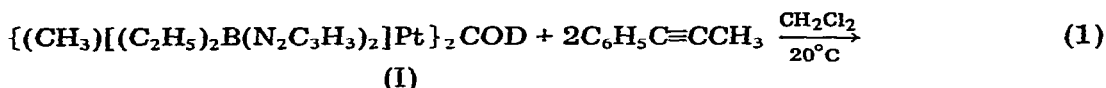
The crystal and molecular structure of [diethylbis(1-pyrazolyl)borato]-methyl(1-phenylpropyne)platinum(II),  $[(C_2H_5)_2B(N_2C_3H_3)_2](CH_3)Pt(C_6H_5C\equiv CCH_3)$ , has been determined by a single crystal X-ray diffraction study using diffractometer techniques. The compound crystallizes in the monoclinic space group  $P2_1/c$  with  $a = 13.239(6)$ ,  $b = 11.077(5)$ ,  $c = 15.619(7)$  Å and  $\beta = 114.53(2)^\circ$ . The observed density of  $1.71(2)$  g cm<sup>-3</sup> agrees well with the calculated value,  $1.687$  g cm<sup>-3</sup>, assuming four molecules in the cell. A conventional agreement factor of 0.036 was obtained by least-squares refinement on  $F$  using 3289 observations and 194 variables. The coordination about the platinum atom is square planar, if the acetylene is assumed to occupy one coordination site. The substituents of the acetylene are *cis*-bent away from the Pt atom, the methyl substituent by  $17.7(1.0)^\circ$ , and the phenyl substituent by  $21.2(9)^\circ$ . The coordinated triple bond length is  $1.227(10)$  Å. These results indicate that the acetylene is moderately perturbed on coordination, consistent with the observation that  $\Delta\nu(C\equiv C)$  is  $211$  cm<sup>-1</sup>. The conformation of the ring formed by the bidentate polypyrazolylborate ligand is that of a "shallow" boat. One of the methylene H atoms on the ethyl substituents on the polypyrazolylborate ligand when placed in an idealized position is  $2.65$  Å distant from the Pt atom.

#### Introduction

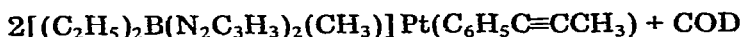
The title compound (II) was prepared by Clark and von Werner [1] according to reaction 1

\* For part V see ref. XX.

\*\* Present address: Chemistry Division (B429), A.E.R.E. Harwell, Oxfordshire, OX11 0RA, (United Kingdom).



(I)



(II)

Compound I, believed to be polymeric with bridging 1,5-cyclooctadiene (COD)\* ligands, dissolved in methylene chloride at room temperature in the presence of 1-phenylpropyne to produce II and cyclooctadiene. II was formulated as a square planar platinum(II)—acetylene complex. We undertook the structural investigation of II as part of our continuing studies of platinum—acetylene complexes [2-6]. In addition, the results obtained in conjunction with those from our previous study of bis(triphenylphosphine)(1-phenylpropyne)platinum(0) would permit a comparison of the geometries of the same acetylene ligand coordinated to a Pt atom in two different coordination geometries.

## Experimental

A crystalline sample was kindly furnished by Dr. K. von Werner. The results of a preliminary photographic examination are summarized in Table 1. The systematic absences observed uniquely determine the space group as  $P2_1/c$  [7]. The observed density is consistent with four formula units in the unit cell, and there are no symmetry constraints upon the molecules.

A Picker FACS-1 automatic four circle diffractometer was used for the intensity data collection. The crystal was mounted such that [100] was deliberately offset from coincidence with the diffractometer  $\phi$  axis to minimize the possibility of multiple reflections [8]. Refined cell constants and their e.s.d.'s were determined by a least-squares process\*\* using the angular settings of 22 reflections in the  $2\theta$  range  $13^\circ < 2\theta < 32^\circ$ . The crystal quality, as indicated by the  $\omega$  scan method of Furnas [9] was judged to be satisfactory. The conditions employed for data collection are summarized in Table 2.

Intensities were recorded by the  $\theta/2\theta$  scan technique. In all, 6288 reflections were recorded. During this period, the behaviour of the standard reflections (400, 402, 006, 060 and 006) was satisfactory, only random variations being

TABLE 1  
CRYSTAL DATA FOR *cis*-[(Et<sub>2</sub>Bpz<sub>2</sub>)(Me)Pt(PhC≡CMe)]

C <sub>20</sub> H <sub>27</sub> BN <sub>4</sub> Pt	mol. wt. 529.4
Crystal habit	Colourless prisms
Crystal system	Monoclinic, Laue symmetry 2/m
Systematic absences	$h0l, l \neq 2n : 0k0, k \neq 2n$
Space group	$P2_1/c$ ( $C_2^5$ , No 14)
Cell constants	$a = 13.239(6), b = 11.077(5), c = 15.619(7) \text{ \AA}, \beta = 114.53(2)^\circ$
Cell volume	$2084 \text{ \AA}^3$
Density determination	By flotation, C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> /CCl <sub>4</sub> , obs. $1.71(2) \text{ g cm}^{-3}$ ; calcd. $1.687 \text{ g cm}^{-3}$ for $Z = 4$

\* The following abbreviations have been used: COD, 1,5-cyclooctadiene; Me, methyl; Et, ethyl; Ph, phenyl; pz, pyrazolyl; t-Bu, tert-butyl.

\*\* Details of computing programs used are given in ref. 6.

TABLE 2  
EXPERIMENTAL CONDITIONS FOR DATA COLLECTION

Radiation	Mo- $K_{\alpha}$ ( $\lambda$ 0.70926 Å)
Filter	Nb foil (0.07 mm thick) prefilter
Temperature	22°C
Mean ' $\omega$ ' scan width at half height	0.10°
Scan range, speed	1.2° (1.4° for $2\theta > 45^\circ$ ), 1° min <sup>-1</sup>
Stationary background count time	10 sec (20 sec for $2\theta > 45^\circ$ )
Standard reflections	400, 402, 006, 060, 006
2 $\theta$ range	$2 \leq 2\theta \leq 55^\circ$
Take-off angle	1.6°
% intensity obtained for a given reflection	87% of maximum possible
Aperture size, distance from crystal	5 × 5 mm, 32 cm
$\mu$ (Mo- $K_{\alpha}$ )	64.7 cm <sup>-1</sup>
Crystal faces: prismatic end	{011} and {001} {110}
Crystal dimensions	0.23 × 0.26 × 0.46 mm
Absorption correction	Gaussian with a 24 × 8 × 10 grid

observed. The measurements were then corrected for background, Lorentz and polarization effects, and values of  $\sigma(I)$  were assigned as described earlier [5]. A statistical examination of the variations in the standard reflections suggested a suitable value for " $p$ " would be 0.009. This was later increased to 0.01 as the refinement proceeded, a value which resulted in a suitable weighting scheme.

The crystal was measured with a micrometer filar eyepiece, and as absorption trials indicated transmission factors varying from 0.245 to 0.404, an absorption correction was applied. The Gaussian method was employed, with a 24 × 8 × 10 grid. In all, 3456 reflections had  $I > 3\sigma(I)$  and were considered "observed".

### Structure solution and refinement

The position of the Pt atom was readily located from a three-dimensional Patterson synthesis using the first "shell" of intensity data ( $2\theta < 35^\circ$ ). Two cycles of full matrix least-squares refinement on  $F$ , varying an overall scale factor and positional parameters for the Pt atom, led to residuals  $R_1 = 0.183$  and  $R_2 = 0.238$  where

$$R_1 = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|} \text{ and } R_2 = \left( \frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2} \right)^{1/2}$$

where the weight  $w$  is  $w = 4F_o^2/\sigma^2(F_o^2)$ , and the function minimized is  $\sum w(|F_o| - |F_c|)^2$ .

The atomic scattering factors for neutral Pt, N, C and B atoms were those of Cromer and Waber [10], whilst those of H were taken from Stewart et al. [11]. Anomalous dispersion contributions to  $F_c$  [12] values were included for the Pt atom, and were taken from Cromer and Liberman [13]. A series of difference Fourier syntheses and least-squares refinements resulted in the location of the 25 other non-hydrogen atoms in the structure. Refinement with all 20 non-group atoms refined anisotropically, the phenyl C atoms refined as a rigid group ( $D_{6h}$  symmetry), C—C = 1.392 Å [14] with individual group atom temperature factors led to residuals  $R_1 = 0.041$  and  $R_2 = 0.046$  (3394 observations, 193 variables,  $p = 0.01$ ). An examination of a difference Fourier synthesis at

TABLE 3  
ATOMIC POSITIONAL AND THERMAL PARAMETERS<sup>a</sup>

Atom	x	y	z	U(1,1) <sup>b</sup>	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Pt	.22843(3)	.09416(3)	.02084(2)	463(2)	376(2)	280(1)	-57(2)	130(1)	-3(2)
N(11)	.1923(6)	.3497(6)	.0656(5)	586(45)	400(40)	468(38)	-23(37)	248(34)	13(34)
N(12)	.1694(5)	.2320(6)	.0631(4)	516(43)	515(44)	379(34)	-41(36)	268(32)	24(33)
C(13)	.0667(7)	.2319(10)	.0764(6)	574(59)	757(72)	526(51)	-84(54)	274(46)	22(50)
C(14)	.0895(8)	.3467(10)	.0900(7)	595(63)	797(77)	809(69)	120(58)	391(56)	50(60)
C(15)	.1198(8)	.4178(9)	.0826(6)	806(68)	580(65)	674(57)	169(59)	362(54)	-30(54)
N(21)	.2839(5)	.3359(6)	-.0381(4)	540(44)	443(41)	345(35)	-8(34)	199(30)	73(30)
N(22)	.2728(5)	.2169(6)	-.0621(4)	541(42)	398(39)	365(33)	12(33)	255(32)	5(31)
C(23)	.2755(7)	.2016(6)	-.1454(5)	620(56)	677(63)	328(40)	50(49)	210(40)	14(42)
C(24)	.3012(8)	.3099(9)	-.1770(6)	811(68)	732(70)	422(47)	77(57)	326(48)	100(49)
C(25)	.3116(7)	.3897(9)	-.1080(6)	617(66)	630(64)	523(48)	-26(52)	272(44)	201(50)
B	.3038(8)	.3857(9)	.0604(6)	597(61)	404(64)	393(47)	-89(50)	185(45)	-9(44)
C(1)	.4520(8)	-.0565(10)	.0873(7)	677(67)	1095(99)	721(66)	164(64)	-17(54)	72(64)
C(2)	.3402(7)	-.0380(8)	.0151(6)	469(62)	605(67)	460(46)	78(46)	103(42)	32(44)
C(3)	.2523(7)	-.0523(7)	-.0543(5)	517(53)	412(51)	445(43)	18(39)	198(41)	-12(36)
C(4)	.1825(8)	-.0220(8)	.0999(6)	902(73)	570(60)	569(54)	-184(56)	417(54)	-5(48)
C(5)	.3158(8)	.5321(9)	.0602(6)	892(74)	488(58)	713(62)	-81(55)	346(57)	-57(51)
C(6)	.3456(10)	.5959(10)	.1556(8)	1402(104)	657(70)	1011(82)	-200(79)	441(77)	-296(73)
C(7)	.4055(7)	.3186(8)	.1434(5)	517(52)	605(58)	421(44)	-151(45)	131(39)	-53(42)
C(8)	.5190(8)	.3389(11)	.1408(7)	595(65)	1123(93)	859(72)	-19(63)	254(57)	224(59)

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

this stage showed clear evidence for most of the H atoms. The largest peak on the synthesis was  $0.48(14) \text{ e } \text{Å}^{-3}$ . Of the twelve methyl H atoms, eight were readily located at peak heights of 0.20 to  $0.41 \text{ e } \text{Å}^{-3}$ , in geometrically feasible locations. The other four, for which idealized positions were calculated, all lay in regions of positive electron density. Of the remaining 15 H atoms, 12 were present as peaks on the map between 0.48 and  $0.30 \text{ e } \text{Å}^{-3}$ . With this encouraging evidence, it was decided to include all 27 H atoms, employing idealized geometries. Methyl H atom positions were calculated from a least-squares refinement to the observed peaks, maintaining a tetrahedral geometry at the C atom. Two cycles of least-squares refinement, including, but not refining the H atoms, resulted in a significant improvement in the model,  $R_1$  being reduced to 0.0370, and  $R_2$  to 0.0387.

The H atom positions were then recalculated on the basis of the improved model. An examination of intense, low angle reflections suggested that secondary extinction might be a problem, so an extinction coefficient was included in the refinement.

The conditions for the final cycles of refinement were:

i) the 20 non-group atoms were refined with anisotropic temperature factors.

ii) the phenyl ring was refined as a rigid group, with individual isotropic temperature factors assigned to each C atom.

iii) anomalous dispersion contributions to the calculated structure factors were included for the Pt atom.

iv) H atom contributions were included for the 27 H atoms in the molecule, each atom being given an isotropic temperature factor of magnitude  $1.0 \text{ Å}^2$  greater than the equivalent isotropic temperature factor of the C atom to which it is bonded. No H parameters were refined.

v) the  $p$  value was chosen as 0.01, and an extinction coefficient was refined.

Under these conditions refinement converged at  $R_1 = 0.0362$  and  $R_2 = 0.0355$  (3289 unique observations, 194 variables). The error on an observation of unit weight is 2.13 electrons, and the extinction coefficient  $2.3(2) \times 10^{-6}$ . In the final cycle no parameter shift exceeded 0.10 of its standard deviation. A final difference Fourier synthesis showed no peak in excess of  $0.96(18) \text{ e } \text{Å}^{-3}$ . The largest peak, at (0.30, 0.10, 0.04) is in a position of no chemical significance.

A statistical examination of the observed and calculated structure factors in terms of magnitude, indices,  $\lambda^{-1} \sin \theta$ , and diffractometer angles ( $\chi$  and  $\phi$ ) showed no unusual trends.

The final atomic positional and thermal parameters of the non-group atoms are given in Table 3. Table 4 lists the group parameters and the derived phenyl C atom parameters. Table 5 gives the idealized H atom positional and thermal parameters. Table 6 lists the root-mean-square amplitudes of vibration of the non-group atoms. A listing of observed and calculated structure factors ( $\times 10$  in electrons) can be obtained\*.

\* A Table of observed and calculated structure factors ( $\times 10$  in electrons) has been deposited as NAPS document No. 02638 (9 pages), with ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document and remitting \$3.00 for microfiche, or \$5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications. Outside of the United States or Canada, postage is \$2.00 for a photocopy or \$1.00 for a fiche.

TABLE 4  
GROUP PARAMETERS

$x_g$	$y_g$	$z_g$	$\delta$	$\epsilon$	$\eta$
0.0992(3)	-0.1582(4)	-0.2237(3)	0.694(4)	-3.013(4)	-2.435(4)

DERIVED GROUP ATOM PARAMETERS

Atom	x	y	z	$B(\text{\AA}^2)$
1C1	0.1729(4)	-0.1051(6)	-0.1403(3)	3.57(14)
1C2	0.0725(5)	-0.0486(5)	-0.1945(4)	4.66(19)
1C3	-0.0012(4)	-0.1017(6)	-0.2778(4)	5.93(21)
1C4	0.0255(5)	-0.2113(6)	-0.3070(4)	6.45(24)
1C5	0.1259(6)	-0.2677(5)	-0.2529(5)	7.93(29)
1C6	0.1996(4)	-0.2146(6)	-0.1695(4)	6.24(23)

<sup>a</sup>  $x_g$ ,  $y_g$  and  $z_g$  are the fractional coordinates of the group origin;  $\delta$ ,  $\epsilon$  and  $\eta$  (in radians) are the group orientation angles [14].

TABLE 5  
HYDROGEN ATOM POSITIONAL AND THERMAL PARAMETERS

Atom	x	y	z	$B(\text{\AA}^2)$
H1C(1) <sup>a</sup>	0.4484	-0.0840	0.1474	8.31
H2C(1)	0.4902	-0.1219	0.0662	8.31
H3C(1)	0.4951	0.0193	0.0982	8.31
H1C(4)	0.0988	-0.0280	0.0743	6.30
H2C(4)	0.2117	-0.1067	0.0978	6.30
H3C(4)	0.2122	0.0042	0.1671	6.30
H1C(5)	0.2448	0.5672	0.0121	6.79
H2C(5)	0.3771	0.5530	0.0388	6.79
H1C(6)	0.4242	0.5803	0.2010	9.34
H2C(6)	0.3323	0.6852	0.1487	9.34
H3C(6)	0.2955	0.5623	0.1863	9.34
H1C(7)	0.3904	0.2296	0.1401	5.30
H2C(7)	0.4110	0.3502	0.2052	5.30
H1C(8)	0.5812	0.3068	0.1996	8.31
H2C(8)	0.5225	0.2918	0.0851	8.31
H3C(8)	0.5323	0.4253	0.1326	8.31
HC(13)	0.0221	0.1579	0.0778	5.91
HC(14)	-0.0264	0.3737	0.1030	6.57
HC(15)	0.1237	0.5083	0.0890	6.24
HC(23)	0.2639	0.1211	-0.1806	5.29
HC(24)	0.3093	0.3276	0.2365	6.00
HC(25)	0.3309	0.4797	-0.1081	5.67
H(1C2)	0.0535	0.0301	-0.1746	5.68
H(1C3)	-0.0729	-0.0622	-0.3175	7.17
H(1C4)	-0.0272	-0.2515	-0.3662	7.69
H(1C5)	0.1449	-0.3486	-0.2720	8.79
H(1C6)	0.2712	-0.2533	-0.1291	7.28

<sup>a</sup> Hydrogen atoms are numbered according to the atom to which they are bonded. Thus, HC(13) is bonded to C(13), H1C(5) and H2C(5) to C(5), etc.

TABLE 6  
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION ( $\text{\AA} \times 10^3$ ).

Atom	Minimum	Median	Maximum
Pt <sup>a</sup>	1671(4)	1870(6)	2269(5)
N(11)	196(11)	212(10)	243(9)
N(12)	164(11)	224(10)	236(10)
C(13)	210(13)	240(12)	282(13)
C(14)	213(14)	275(13)	298(13)
C(15)	206(15)	261(12)	300(13)
N(21)	168(10)	219(10)	234(10)
N(22)	171(10)	199(10)	234(9)
C(23)	175(12)	244(12)	266(12)
C(24)	183(12)	264(13)	293(13)
C(25)	178(14)	249(11)	284(13)
B	192(16)	199(12)	256(13)
C(1)	212(13)	329(15)	356(14)
C(2)	195(12)	241(12)	258(13)
C(3)	200(13)	212(11)	230(12)
C(4)	195(14)	238(13)	314(12)
C(5)	217(13)	265(12)	302(13)
C(6)	220(15)	341(15)	385(15)
C(7)	191(12)	225(12)	271(12)
C(8)	244(13)	272(14)	360(15)

<sup>a</sup> ( $\text{\AA} \times 10^4$ ).

### Description of the structure

The structure consists of discrete molecules. One intermolecular distance of approach, 2.26 Å, between HC(25) and H3C(8), a methyl H atom, is smaller than the sum of the Van der Waal's H atom radii, 2.4 Å, [15], but other intermolecular contacts are satisfactory. A view of the molecule, showing the atom numbering scheme used is given in Fig. 1. Fig. 2 shows the inner coordination sphere, Fig. 3 a stereoview of the molecule, and Fig. 4 a view of the BN<sub>4</sub>Pt ring. Selected intramolecular bond distances and angles are given in Table 7 and least-squares planes in Table 8.

The coordination about the Pt atom is approximately square planar if the acetylene is regarded as occupying one coordination site. The Pt, N(22), N(12) and C(4) atoms are planar within experimental error and none of the angles subtended by the N(12), N(22) and C(4) atoms at the Pt atom is significantly different from its ideal value (90° or 180°). The acetylenic C atoms C(2) and C(3) are displaced by 0.612 and 0.587 Å respectively from the coordination plane of the Pt atom (Table 8). The acetylene is approximately perpendicular to the coordination plane of the Pt atom, for the dihedral angle (the angle between the normals to the planes defined by Pt, N(22) and N(12) and by C(1), C(2) and C(3)) is 86.9(6)°. The Pt—C(4) distance, 2.043(8) Å, lies in the normal range for Pt—CH<sub>3</sub> distances, the sum of the covalent radii being 2.09 Å [15]. The Pt—N distances are significantly different, Pt—N(12) being 2.026(7) Å, and Pt—N(22) being 2.120(6) Å. This considerable difference ( $\Delta/\sigma = 10$ ) could be attributed to the steric requirements of the (Et<sub>2</sub>Bpz<sub>2</sub>)<sup>-</sup> ligand or to the *trans* influence of the methyl ligand. The latter explanation seems more likely be-

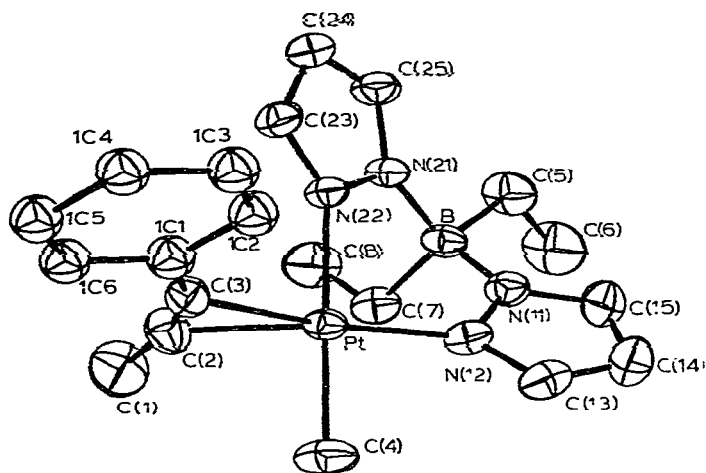


Fig. 1.

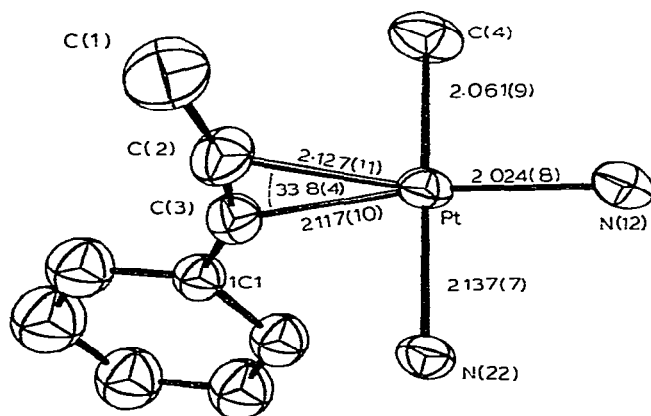


Fig. 2.

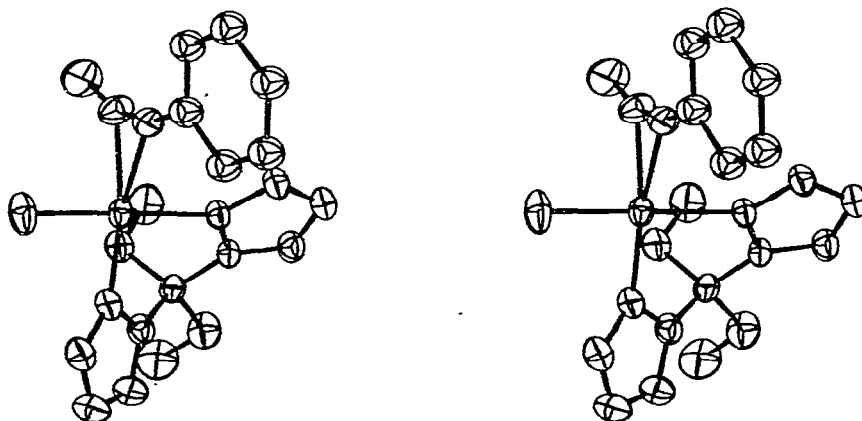


Fig. 3.



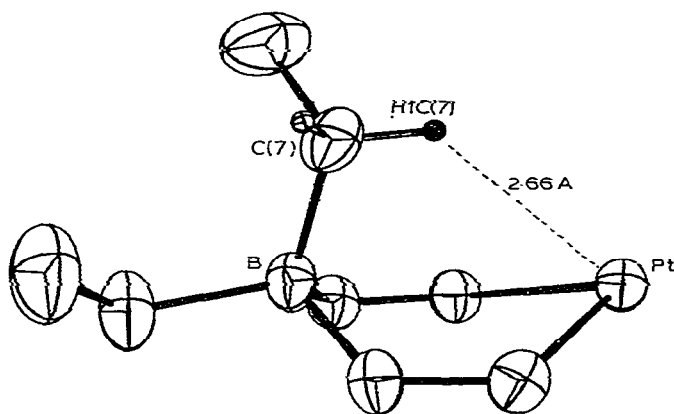


Fig. 4.

cause the steric requirements of the ligand, as evidenced by the N(12)—Pt—N(22) angle of  $89.5(3)^\circ$ , appear to be small. These requirements would be expected to be less than those of the tridentate (HBpz<sub>3</sub>)<sup>-</sup> ligand. The departures from an ideal trigonal bipyramidal geometry in (Me)(HBpz<sub>3</sub>)Pt(F<sub>3</sub>CC≡CCF<sub>3</sub>) [4] are much greater than the departures from a square planar geometry observed in this study. In the compound *cis*-[(Me)(CO)Pt(HBpz<sub>3</sub>)], in which the (HBpz<sub>3</sub>)<sup>-</sup> ligand is bidentate, the Pt—N distance *trans* to the methyl is 2.068(7) Å, intermediate between the Pt—N distances observed in this study. The Pt—C(acetylene) distances are equivalent, Pt—C(2) being 2.110(9) Å and Pt—C(3), 2.102(8) Å.

The diethylbis(pyrazolyl)borate ligand is bidentate, occupying *cis* positions in the coordination sphere. The geometries of the pyrazolyl rings agree well with those obtained in previous studies [17,18] of complexes of this and other bidentate polypyrazolylborate ligands [19], and even with those obtained for the tridentate (HBpz<sub>3</sub>)<sup>-</sup> ligand [19].

The B—N distances are 1.563(12) and 1.587(11) Å, in agreement with values previously found. The B—C(ethyl) distances are 1.630(13) and 1.618(12) Å, comparable with the values of 1.635(10) and 1.608(10) Å found in [(Et<sub>2</sub>Bpz<sub>2</sub>)-(π-CH<sub>2</sub>C(Ph)CH<sub>2</sub>)(CO)<sub>2</sub>Mo] [17], and the values of 1.605(6) and 1.625(6) Å observed in [(Et<sub>2</sub>Bpz<sub>2</sub>)(Hpz)(π-C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>Mo] [18]. The four independent angles subtended at the B atom have a mean value of  $109.4(10)^\circ$ , indicating an essentially tetrahedral environment. The ethyl moiety geometries are satisfactory, C(5)—C(6) being 1.544(13) Å and C(6)—C(5)—B  $116.0(8)^\circ$  for one ethyl group, and C(7)—C(8) being 1.523(12) Å and B—C(7)—C(8)  $114.6(7)^\circ$  for the other ethyl group.

The pyrazolyl rings, which are planar within experimental error (Table 8) are inclined at angles of  $32.4$  and  $31.9^\circ$  with the coordination plane of the Pt atom. The conformation of the six-membered ring formed by the Pt, N(12), N(11), B, N(21) and N(22) atoms is best described as a "shallow boat" and is shown in Fig. 4. The B atom and Pt atom are 0.70 and 0.58 Å above the plane of the four N atoms. The angle between the plane of the four N atoms and the plane of B, N(11) and N(21) is  $46.8^\circ$ , whilst that between the plane of the four N atoms and the plane of Pt, N(12) and N(22) is  $23.3^\circ$ . With this conformation

TABLE 7  
SELECTED INTRAMOLECULAR BOND DISTANCES AND ANGLES

Atoms			
<i>(a) Coordination about the Pt atom</i>			
Pt—N(12)	2.026(7)	N(12)—Pt—N(22)	89.5(3)
Pt—N(22)	2.120(6)	N(12)—Pt—C(2)	163.0(3)
Pt—C(4)	2.043(8)	N(12)—Pt—C(3)	163.0(3)
Pt—C(3)	2.102(8)	N(12)—Pt—C(4)	89.4(3)
Pt—C(2)	2.110(9)	N(22)—Pt—C(2)	92.5(3)
		N(22)—Pt—C(3)	90.6(3)
		N(22)—Pt—C(4)	178.7(3)
		C(2)—Pt—C(3)	33.9(3)
<i>(b) The (Et<sub>2</sub>Bpz<sub>2</sub>)<sup>-</sup> ligand</i>			
N(21)—N(22)	1.368(8)	N(21)—N(22)—C(23)	107.6(7)
N(22)—C(23)	1.335(9)	N(22)—C(23)—C(24)	110.3(8)
C(23)—C(24)	1.386(12)	C(23)—C(24)—C(25)	104.0(7)
C(24)—C(25)	1.356(12)	C(24)—C(25)—N(21)	111.2(8)
C(25)—N(21)	1.347(9)	C(25)—N(21)—N(22)	106.8(7)
		B—N(21)—N(22)	121.7(6)
		B—N(21)—C(25)	131.3(7)
		Pt—N(22)—N(21)	121.9(5)
		Pt—N(22)—C(23)	130.3(6)
N(11)—N(12)	1.370(8)	N(11)—N(12)—C(13)	107.5(7)
N(12)—C(13)	1.327(10)	N(12)—C(13)—C(14)	110.2(8)
C(13)—C(14)	1.362(13)	C(13)—C(14)—C(15)	105.1(9)
C(14)—C(15)	1.366(13)	C(14)—C(15)—N(11)	110.0(9)
C(15)—N(11)	1.332(11)	C(15)—N(11)—N(12)	107.3(8)
		B—N(11)—N(12)	122.5(7)
		B—N(11)—C(15)	129.8(8)
		Pt—N(12)—N(11)	123.0(5)
		Pt—N(12)—C(13)	128.5(6)
B—C(5)	1.630(13)	C(5)—B—C(7)	114.1(7)
B—C(7)	1.618(12)	C(5)—B—N(21)	108.2(7)
B—N(21)	1.587(11)	C(5)—B—N(11)	110.4(8)
B—N(11)	1.563(12)	N(11)—B—N(21)	105.2(6)
C(5)—C(6)	1.544(13)	N(11)—B—C(7)	109.8(7)
C(7)—C(8)	1.523(12)	N(21)—B—C(7)	108.7(7)
		B—C(7)—C(8)	114.6(7)
		B—C(5)—C(6)	116.0(8)
<i>(c) The coordinated 1-phenylpropyne</i>			
C(1)—C(2)	1.455(11)	C(1)—C(2)—C(3)	162.3(10)
C(2)—C(3)	1.227(10)	C(2)—C(3)—1C1	158.8(9)
C(3)—1C1	1.442(10)	Pt—C(3)—C(2)	73.4(6)
		Pt—C(2)—C(3)	72.7(6)
		Pt—C(2)—C(1)	124.7(7)
		Pt—C(3)—1C1	127.8(6)
		C(3)—1C1—1C2	121.8(6)
		C(3)—1C1—1C6	116.2(6)

of the "boat", one of the methylene H atoms, H1C(7) is positioned 2.65 Å away from the Pt atom and this interaction is depicted in Fig. 4. A comparable "boat" conformation was observed in (Et<sub>2</sub>Bpz<sub>2</sub>)( $\pi$ -CH<sub>2</sub>C(Ph)CH<sub>2</sub>)(CO)<sub>2</sub>Mo [17].

The acetylene C atoms, C(2) and C(3), subtend an angle of 33.9(3)<sup>o</sup> at the Pt atom. The triple bond length of 1.227(10) Å is not significantly different from a normal triple bond length, 1.202(5) Å [20]. The C(1)—C(2) distance is 1.455(11) Å and the C3—1C1 distance is 1.442(10) Å. The methyl substituent

TABLE 8  
SELECTED WEIGHTED LEAST-SQUARES PLANES

Plane	Atoms in plane	Departure (Å) from plane		
1	Pt	0.0001(3)		
	N(12)	0.000(6)		
	N(22)	-0.008(6)		
	C(4)	-0.021(9)		
	C(2) <sup>a</sup>	0.587		
	C(3) <sup>a</sup>	-0.612		
2	N(11)	-0.006(7)		
	N(12)	0.006(6)		
	C(13)	-0.008(8)		
	C(14)	0.005(10)		
	C(15)	0.004(9)		
3	N(21)	-0.003(6)		
	N(22)	0.003(6)		
	C(23)	-0.003(8)		
	C(24)	-0.002(9)		
	C(25)	0.005(8)		
Equations of planes $Ax + By + Cz - D = 0$				
1	8.031	1.846	7.111	2.156
2	2.025	-0.943	13.00	0.918
3	11.40	-2.293	1.016	2.544

<sup>a</sup> Not included in calculation of plane equation.

is bent back away from the Pt by 17.7(10)°, and the phenyl substituent by 21.2(9)°, values perhaps significantly different ( $\Delta/\sigma = 2.6$ ). Any such variation could either be due to a difference in the mode of bonding from the Pt atom to C(2) and C(3), due to the different nature of the substituents attached to these atoms, or from steric reasons, the phenyl substituent being bulkier than the methyl substituent. The fact that the Pt—C(acetylene) distances are not significantly different could be used to argue against the former reason, or may merely reflect the fact that such changes are too small to be detected by X-ray techniques. The plane of the phenyl substituent is inclined at an angle of 4.1° with the plane of the acetylene C atoms, C(1), C(2) and C(3). Thus the orientation of the phenyl substituent in this study is similar to that observed in  $(PPh_3)_2Pt(C_6H_5C\equiv CMe)$  (preceding paper), in which the analogous angle is 10.4°. The significance of this orientation has been discussed by McGinnety [21].

## Discussion

The structural results confirm the original formulation [1], and indicate that the coordinated triple bond is approximately perpendicular to the coordination plane of the Pt atom. The acetylene ligand is moderately perturbed on coordination, consistent with the observation that  $\Delta\nu(C\equiv C)$  is 211  $cm^{-1}$ . Similar acetylene perturbations were obtained in the other square planar platinum(II)—acetylene complexes studied by X-ray methods, *trans*-[(PMe<sub>2</sub>Ph)<sub>2</sub>(Me)Pt-(MeC≡CMe)]PF<sub>6</sub> [3], *trans*-[Cl<sub>2</sub>(PH<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)Pt(*t*-BuC≡C-*t*-Bu)] [22,23] and K[Cl<sub>3</sub>Pt(HOEt<sub>2</sub>CC≡CCEt<sub>2</sub>OH)] [24].

The results obtained in this study and that of  $(\text{PPh}_3)_2\text{Pt}(\text{PhC}\equiv\text{CMe})$  [6] provide support for the molecular orbital continuum of bond types model [25]. The platinum—acetylene interaction is stronger in the platinum(0) complex ( $\text{Pt}-\text{C}$ , 2.029(15) Å;  $\text{C}\equiv\text{C}$ , 1.277(25) Å;  $\Delta\nu(\text{C}\equiv\text{C})$ , 478  $\text{cm}^{-1}$  and bend back angles of Me, 38.2(17) and Ph, 41.0(16)°). In this study we observe a weaker interaction ( $\text{Pt}-\text{C}$ , 2.106(4) Å,  $\text{C}\equiv\text{C}$ , 1.227(10) Å;  $\Delta\nu(\text{C}\equiv\text{C})$ , 211  $\text{cm}^{-1}$ , and bend back angles of Me, 17.7(10) and Ph, 21.2(9)°). This is consistent with greater  $\pi$  back-donation from the Pt to the acetylene  $\pi^*$  orbitals in  $(\text{PPh}_3)_2\text{Pt}(\text{PhC}\equiv\text{CMe})$  than in the square planar platinum(II) complex, and molecular orbital calculations have indicated [26] that the departure from linearity of the ligand increases with increased  $\pi$  back-donation.

Recently Cotton et al. [17,18,27] have determined the structures of three molybdenum complexes containing  $(\text{Et}_2\text{Bpz}_2)^-$  ligands. In two of the complexes,  $[(\text{Et}_2\text{Bpz}_2)(\pi\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2)(\text{CO})_2\text{Mo}]$  [17] and  $[(\text{Et}_2\text{Bpz}_2)(\pi\text{-C}_7\text{H}_7)(\text{CO})_2\text{Mo}]$  [27], the conformation of the  $\text{BN}_4\text{Mo}$  ring was such that a methylene H atom of the  $(\text{Et}_2\text{Bpz}_2)^-$  ligand approached to a distance of approximately 2 Å away from the Mo atom ( $\sim 1.93$  Å in  $[(\text{Et}_2\text{Bpz}_2)(\pi\text{-C}_7\text{H}_7)(\text{CO})_2\text{Mo}]$  and 2.15 Å in  $[(\text{Et}_2\text{Bpz}_2)(\pi\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2)(\text{CO})_2\text{Mo}]$ ). Chemical evidence (abnormal  $\nu(\text{C}-\text{H})$  and  $^1\text{H}$  NMR chemical shift values) [28,29] predicted such an interaction. The conformation of the  $\text{BN}_4\text{Mo}$  ring in the above two compounds was that of a "boat" whilst in  $[(\text{Et}_2\text{Bpz}_2)(\text{Hpz})(\pi\text{-C}_3\text{H}_5)(\text{CO})_2(\text{Mo})]$  [18], in which no such Mo—H interaction was postulated, it was a "shallow chair".

For the title compound there was no chemical evidence predicting such an interaction. The structural results suggest that a methylene H atom approaches to within 2.7 Å of the Pt atom. The conformation of the  $\text{BN}_4\text{Pt}$  ring, a "shallow boat", more closely resembles the "boat" observed in  $[(\text{Et}_2\text{Bpz}_2)(\pi\text{-CH}_2\text{C}(\text{Ph})\text{-CH}_2)(\text{CO})_2\text{Mo}]$  [17] than it does the "shallow chair" observed in  $[(\text{Et}_2\text{Bpz}_2)(\text{Hpz})(\pi\text{-C}_3\text{H}_5)(\text{CO})_2\text{Mo}]$  [18].

It is a moot point therefore, as to whether the observed Pt—H distance corresponds to a significant bonding interaction or not. Generally, it is assumed [17] that metal H interactions in the range 2.5-3.0 Å do not represent an appreciable interaction. This, together with the chemical evidence [1], leads us to conclude that the Pt—H distance of 2.65 Å does not represent a "bond". It is interesting to note that the three H atoms on the methyl group C atom bonded to the Pt atom are 2.58 Å distant from the Pt atom, and that this interaction would certainly be considered non-bonding.

## Acknowledgements

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

## References

- 1 H.C. Clark and K. von Werner, personal communication.
- 2 B.W. Davies, R.J. Puddephatt and N.C. Payne, *Canad. J. Chem.*, 50 (1972) 2276.
- 3 B.W. Davies and N.C. Payne, *Canad. J. Chem.*, 51 (1973) 3477.
- 4 B.W. Davies and N.C. Payne, *Inorg. Chem.*, 13 (1974) 1843.
- 5 B.W. Davies and N.C. Payne, *Inorg. Chem.*, 13 (1974) 1848.

- 6 B.W. Davies and N.C. Payne, *J. Organometal. Chem.*, **99** (1975) 315.
- 7 *International Tables for X-ray Crystallography*, 3rd Ed., Kynoch Press, Birmingham, England, Vol. I, 1969.
- 8 W.A. Zachariasen, *Acta Crystallogr.*, **18** (1965) 705.
- 9 T.C. Furnas, *Single Crystal Orienter Instruction Manual*, General Electric Company, Milwaukee, Wis., 1957.
- 10 D.T. Cromer and S.H. Waber, *Acta Crystallogr.*, **18** (1965) 104.
- 11 R.F. Stewart, E.R. Davidson and W.T. Simpson, *J. Chem. Phys.*, **42** (1965) 3175.
- 12 J.A. Ibers and W.C. Hamilton, *Acta Crystallogr.*, **17** (1964) 781.
- 13 D.T. Cromer and D. Liberman, *J. Chem. Phys.*, **53** (1970) 1891.
- 14 R. Eisenberg and J.A. Ibers, *Inorg. Chem.*, **4** (1965) 773.
- 15 L. Pauling, *The Nature of the Chemical Bond*, 3rd Ed. Cornell University Press, Ithaca, New York, 1960.
- 16 P.E. Rush and J.D. Oliver, personal communication.
- 17 F.A. Cotton, T. LaCour and A.G. Stanislawski, *J. Amer. Chem. Soc.*, **96** (1974) 754.
- 18 F.A. Cotton, B.A. Frenz and A.G. Stanislawski, *Inorg. Chim. Acta*, **7** (1973) 503.
- 19 L.J. Guggenberger, C.T. Prewitt, P. Meakin, S. Trofimenko and J.P. Jesson, *Inorg. Chem.*, **12** (1973) 508.
- 20 *Interatomic Distances Supplement*. Special Publication No. 18, The Chemical Society, London, p. S16s, 1965.
- 21 J.A. McGinnety, *J. Chem. Soc., Dalton*, (1974) 1038.
- 22 G.R. Davies, W. Hewertson, R.H.B. Mais and P.G. Owston, *Chem. Commun.*, (1967) 423.
- 23 G.R. Davies, W. Hewertson, R.H.B. Mais, P.G. Owston and C.G. Patel, *J. Chem. Soc., (A)*, (1970) 1873.
- 24 A.L. Beauchamp, F.D. Rochon and T. Theophanides, *Canad. J. Chem.*, **51** (1973) 126.
- 25 E.O. Greaves, C.J.L. Lock and P.M. Maitlis, *Canad. J. Chem.*, **46** (1968) 3879.
- 26 A.C. Blizzard and D.P. Santry, *J. Amer. Chem. Soc.*, **90** (1968) 5749.
- 27 F.A. Cotton and V.W. Day, *Chem. Commun.*, (1974) 415.
- 28 S. Trofimenko, *J. Amer. Chem. Soc.*, **90** (1968) 4754.
- 29 S. Trofimenko, *Inorg. Chem.*, **9** (1970) 2493.