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A PLATINUM-CYCLOBUTENE COMPLEX: PREPARATION AND STRUCTURE OF BIS(TRIPHENYLPHOSPHINE)-(1,2-DICYANOCYCLOBUTENE)PLATINUM(0)

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Summary

The reaction of $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ with 1,2-dicyanocyclobutene affords the new complex bis(triphenylphosphine)(1,2-dicyanocyclobutene)platinum(0), $\text{Pt}((\text{NC})\overline{\text{C}=\text{C}(\text{CN})\text{CH}_2\text{CH}_2})(\text{PPh}_3)_2$. The complex has been characterized spectroscopically and by means of a low-temperature X-ray diffraction study. The ^{31}P NMR spectrum displays a singlet at 24.34 ppm downfield from external 85% H_3PO_4 with ^{195}Pt satellites ($^1J(^{195}\text{Pt}-^{31}\text{P}) = 3561$ Hz), consistent with the equivalence of the two PPh_3 groups in the complex. The material crystallizes in space group $C_{2h}^5 - P2_1/n$ of the monoclinic system with four formula units in a cell at -150°C of $a = 14.525(3)$, $b = 11.981(3)$, $c = 19.721(6)$ Å, $\beta = 98.22(1)^\circ$. Based on a total of 14 108 observations and 173 variables the structure has been refined to values of R and R_w on F_o^2 of 0.044 and 0.073, respectively. The cyclobutene is attached to the P_2Pt moiety through interaction with the double bond. The resultant P_2PtC_2 portion of the molecule is essentially planar. The Pt–P distances are 2.284(1) and 2.301(1) Å and the Pt–C distances are 2.091(3) and 2.077(3) Å. The 1,2-dicyanocyclobutene portion of the complex is essentially planar, with the angle between this plane and that of the P_2PtC_2 plane being 62.6° . The single bonds within the ring have lengths of 1.542(4), 1.546(5), and 1.541(5) Å, while the former double bond has on coordination lengthened to a value of 1.504(4) Å.

Introduction

The discovery of platinacyclobutanes by Tipper in 1955 [1] from the ring opening of cyclopropane by Pt^{II} initiated the study of the interactions of Group VIII metals with small rings [2–4]. Ring-opening insertions of Pt^0 , Pt^{II} , and Ir^{I} into cyclopropanes proceed by concerted pathways [5]; ring openings into heterocyclic oxiranes proceed by dipolar intermediates [6]. When the ring

is unsaturated, the double bond plays a role in initial coordination before the ring is opened [7,8]. Several structures of π -bound cyclopropenes have shown considerable lengthening of the C=C bond, perhaps because the metal orbitals interact to relieve ring strain in the molecule [8,9]. Some of these π -bound complexes can be converted into metallocycles by insertion of the metal into an adjacent C—C bond [7]. Activated cyclopropenes may undergo insertion of Pt into the adjacent C—C bond in solution [10].

Interactions of this type have not been as extensively documented for four-membered rings. Most of the work to date has involved metal-assisted catalysis of the rearrangements of cubanes or strained cyclobutenes to less strained products [11]. This usually involves scission of a cyclobutane by Ag^{I} , Cu^{I} , Pd^{II} , or Rh^{I} , and the release of a diolefin product, comprising a $4\sigma \rightarrow 2\pi + 2\pi$ transformation. Much of the evidence suggests that metallocyclic intermediates are often important in such processes. The compound $\text{Fe}(\text{CO})_5$ reacts with strained cyclobutenes to form an initial π -adduct, and then isomerizes the ligand by ring-opening of the cyclobutene. The result is a cyclobutene-to-butadiene rearrangement [11]. The use of cyclobutadiene as a 4π ligand has been extensive and many of its complexes have been analyzed structurally [12].

An area which has received much less attention than either of these is the study of the π -coordination and C—C bond activation of cyclobutenes. The only compounds that have been observed to coordinate and undergo subsequent insertions have been substituted cyclobutenediones [13,14]. Usually, these first bind in a π -fashion to the metal (a Pt^0 species) before the Pt center oxidatively inserts into an adjacent C—C single bond [14]. An intermediate π -complex has been characterized [15]. Platinum(0) may also be used to trap unstable organic moieties containing a cyclobutene ring. Thus, bicyclo[2.2.0]-cyclohexene forms a stable π -complex with Pt^0 at low temperature [16].

An objective of the present work was to analyze the product of the reaction of an electron-rich metal species with 1,2-dicyanocyclobutene. This ring is different from the cyclobutenediones in that the olefin carbon atoms are relatively electron poor and the other carbon atoms are saturated. We thus expected the formation and stabilization of a π -bound species leaving the ring intact.

Experimental

Synthesis of $\text{Pt}((\text{NC})\overline{\text{C}=\text{C}(\text{CN})\text{CH}_2\text{CH}_2})(\text{PPh}_3)_2$

The previously unreported complex bis(triphenylphosphine)(1,2-dicyanocyclobutene)platinum(0) was synthesized by refluxing $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ [17] (0.75 g, 1.0 mmol) and 1,2-dicyanocyclobutene [18] (0.27 g, 2.6 mmol) in benzene (19 ml) for 16 h. Reduction of the volume by half, followed by addition of absolute ethanol, gave a white precipitate. This precipitate was collected on a filter, washed with absolute ethanol, and dried in vacuo. Yield = 0.57 g (68%) (Anal. Found: C, 61.45; H, 4.06; N, 3.34. $\text{C}_{42}\text{H}_{34}\text{N}_2\text{P}_2\text{Pt}$ calcd.: C, 61.24; H, 4.16; N, 3.40%). The ^{31}P NMR spectrum (CDCl_3) consisted of a singlet at 24.34 ppm downfield from external 85% H_3PO_4 with ^{195}Pt satellites ($^1J(^{195}\text{Pt}-^{31}\text{P}) = 3561$ Hz). The IR spectrum (KBr pellet) contained a sharp band at 2200 cm^{-1} which we assign to the $\nu(\text{CN})$ stretching frequency.

Collection of X-ray data

The title compound was recrystallized from absolute EtOH to give large, clear crystals. Preliminary film work revealed symmetry and systematic extinctions consistent with the space group $C_{2h}^5 - P2_1/n$ of the monoclinic system. Acquisition of a low-temperature (-150°C) diffraction data set proceeded using methods described previously [19]. Some details are given in Table 1.

The positions of the Pt atom and the two *cis*-phosphorus atoms were found from a sharpened, origin-removed Patterson map. The other atoms in the asymmetric unit were found in a succession of difference Fourier maps.

Up to the final calculations, each successive refinement was carried out on a random 20% of the 10 796 unique data for which $F_0^2 > 3\sigma(F_0^2)$. Full matrix, least-squares refinement was on F_0 with minimization of $\sum w(|F_0| - |F_c|)^2$. The phenyl groups were constrained as rigid groups of D_{6h} symmetry with a C—C distance of 1.392 Å.

The isotropic refinement of non-hydrogen atoms converged to values for R

TABLE 1

DATA COLLECTION PROCEDURES AND REFINEMENT RESULTS FOR
 $\text{Pt}((\text{NC})\text{C}=\text{C}(\text{CN})\text{CH}_2\text{CH}_2)(\text{PPh}_3)_2$

Formula	$\text{C}_{42}\text{H}_{34}\text{N}_2\text{P}_2\text{Pt}$
Formula weight (a.m.u.)	823.79
Space group	monoclinic $C_{2h}^5 - P2_1/n$
Cell constants	
a (Å)	14.525(3)
b (Å)	11.981(3)
c (Å)	19.721(6)
β	93.22(1)
V (Å ³)	3397
Z	4
Density	
Calcd. (g/cm ³)	1.61 (-150°C) ^a
Measured (g/cm ³)	1.50 (23°C)
Crystal shape	irregular decahedral prism, bounded by faces of the forms {110}, {111}, {001}
Crystal volume (mm ³)	0.11
Radiation	graphite monochromated Mo- K_{α} ; ($\lambda(K_{\alpha 1}) = 0.7093$ Å)
μ (cm ⁻¹)	43.0
Transmission factors	0.13 to 0.25
Takeoff angle (°)	2.8
Receiving aperture (mm)	5 × 5, 34 cm from the crystal
Scan speed (°/min)	2
Scan width	1.0° below $K_{\alpha 1}$ to 1.0° above $K_{\alpha 2}$
Data collection	$\theta/2\theta$ method, $4.0^\circ \leq 2\theta \leq 67.8^\circ$
Background counts	10 seconds with the rescans option ^b
Number of unique reflections measured	14 108
Unique data with $F_0^2 > 3\sigma(F_0^2)$	10 796
Number of variables	173
Error in observation of unit weight	1.12 e^2
R (on F_0^2)	0.044
R_w (on F_0^2)	0.073
R (on $ F_0 $ for $F_0^2 > 3\sigma(F_0^2)$)	0.034
R_w (on $ F_0 $ for $F_0^2 > 3\sigma(F_0^2)$)	0.038

^a The low-temperature system is based on a design by J.C. Huffman [37].

^b The diffractometer was run under the disk-oriented Vanderbilt system [38].

TABLE 2

POSITIONAL AND THERMAL PARAMETERS OF NON-GROUP ATOMS OF
Pt(CN) $\overline{C=C(CN)CH_2CH_2}$ (PPh₃)₂

ATOM	X ^A	Y	Z	B ₁₁ ^B	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
PT	0.265935(65)	0.1156153(83)	0.2236839(58)	13.16(4)	19.05(6)	0.33(2)	-2.10(6)	1.25(2)	2.56(3)
P(1)	-0.096909(46)	0.019808(57)	0.166262(35)	14.72(26)	16.46(39)	0.76(15)	-0.05(26)	2.49(16)	0.24(19)
P(2)	0.032656(47)	0.055566(68)	0.335178(36)	15.68(27)	26.08(41)	9.63(15)	-2.48(27)	0.86(16)	2.36(28)
C(1)	0.13369(21)	0.23105(27)	0.22150(15)	18.5(12)	37.1(23)	12.79(69)	-0.1(13)	-1.74(73)	5.68(97)
C(2)	0.07635(28)	0.21766(25)	0.15219(15)	17.2(11)	27.2(18)	10.03(68)	-2.3(12)	2.82(78)	5.58(89)
C(3)	0.16166(22)	0.17193(28)	0.12275(17)	22.3(13)	45.9(22)	17.96(80)	3.6(14)	0.47(83)	8.4(11)
C(4)	0.22086(21)	0.18808(32)	0.19633(22)	15.5(11)	61.8(26)	24.7(13)	-2.3(14)	2.0(19)	18.5(15)
C(5)	0.13681(24)	0.33181(33)	0.26841(17)	33.2(16)	49.3(27)	14.33(78)	-22.7(18)	-3.29(88)	8.3(12)
C(6)	0.01571(20)	0.30867(25)	0.11961(16)	23.7(12)	23.9(16)	9.89(61)	-6.0(12)	0.36(68)	8.87(87)
N(1)	0.13933(27)	0.41371(31)	0.29846(18)	65.6(21)	57.5(27)	17.63(91)	-31.8(19)	-8.3(12)	-1.2(13)
N(2)	-0.03264(28)	0.36983(21)	0.09341(16)	39.5(13)	28.0(17)	16.16(76)	0.4(11)	-2.37(78)	1.19(85)

^A ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. ^B THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B_{11}H^2 + B_{22}K^2 + B_{33}L^2 + 2B_{12}HK + 2B_{13}HL + 2B_{23}KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS $\times 10^{-4}$.

and R_w of 0.080 and 0.091. Next, the hydrogen atom positions of the phenyl groups were idealized ($C-H = 0.95 \text{ \AA}$). The positions of the cyclobutene hydrogen atoms were also idealized using a $C-H$ distance of 0.95 \AA and an $H-C-H$ angle of 114° [20]. The contributions of these atoms to the structure factors were fixed in subsequent refinements. Each hydrogen atom was given a thermal parameter 1.0 \AA^2 greater than that of the carbon atom to which it is attached.

TABLE 3

DERIVED PARAMETERS FOR GROUP ATOMS OF Pt(CN) $\overline{C=C(CN)CH_2CH_2}$ (PPh₃)₂

ATOM	X	Y	Z	B ₁₁ ²	ATOM	X	Y	Z	B ₁₁ ²
C(11)	-0.07288(12)	-0.12331(12)	0.142838(19)	1.40(4)	C(41)	0.158865(98)	0.05756(17)	0.381577(83)	1.42(4)
C(12)	-0.00999(12)	-0.18896(15)	0.183317(17)	1.78(4)	C(42)	0.22221(12)	0.0198(17)	0.367518(67)	1.75(4)
C(13)	0.02045(12)	-0.24981(15)	0.186438(19)	2.14(5)	C(43)	0.31221(10)	0.0094(18)	0.382482(87)	1.93(5)
C(14)	-0.02693(13)	-0.34896(12)	0.189878(19)	1.98(4)	C(44)	0.338894(92)	0.03853(18)	0.451365(86)	1.97(4)
C(15)	-0.09974(13)	-0.28331(15)	0.088598(18)	1.93(5)	C(45)	0.25951(12)	0.0778(18)	0.445846(87)	2.05(4)
C(16)	-0.12118(12)	-0.17648(16)	0.085478(18)	1.76(4)	C(46)	0.16951(12)	0.08660(17)	0.458528(84)	1.73(4)
C(21)	-0.14560(11)	0.07688(16)	0.082195(16)	1.36(4)	C(51)	-0.00392(12)	-0.08015(13)	0.35885(11)	1.47(4)
C(22)	-0.082688(88)	0.08622(17)	0.035585(18)	1.71(4)	C(52)	-0.09778(11)	-0.11435(14)	0.36067(11)	1.88(4)
C(23)	-0.11834(12)	0.12963(18)	-0.030887(18)	2.15(5)	C(53)	-0.129317(91)	-0.22933(16)	0.35118(11)	2.17(5)
C(24)	-0.21370(13)	0.14169(20)	-0.058749(17)	2.48(5)	C(54)	-0.05916(13)	-0.31012(12)	0.35611(12)	2.39(5)
C(25)	-0.275812(92)	0.12834(20)	-0.084139(19)	2.46(6)	C(55)	0.03661(11)	-0.28391(13)	0.35858(11)	2.05(4)
C(26)	-0.24897(18)	0.04634(18)	0.062333(18)	1.83(4)	C(56)	0.06232(18)	-0.17293(15)	0.35587(10)	1.78(4)
C(31)	-0.19775(18)	0.01138(16)	0.211338(16)	1.33(3)	C(61)	-0.02957(13)	0.14733(15)	0.386972(96)	1.83(4)
C(32)	-0.21228(12)	0.18861(12)	0.253747(15)	1.59(4)	C(62)	-0.08409(15)	0.43487(11)	0.43487(11)	2.15(5)
C(33)	-0.24866(13)	0.09695(13)	0.292771(16)	1.90(5)	C(63)	-0.12661(16)	0.18588(18)	0.47388(18)	2.61(6)
C(34)	-0.34291(11)	0.08487(16)	0.289388(17)	2.15(5)	C(64)	-0.11661(16)	0.25998(18)	0.46658(11)	2.65(6)
C(35)	-0.32838(12)	-0.08516(13)	0.24696(18)	1.98(4)	C(65)	-0.08089(17)	0.33786(12)	0.41668(12)	2.73(6)
C(36)	-0.25540(13)	-0.08150(13)	0.207939(19)	1.71(4)	C(66)	-0.01757(14)	0.26135(16)	0.37788(18)	2.24(5)

RIGID GROUP PARAMETERS

GROUP	X _C ^A	Y _C	Z _C	DELTA ^B	EPSILON	ETA
PPh1P1	-0.058364(83)	-0.23224(11)	0.125958(16)	1.5258(16)	2.3788(12)	-2.7548(15)
PPh2P1	-0.179656(88)	0.10826(11)	0.015723(16)	1.6281(16)	-2.77996(18)	-1.2618(14)
PPh3P1	-0.278338(81)	0.00772(10)	0.250355(16)	2.8624(11)	2.7977(11)	0.7767(13)
PPh1P2	0.248659(84)	0.04804(18)	0.416461(16)	0.7520(25)	-2.8488(11)	0.6964(25)
PPh2P2	-0.031542(87)	-0.19913(11)	0.353482(16)	-1.06789(16)	3.8642(12)	0.0788(13)
PPh3P2	-0.072891(95)	0.22361(12)	0.425777(17)	-0.4842(15)	2.5987(13)	2.3325(16)

^A X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. ^B THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (DEGREES) HAVE BEEN DEFINED PREVIOUSLY S.-J. LA PLAGA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

TABLE 4

IDEALIZED HYDROGEN PARAMETERS OF $\text{Pt}((\text{CN})\overline{\text{C}=\text{C}(\text{CN})\text{CH}_2\text{CH}_2})(\text{PPh}_3)_2$

ATOM	X	Y	Z	R	ATOM	X	Y	Z	R
H1C(3)	.1542	.0976	.1084	3.18	H1C(35)	-.3696	-.1453	.2454	2.19
H2C(3)	.1809	.2218	.0901	3.18	H1C(36)	-.2477	-.1414	.1794	2.31
H1C(4)	.2412	.1147	.2133	3.94	H1C(42)	.2107	.0011	.3002	2.87
H2C(4)	.2693	.2382	.1945	3.94	H1C(43)	.3622	-.0134	.3589	2.78
H1C(12)	.0331	-.1465	.2222	2.73	H1C(44)	.3927	.0331	-.4753	3.02
H1C(13)	.0698	-.3291	.1933	2.93	H1C(45)	.2717	.0941	.5330	3.26
H1C(14)	-.0137	-.4153	.0970	3.25	H1C(46)	.1202	.1086	.4742	2.73
H1C(15)	-.1339	-.3188	.0296	2.71	H1C(52)	-.1432	-.0570	.3451	2.95
H1C(16)	-.1705	-.1361	.0545	2.47	H1C(53)	-.1887	-.2440	.3498	3.72
H1C(22)	-.0191	.0862	.0491	2.67	H1C(54)	-.0767	-.3859	.3586	3.53
H1C(23)	-.0762	.1442	-.0624	3.35	H1C(55)	.0809	-.3408	-.3628	3.13
H1C(24)	-.2366	.1654	-.0958	3.45	H1C(56)	.1264	-.1538	.3581	2.82
H1C(25)	-.3399	.1285	-.0176	3.83	H1C(62)	-.0912	.0318	.4416	2.64
H1C(26)	-.2828	.0704	.0939	2.60	H1C(63)	-.1638	.1596	.5066	3.67
H1C(32)	-.1704	.1637	.2547	2.82	H1C(64)	-.1443	.3516	.4913	3.67
H1C(33)	-.2923	.1598	.3226	2.54	H1C(65)	-.0522	.4158	.4112	3.80
H1C(34)	-.3918	.0052	.3170	2.66	H1C(66)	.0204	.2880	.3462	3.02

The final refinement on F_0^2 , with $w = 1/\sigma^2(F_0^2)$, and minimization of $\sum w(F_0^2 - F_c^2)^2$, was based on 173 variables and 14 108 unique data and converged to values for R and R_w (on F_0^2) of 0.044 and 0.073, and to an error in an observation of unit weight of $1.12 e^2$. For unique data having $F_0^2 > 3\sigma(F_0^2)$ the values of R and R_w (on F_0) are 0.034 and 0.038. A final difference Fourier map displays peaks no higher than $1.3 e/\text{\AA}^3$, approximately 12% of the height of a C atom in the structure. An analysis of the $\sum w(F_0^2 - F_c^2)^2$ as a function of $|F_0|$, Miller indices, and $\lambda^{-1} \sin \theta$ exhibited no unusual trends.

The final positional, thermal, and group parameters are given in Tables 2 and 3. The idealized parameters for the hydrogen atoms are given in Table 4. Root-mean-square amplitudes of vibration for the nongroup atoms are given in Table 5. A listing of observed and calculated structure amplitudes is available ∞ .

Results and discussion

The crystal structure consists of the packing of monomers of $\text{Pt}((\text{CN})\overline{\text{C}=\text{C}(\text{CN})\text{CH}_2\text{CH}_2})(\text{PPh}_3)_2$; a stereo view of the unit cell is shown in Fig. 1. There are

* Table 5 and the table of structure amplitudes have been deposited as NAPS document no. 03763 (49 pages). Order from NAPS % Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only \$ 12.25 for photocopies or \$ 3.00 for microfiche. Outside the U.S. and Canada add postage of \$ 3.00 for photocopy and \$ 1.00 for microfiche.

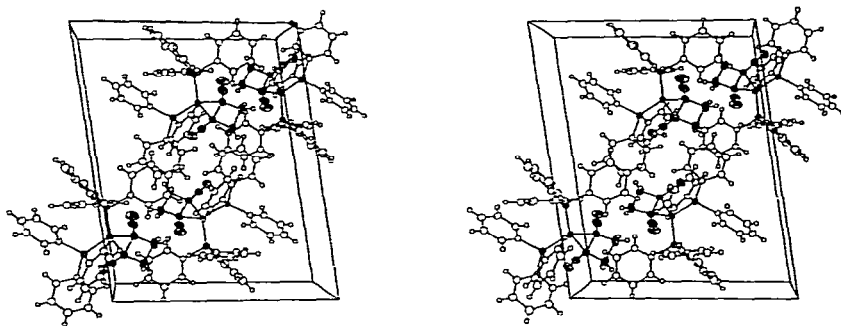


Fig. 1. A stereo view of the unit cell of $\text{Pt}((\text{CN})\overline{\text{C}=\text{C}(\text{CN})\text{CH}_2\text{CH}_2})(\text{PPh}_3)_2$. The view is down the b axis. The 50% probability ellipsoids are shown here and in subsequent figures.

no significant intermolecular interactions, the closest contact being the $\text{H}(2)\text{C}(4)\cdots\text{H}(1)\text{C}(56)$ distance of 2.34 Å. There are four other $\text{H}\cdots\text{H}$ contacts in the range 2.36 Å to 2.46 Å; other contacts of $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{H}$, and $\text{N}\cdots\text{H}$ are greater than 2.5 Å.

A stereo view of the molecule is shown in Fig. 2. The structure is the anticipated one, with coordination of the cyclobutene to the P_2Pt moiety through the olefinic bond. The inner coordination sphere around the Pt atom is nearly planar; the dihedral angle (θ) between the Pt, C(1), C(2) plane and the Pt, P(1), P(2) plane is only $2.4(1)^\circ$, compared with typical values of 8° to 9° in similar Pt^0 olefin complexes [21]*. The deviations of atoms Pt, P(1), P(2), C(1), and C(2) from the best weighted least-squares plane are 0.002(1), $-0.0022(7)$, $-0.0040(7)$, $-0.020(4)$, and $-0.069(3)$ Å. The P(1)–Pt–P(2) angle of $103.90(3)^\circ$ and the C(1)–Pt–C(2) angle of $42.3(1)^\circ$ are typical for Pt complexes with electron-poor olefins [23]. Other important bond distances and angles are tabulated in Table 6, and a comparison with similar structures is made in Table 7 [24–26]. The cone angles and P–C distances of the phosphines are normal. The phenyl groups around phosphorus display a propeller conformation.

The 1,2-dicyanocyclobutene ligand has retained the planarity of its four-membered ring on complexation to Pt; the deviations of atoms C(1), C(2), C(3), and C(4) from the best weighted least-squares plane are 0.006(3), $-0.005(3)$, 0.006(3), and $-0.008(4)$ Å. This plane makes an angle of 62.6° with the PtP_2C_2 plane. A detailed view of the coordinated ligand is shown in Fig. 3. Backbonding of Pt d -electrons into the π^* -orbital of the 1,2-dicyanocyclobutene ligand has lengthened the carbon–carbon double bond to 1.504(4) Å from the average length of 1.35 Å found in some substituted cyclobutenes [27]. Structures of cyclobutenes provide a wide range of lengths for this bond, from 1.342 Å in cyclobutene itself to 1.41 Å in substituted cyclobutenediones (squaric acid and its derivatives) [28–30]. But the length of this bond in the present complex is comparable with those in other coordinated olefins (Table 7) which may be formally described as Pt^{II} -metallocyclopropanes.

* A dihedral angle of $3.2(5)^\circ$ is found in the $\text{Pt}(\text{bicyclo}[2.2.0]\text{cyclohexene})$ complex [22].

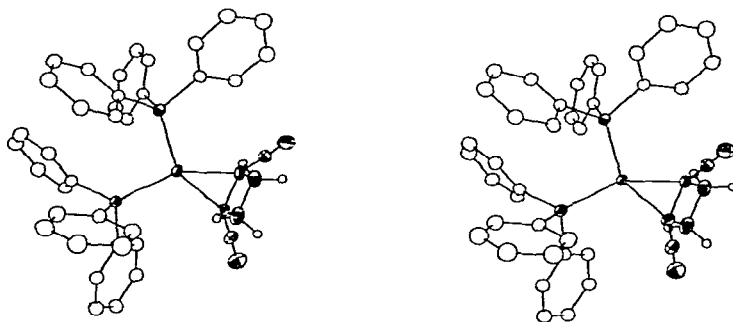


Fig. 2. A stereo view of the $\text{Pt}((\text{CN})\overline{\text{C}=\text{C}(\text{CN})\text{CH}_2\text{CH}_2})(\text{PPh}_3)_2$ molecule. Only the cyclobutene hydrogen atoms have been included.

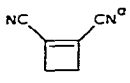
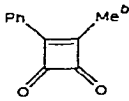
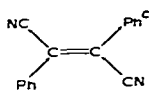
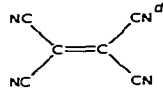
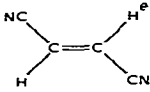
TABLE 6

DISTANCE AND ANGLES FOR $\text{Pt}((\text{CN})\overline{\text{C}=\text{C}(\text{CN})\text{CH}_2\text{CH}_2})(\text{PPh}_3)_2$

Distances (Å)		Angles (°)	
Pt—P(1)	2.284(1)	P(1)—Pt—P(2)	103.90(3)
Pt—P(2)	2.301(1)	P(1)—Pt—C(2)	106.48(8)
Pt—C(1)	2.091(3)	P(2)—Pt—C(1)	107.31(8)
Pt—C(2)	2.077(3)	C(1)—Pt—C(2)	42.3(1)
C(1)—C(2)	1.504(4)	C(1)—C(2)—C(3)	90.6(2)
C(2)—C(3)	1.542(4)	C(2)—C(3)—C(4)	89.4(2)
C(3)—C(4)	1.546(5)	C(3)—C(4)—C(1)	89.1(2)
C(4)—C(1)	1.541(5)	C(4)—C(1)—C(2)	91.0(3)
C(1)—C(5)	1.428(5)	C(4)—C(1)—C(5)	122.2(3)
C(2)—C(6)	1.420(4)	C(4)—C(1)—Pt	114.1(2)
C(5)—N(1)	1.144(5)	C(3)—C(2)—C(6)	123.9(3)
C(6)—N(2)	1.152(4)	C(3)—C(2)—Pt	114.9(2)
F(1)—C(11) ^a	1.827(2)	C(2)—C(1)—Pt	68.3(2)
P(1)—C(21)	1.830(2)	C(1)—C(2)—Pt	69.4(2)
P(1)—C(31)	1.822(2)	C(2)—C(1)—C(5)	123.3(3)
P(2)—C(41)	1.824(2)	C(1)—C(2)—C(6)	124.3(3)
F(2)—C(51)	1.842(2)	C(1)—C(5)—N(1)	178.7(4)
P(2)—C(61)	1.827(2)	C(2)—C(6)—N(2)	179.1(3)
Dihedral Angles ^b (°)			
C(5)C(1)C(4)—C(6)C(2)C(3)	84.6(4) (α)		
PtP(1)P(2)—PtC(1)C(2)	2.4(1) (θ)		
Vector-Plane Normal Angles ^b (°)			
C(1)C(2)—C(5)C(1)C(4)	41.3(4) (β ₁)		
C(1)C(2)—C(6)C(2)C(3)	43.3(4) (β ₂)		
C(1)C(2)—PtP(1)P(2)	88.1(2) (ψ)		
Torsion Angles ^b (°)			
C(5)C(1)C(2)C(3)	129.5(3) (γ ₁)		
C(4)C(1)C(2)C(6)	134.0(3) (γ ₂)		
PtC(1)C(2)C(3)	116.5(2) (δ ₁)		
PtC(2)C(1)C(4)	115.6(2) (δ ₂)		
PtC(2)C(1)C(5)	113.9(3) (δ ₃)		
PtC(1)C(2)C(6)	110.4(3) (δ ₄)		

^a Atom C(n1) of phenyl ring n is attached to a P atom, and the other atoms of the ring are C(n2) through C(n6). ^b These are defined in ref. 21.

TABLE 7
COMPARISON OF STRUCTURAL PARAMETERS OF Pt(olefin)(PPh₃)₂ COMPLEXES

					
Distances (Å)					
Pt—P(1)	2.284(1)	2.271(4)	2.295(2)	2.291(9)	2.277(5)
Pt—P(2)	2.301(1)	2.309(4)	2.289(2)	2.288(8)	2.296(4)
Pt—C(1)	2.091(3)	2.12(2)	2.102(7)	2.12(3)	2.05(2)
Pt—C(2)	2.077(3)	2.00(2)	2.113(8)	2.10(3)	2.16(2)
C(1)—C(2)	1.504(4)	1.53(3)	1.50(1)	1.49(5)	1.53(4)
P—C ^f	1.829(7)	1.84(2)	1.830(8)	1.82(4)	1.829(8)
C≡N ^f	1.149(6)	—	1.16(2)	1.15(3)	1.15(3)
Angles (°)					
P(1)—Pt—P(2)	103.90(3)	103.9(2)	103.51(9)	101.4(3)	104.4(2)
P(1)—Pt—C(2)	106.48(8)	108.2(5)	104.6(2)	111(1)	102.7(7)
P(2)—Pt—C(1)	107.31(8)	103.5(5)	110.0(2)	106(1)	110.5(7)
C(1)—Pt—C(2)	42.3(1)	43.5(7)	41.7(3)	42(1)	43(1)
C(4)—C(1)—C(5)	122.2(3)	131(2)	111.5(6)	110(4)	—
C(3)—C(2)—C(6)	123.9(3)	120(2)	114.6(6)	116(3)	—
Pt—P—C ^f	115(2)	114(7)	115(5)	114(4)	114(3)
C—P—C ^f	103(3)	104(4)	104(3)	105(4)	105(2)
Dihedral Angles^g (°)					
α	84.6(4)	72(3)	64.1(8)	66.1	—
β _{1,2}	41.3(4)	63(3)	55.2(8)	63.8	—
	43.3(4)	45(2)	60.8(9)	—	—
γ _{1,2}	129.5(3)	147(1)	144.2(7)	141.3	—
	134.0(3)	136(2)	138.0(6)	—	—
δ _{1→4}	116.5(2)	104(2)	110.5(5)	—	—
	115.6(2)	99(1)	105.3(6)	—	—
	113.9(3)	109(3)	112.0(7)	—	—
	110.4(3)	125(2)	110.0(6)	—	—
θ	2.4(1)	22(1)	8.9(4)	8.3	—
ψ	88.1(2)	73(1)	83.2(4)	—	—

^a This paper. ^b Ref. 15. ^c Ref. 24. ^d Ref. 25. ^e Ref. 26. ^f These are average quantities. ^g Ref. 21.

The Pt—C distances of 2.091(3) and 2.077(3) Å do not differ from those of similar structures. The olefin is bound so as to minimize steric repulsions with the phosphine groups. The various angles useful for defining the non-planarity of the bound olefin are summarized in Table 6. The α, β, and γ angles, which describe the disposition of the olefin, are significantly different from those of other Pt(olefin)P₂ complexes; this is presumably the result of the C(3) and C(4) carbon atoms being tied back in the four-membered ring. The dihedral angles, δ, which describe the disposition of the cyano groups and ring carbon atoms, are similar to those in related complexes (Table 7).

Although cyclobutene π-complexes appear to be rare, many structures involving the 1,2-bis(dimethylarsino)-3,3,4,4-tetrafluorocyclobutene ligand are known [27,31–36]. In most cases, this molecule is used to provide a rigid, planar diarsine ligand (or an analogous phosphine) for binding to a single metal or chelation to a metal cluster [31,32]. In all instances, the arsenic atoms are

benzene, even though the cyanocyclobutene has minimal steric requirements.

Upon coordination, both cyclopropenes and cyclobutenes show considerable lengthening of the olefinic bond. Concomitant opening of the acute bond angles opposite to this bond occurs, thus reducing the strain energy of the molecule. Upon coordination, the olefinic double bond of unstrained polycyano-olefins is also lengthened to about the same degree. These polycyano-olefins have low energy π^* -orbitals to match the energy of the d -orbital of the metal, thus maximizing orbital overlap. On the basis of the resultant bond lengths, it appears that these two factors, namely the relief of ring strain in strained olefins and the presence of electron-withdrawing substituents on unstrained olefins, have about the same effect on the degree of backbonding from metal to olefin. The present complex, a π -bonded cyano-cyclobutene, has both factors operating to enhance this backbonding. The effects are clear in the lengthening of the olefinic double bond to 1.504(4) Å and in the opening of the C(2)–C(3)–C(4) and C(3)–C(4)–C(1) angles to nearly 90°, as detailed in Fig. 3. The upper limit to which the coordinated olefinic bond may be lengthened with strong π -backbonding appears to be 1.53 Å.

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