

THE STRUCTURE OF BIS(TRIPHENYLPHOSPHINE)(1,1-DICHLORO-2,2-DICYANOETHYLENE)PLATINUM(0), $\text{Pt}[\text{Cl}_2\text{C}=\text{C}(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$

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SUMMARY

The structure of bis(triphenylphosphine) (1,1-dichloro-2,2-dicyanoethylene)-platinum(0), $\text{Pt}[\text{Cl}_2\text{C}=\text{C}(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$ has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The structure has been refined by least-squares techniques to a final *R* factor on *F* of 5.3%, based on 1777 observations above background. The material crystallizes in space group $C_{2h}^5-P2_1/c$ of the monoclinic system, with four molecules in a cell of dimensions $a=10.507(7)$, $b=15.264(9)$, $c=23.340(13)$ Å, $\beta=107.32(2)^\circ$. The observed and calculated densities are 1.63(1) and 1.610 g/cm³, respectively. If one counts the olefin as a single ligand, the coordination about the Pt atom is trigonal. The two central atoms of the olefin ligand are not equidistant from the metal, the Pt-CCl₂ bond length of 2.00(2) Å being significantly shorter than the Pt-C(CN)₂ bond length of 2.10(2) Å. The central C-C bond length of 1.42(3) Å is longer than the value of 1.339(2) Å found in free ethylene, but shorter than the values of 1.49(5) Å and 1.62(3) Å found in the analogous complexes of tetracyanoethylene and tetrachloroethylene, respectively. As expected the olefinic ligand is non-planar with the CCl₂ and C(CN)₂ groups bent away from the Pt atom. However, the groups are not bent back equally. The angle between the central C-C bond and the normal to the CCl₂ plane is $48.4 \pm 2.3^\circ$, compared with a value of $69.9 \pm 3.3^\circ$ for the angle between C-C and C(CN)₂. Thus the CCl₂ group is bent back by about twice as much as the C(CN)₂ group. The central C-C vector is, within experimental error, perpendicular to the normal to the Pt-P(1)-P(2) plane, *i.e.*, the olefinic C atoms lie strictly in the plane of the Pt and the two P atoms.

INTRODUCTION

Despite the growing number of structural studies on organometallic complexes, there is still insufficient structural information that bears on the finer details of the bonding of olefins to transition metals. As part of a program to study the structural effects of substituting electron-withdrawing atoms and groups onto the olefinic carbon atoms in platinum-olefin π -complexes, we have previously determined the crystal and molecular structure of bis(triphenylphosphine)(tetrachloroethylene)-platinum(0)¹. The crystal structure of the analogous complex of tetracyanoethylene (TCNE) has also been published², and there appear to be important differences between the two molecules. The most significant differences are to be found in the Pt-C

distances [2.03 Å in the $\text{Cl}_2\text{C}=\text{CCl}_2$ (TCLE) complex *vs.* 2.11 Å in the TCNE complex], and to a lesser extent in the degree of bending back from the platinum atom of the CX_2 groups. Each of the CCl_2 groups is bent back by about 41° *³ from the original planar configuration, whereas the $\text{C}(\text{CN})_2$ groups are bent back by about 32° . However the average Pt–P bond lengths in the two complexes are strictly comparable [2.285(8) Å *vs.* 2.289(9) Å]. In view of these results we felt it would be useful to study the complex of the mixed olefin 1,1-dichloro-2,2-dicyanoethylene, for which one could compare directly the electron-withdrawing properties of Cl *vs.* CN. Whereas the complexes prepared from halogen-substituted ethylenes proved to be very unstable in the X-ray beam, the tetracyanoethylene complex is relatively stable. We thus hoped that two cyano groups on the chloro olefin might stabilize the resultant complex. The results of this study are presented here.

EXPERIMENTAL

Preparation and characterization

The previously unreported complex bis(triphenylphosphine)(1,1-dichloro-2,2-dicyanoethylene)platinum(0) was synthesized from 1,1-dichloro-2,2-dicyanoethylene⁴ and bis(triphenylphosphine) (stilbene)platinum⁵, and recrystallized from an acetone/water mixture. The compound melts at $310\text{--}312^\circ$, with partial melting and resolidification at about 150° caused by its irreversible isomerization to a vinyl complex, as occurs with the TCLE complex⁶.

Infrared spectrum (nujol mull): 3.29 w, 4.52 m, 6.75 m, 6.98 s, 7.49 vw(br), 7.62 w, 7.80 vw, 8.42 w, 8.60 m, 9.10 s, 9.30 w, 9.71 w, 9.97 w, 10.08 vw, 10.25 vw(br), 11.65 w(br), 12.03 m, 12.55 m, 13.19 m, 13.42 s, 14.02 m, 14.22 s, 14.42 vs, 14.81 s.

The compound may be recrystallized from either methylene chloride or a mixture of acetone/water. A preliminary crystallographic examination of the crystals obtained from methylene chloride indicated a monoclinic unit cell of dimensions $a = 10.50(2)$, $b = 37.13(5)$, $c = 10.87(2)$ Å, $\beta = 113.4(3)^\circ$. The space group was uniquely determined to be $C_{2h}^5\text{--}P2_1/c$. However, in view of the extremely long b axis, we selected our data crystal from those recrystallized from acetone/water. The crystal data for these are given below.

Crystal data

$\text{C}_{40}\text{Cl}_2\text{H}_{30}\text{N}_2\text{P}_2\text{Pt}$; mol. wt., 866.6; monoclinic, $a = 10.507(7)$, $b = 15.264(9)$, $c = 23.340(13)$ Å, $\beta = 107.32(2)^\circ$; [Temp. 22° , $\lambda(\text{Mo-K}\alpha_1)$ 0.7093 Å]; $U = 3574$ Å³, $d_c = 1.610$ g/cm³ for $Z = 4$, $d_0 = 1.63(1)$ g/cm³ (by flotation in $\text{CH}_3\text{I}/\text{C}_2\text{Cl}_4$). Linear absorption coefficient for Mo-K α X-rays, $\mu = 44.3$ cm⁻¹.

A sample was prepared by the method outlined above, and recrystallized from acetone/water. The crystals were colorless, transparent prisms with well-formed faces. Oscillation, Weissenberg, and precession photographs taken with Cu-K α ($\lambda = 1.5418$ Å) and Mo-K α ($\lambda = 0.7107$ Å) radiations indicated that the crystals belong to the monoclinic system. The systematic absence of $0k0$ reflections when $k \neq 2n$ and $h0l$ reflections when $l \neq 2n$ uniquely determined the space group to be $C_{2h}^5\text{--}P2_1/c$. Since density measurements indicate four molecules per unit cell, no symmetry conditions need be

* This angle is defined as $(90^\circ - \beta)$ where β is defined as the angle the central C–C vector makes with the normal to the CX_2 plane. See also ref. 3.

imposed on the molecules of the complex. On the basis of optical goniometry the crystal faces typically belong to the forms $\{012\}$, $\{102\}$, and $\{1\bar{1}0\}$.

Intensity measurements were made with a Picker Four Circle Diffractometer, using monochromatic Mo- K_{α} radiation produced by Bragg reflection from the (002) plane of a highly oriented graphite crystal. Apart from the use of the monochromator, the procedures employed have been described in detail elsewhere^{7,8}. A crystal of dimensions $0.27 \times 0.13 \times 0.12$ mm was mounted on the instrument so that the a axis was roughly coincident with the Φ axis. The half-widths of a number of narrow-source, open-counter ω -scans ranged from 0.08° to 0.13° , indicating that the mosaicity of the crystal was acceptably low. The setting angles of 13 reflections were determined manually through a narrow vertical slit at 0.7° takeoff angle. From these observations the crystal orientation and preliminary values of the cell parameters were derived by a least-squares procedure^{7,8}.

For data collection Mo- K_{α} radiation was used, the intensities being measured by the θ - 2θ technique at a takeoff angle of 1.65° . The counter was positioned 33 cm from the crystal and was preceded by an aperture of dimensions 3.0 mm \times 3.5 mm. The pulse-height analyzer was set to admit 90% of the Mo- K_{α_1} peak. Copper foil attenuators were automatically inserted if the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan.

The data were collected in four shells: $2\theta \leq 26.2^{\circ}$, $26.2 < 2\theta \leq 31.0^{\circ}$, $31.0 < 2\theta \leq 35.8^{\circ}$, and $35.8 < 2\theta \leq 39.0^{\circ}$. Since the last shell yielded relatively few intensities above background, data collection was terminated. Reflections were scanned at 1° in 2θ per minute, and background counts were taken at each end of the scan range. For the first shell the scan ranged from -0.40° to $+0.50^{\circ}$ from the Mo- K_{α_1} maximum, and the background counting time was 10 sec; thereafter the range was from -0.55° to $+0.60^{\circ}$, and the background counting time was 20 sec.

The intensities of four standard reflections were measured periodically (every 100 reflections for the first shell, every 200 thereafter). At the end of the collection of the first shell (976 reflections) the intensity of one of the standards had dropped by 10%. The crystal was recentered and the intensity of this reflection returned to its original value. At the end of the data collection, the intensities of all four reflections had, on the average, decreased by about 12%. Compensation for this decay was made during the data-processing. In the least-squares refinement of the structure, the data from the first shell were given a separate scale factor because of the crystal recentering. At the end of the refinement the two scale factors differed by 2%.

All data were processed as previously described^{7,8}. A value of p of 0.04 was used in the estimation of the standard deviations. Of the 3094 unique reflections having $2\theta \leq 39.0^{\circ}$, 1777 obeyed the condition $F_o^2 > 3\sigma \cdot (F_o^2)$, and only these reflections were used in subsequent calculations. To correct for the absorption of the crystal, the dimensions of the crystal were determined by means of a micrometer eyepiece, and the faces indexed by optical goniometry. The calculated transmission factors ranged from 0.56 to 0.67*.

* In addition to various local programs for the CDC 6400, computer programs used in this work include local versions of Zalkin's FORDAP Fourier program, Hamilton's GONO9 absorption correction program, Busing and Levy's ORFFE function and error program, and Johnson's ORTEP thermal ellipsoid plotting program. Our least-squares program NUCLS, in its nongroup form, closely resembles the Busing-Levy ORFLS program.

At the end of the data collection, the monochromator was removed and 12 strong reflections were centered manually as before, using a takeoff angle of 0.8° . The cell parameters taken from this refinement are listed at the beginning of this section.

Structure solution and refinement

The structure was solved using conventional Patterson, least-squares, and Fourier methods. From a Patterson synthesis on 903 low-angle reflections it was possible to locate the platinum atom. Refinement, followed by a difference Fourier synthesis, revealed the two phosphorus atoms and one of the chlorine atoms. Repetition of these steps led to positions for the other chlorine atom and two of the phenyl rings. At this point all the data were included in the calculations, and a difference Fourier synthesis revealed all other non-hydrogen atoms. The agreement factors R ($\Sigma\Delta/\Sigma|F_o|$, $\Delta = ||F_o| - |F_c||$) and R_w [$(\Sigma w \cdot \Delta^2 / \Sigma w \cdot F_o^2)^{1/2}$] were 0.134 and 0.157, respectively.

Refinement of the structure was continued by the method of full-matrix least-squares, the function minimized being $\Sigma w \cdot \Delta^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Throughout the refinement the phenyl rings were constrained to D_{6h} symmetry⁹, and the C-C bond distance was fixed at 1.394 Å. The atomic scattering factors used in all calculations were from the usual tabulation¹⁰, with the exceptions of those for Pt¹¹ and H¹². The anomalous dispersion corrections of Cromer for Pt, P, and Cl¹³ were applied to the calculated structure factors¹⁴.

Two cycles of refinement in which all nongroup atoms were assigned isotropic thermal parameters, and each of the phenyl rings an overall group thermal parameter, led to R and R_w values of 0.103 and 0.118, respectively. After correction for absorption, one further cycle of isotropic refinement converged to a value of R of 0.097. Two cycles in which all non-phenyl atoms were allowed to vibrate anisotropically, followed by a cycle in which variable isotropic temperature factors were assigned to each of the phenyl carbon atoms reduced R and R_w to 0.056 and 0.066, respectively. However, the thermal ellipsoid of atom C(3) was nonpositive definite. A difference Fourier map then revealed peaks which could be ascribed to some of the hydrogen atoms of the phenyl rings. Accordingly, fixed contributions for the ring hydrogen atoms were included in all further structure factor calculations; the C-H distance was taken as 1.0 Å, and the temperature factor of each hydrogen atom was set equal to that of the carbon atom to which it was bonded. A further cycle of refinement reduced R to 0.053. The thermal ellipsoid of atom C(3) remained nonpositive definite in the next cycle. Accordingly, in a subsequent cycle of refinement only the Pt, P, and Cl atoms were allowed to vibrate anisotropically. None of the coordinates of the C and N atoms of the coordinated olefin moved by more than two standard deviations, and R and R_w remained constant. Consequently this mode of refinement was continued during the last cycle of least-squares refinement. This converged to R 0.053 and R_w 0.061.

In the final cycle no parameter shifted by more than 0.3 of its estimated standard deviation. The standard deviation of an observation of unit weight is 1.82. However, the relative correctness of the weighting scheme, judged by the variation in mean $\Sigma w \cdot \Delta^2$ with $\lambda^{-1} \sin \theta$ and $|F_o|$, is satisfactory. No extinction corrections were deemed necessary.

The positional and thermal parameters for all nongroup atoms, obtained from

TABLE 1

POSITIONAL AND THERMAL PARAMETERS FOR Pt[Cl₂C=C(CN)₂][P(C₆H₅)₃]₂

Atom	x	y	z	B _{iso} (Å ²) or β ₁₁ ^a	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Pt	0.25177(10)	0.24538(7)	0.13127(4)	114(2)	36.2(7)	25.6(3)	-4.2(1.0)	29.6(4)	-0.8(4)
P(1)	0.0838(6)	0.3261(4)	0.1459(3)	118(9)	30(3)	27(2)	-5(4)	21(3)	-1(2)
P(2)	0.2158(6)	0.1087(4)	0.1691(3)	100(8)	35(3)	23(2)	-4(4)	20(3)	-3(2)
Cl(1)	0.4344(8)	0.4203(5)	0.1371(3)	179(12)	60(4)	64(3)	-30(6)	49(5)	-11(3)
Cl(2)	0.2707(9)	0.3662(6)	0.0166(3)	306(17)	131(7)	40(2)	36(9)	68(5)	26(3)
C(1)	0.3494(23)	0.3315(16)	0.0950(10)	5.0(6)					
C(2)	0.4161(21)	0.2497(18)	0.0979(9)	5.2(5)					
C(3)	0.5310(27)	0.2260(17)	0.1502(12)	6.4(7)					
C(4)	0.4132(27)	0.2051(18)	0.0450(13)	7.1(7)					
N(1)	0.6186(29)	0.2240(18)	0.1891(12)	10.8(8)					
N(2)	0.4101(23)	0.1670(17)	0.0000(11)	9.6(7)					

^a The form of the anisotropic temperature factor is $\exp [-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + 2\beta_{12} \cdot h \cdot k + 2\beta_{13} \cdot h \cdot l + 2\beta_{23} \cdot k \cdot l)]$. The values of β have been multiplied by 10^3 .

TABLE 2

GROUP POSITIONAL PARAMETERS

Group	x _c ^a	y _c	z _c	δ	ε	η
R _{1A}	0.0431(10)	0.3061(5)	0.2777(4)	-1.564(9)	-3.044(9)	-1.641(10)
R _{1B}	-0.1905(11)	0.2932(6)	0.0411(5)	0.512(12)	-2.608(10)	0.608(11)
R _{1C}	0.1437(9)	0.5331(7)	0.1390(4)	-1.408(26)	-1.940(9)	0.431(25)
R _{2A}	0.3081(10)	0.1093(6)	0.3143(4)	-1.151(10)	2.801(9)	-1.708(10)
R _{2B}	-0.0826(10)	0.0370(6)	0.1116(4)	-2.673(13)	2.321(8)	2.929(13)
R _{2C}	0.3933(9)	-0.0471(7)	0.1421(4)	-2.979(22)	-2.009(9)	1.124(22)

^a These quantities have been defined previously (see ref. 9).

the last cycle of refinement, are listed in Table 1, together with the associated standard deviations as estimated from the inverse matrix. In Table 2 are listed the positional and orientation parameters associated with the groups, and in Table 3 are given the derived positional parameters for each of the group carbon atoms, together with the associated isotropic temperature factors.

A comparison of $|F_o|$ and $|F_c|$ for the 1317 reflections omitted from the refinement [$F_o^2 < 3\sigma(F_o^2)$] revealed 18 for which $|F_o^2 - F_c^2|$ lay between 3- and $5\sigma(F_o^2)$. All the others have $|F_o^2 - F_c^2| < 3\sigma(F_o^2)$. Thus these data are omitted from the tabulation of structure amplitudes where we present the final values of $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections used in the refinements*.

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TABLE 3

DERIVED PARAMETERS OF GROUP CARBON ATOMS^a

Atom	x	y	z	β (Å ²)
R _{1A} C(1)	0.0565(16)	0.3125(10)	0.2197(5)	4.6(5)
C(2)	0.1690(11)	0.3098(10)	0.2702(7)	4.6(5)
C(3)	0.1556(13)	0.3033(10)	0.3282(5)	5.0(5)
C(4)	0.0296(17)	0.2966(11)	0.3357(5)	6.8(7)
C(5)	-0.0829(12)	0.3023(11)	0.2852(8)	6.2(6)
C(6)	-0.0694(12)	0.3088(10)	0.2272(6)	6.3(6)
R _{1B} C(1)	-0.0718(14)	0.3069(11)	0.0870(6)	4.8(5)
C(2)	-0.1817(19)	0.3597(9)	0.0836(7)	6.8(7)
C(3)	-0.3004(15)	0.3460(11)	0.0377(9)	9.0(8)
C(4)	-0.3092(13)	0.2796(12)	-0.0049(7)	7.3(7)
C(5)	-0.1993(17)	0.2268(9)	-0.0015(6)	6.5(6)
C(6)	-0.0806(13)	0.2405(10)	0.0444(7)	4.7(5)
R _{1C} C(1)	0.1110(15)	0.4452(7)	0.1436(7)	4.1(5)
C(2)	0.1700(15)	0.4938(10)	0.1959(5)	5.1(5)
C(3)	0.2027(14)	0.5818(10)	0.1913(6)	6.5(6)
C(4)	0.1764(16)	0.6211(7)	0.1344(8)	7.1(7)
C(5)	0.1174(15)	0.5725(10)	0.0822(5)	5.7(6)
C(6)	0.0847(14)	0.4845(10)	0.0868(5)	6.0(6)
R _{2A} C(1)	0.2585(14)	0.1084(10)	0.2512(4)	3.7(5)
C(2)	0.3864(13)	0.1393(10)	0.2794(6)	5.2(6)
C(3)	0.4359(11)	0.1402(10)	0.3426(7)	6.1(6)
C(4)	0.3576(16)	0.1102(11)	0.3774(4)	6.5(6)
C(5)	0.2297(15)	0.0793(10)	0.3491(6)	6.0(6)
C(6)	0.1802(10)	0.0784(9)	0.2860(6)	4.4(5)
R _{2B} C(1)	0.0478(11)	0.0649(9)	0.1382(6)	3.5(5)
C(2)	0.0195(13)	0.0027(9)	0.0918(6)	4.3(5)
C(3)	-0.1108(16)	-0.0251(8)	0.0652(5)	5.6(6)
C(4)	-0.2129(11)	0.0092(10)	0.0850(7)	6.3(6)
C(5)	-0.1846(13)	0.0714(10)	0.1314(7)	5.1(5)
C(6)	-0.0543(15)	0.0992(8)	0.1580(5)	4.9(5)
R _{2C} C(1)	0.3161(14)	0.0204(9)	0.1546(7)	4.2(5)
C(2)	0.3629(16)	-0.0466(11)	0.1967(5)	5.5(6)
C(3)	0.4401(15)	-0.1141(9)	0.1842(6)	7.0(7)
C(4)	0.4705(14)	-0.1146(9)	0.1296(8)	6.8(7)
C(5)	0.4237(16)	-0.0476(11)	0.0874(5)	5.7(6)
C(6)	0.3465(15)	0.0199(9)	0.0999(6)	4.8(5)

^a R_{1A} indicates this is Ring A attached to P(1). C(1) is attached to P and the other C atoms are numbered in succession such that C(4) is para to C(1).

DESCRIPTION OF THE STRUCTURE

The crystal structure consists of discrete molecules. All intermolecular contacts are normal, the shortest being 2.28 Å between R_{1A}H6 and R_{2B}H6 atoms in adjacent molecules. Fig. 1 presents a drawing of the inner coordination sphere of the molecule, and Fig. 2 shows a view of a complete molecule, together with the naming of the phenyl rings. The 50% probability ellipsoids for thermal motion are displayed in both diagrams, and the root-mean-square amplitudes of vibration are listed in Table 4. These appear to be reasonable considering the nature of the structure. The

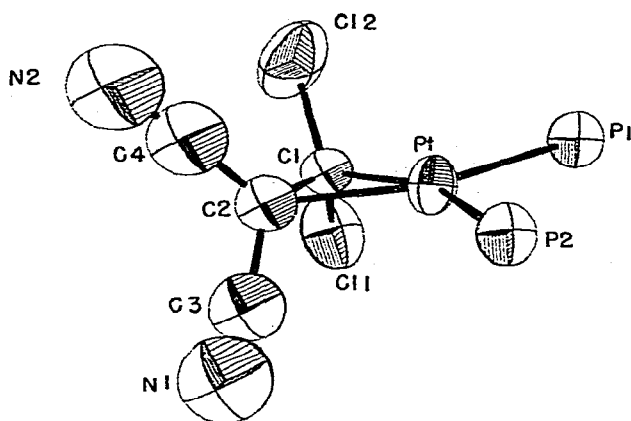


Fig. 1. The inner coordination sphere of $\text{Pt}[\text{Cl}_2\text{C}=\text{C}(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$. The 50% probability ellipsoids are shown.

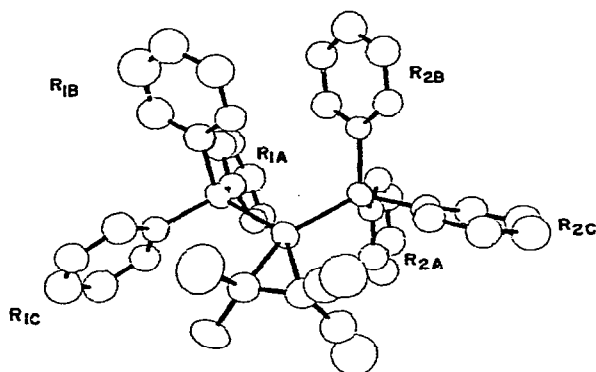


Fig. 2. The molecular geometry of $\text{Pt}[\text{Cl}_2\text{C}=\text{C}(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$. The hydrogen atoms on the phenyl rings have been omitted for the sake of clarity.

TABLE 4

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Minimum	Intermediate	Maximum
Pt	0.196(2)	0.208(2)	0.271(2)
P(1)	0.188(10)	0.239(9)	0.262(9)
P(2)	0.200(10)	0.211(9)	0.250(9)
Cl(1)	0.234(11)	0.299(10)	0.408(10)
Cl(2)	0.235(10)	0.356(11)	0.450(11)

two chlorine atoms exhibit the greatest motion. In Tables 5 and 6 are presented relevant interatomic distances and angles.

The platinum atom has, as expected, a planar environment, being three-coordinate, if one views the olefin as a monodentate ligand. As has been shown for other metal-olefin complexes, the olefin loses its planar geometry on coordination,

TABLE 5

SELECTED INTRAMOLECULAR DISTANCES (Å) IN $\text{Pt}[\text{Cl}_2\text{C}=\text{C}(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$

(i). Bond distances

Pt-P(1)	2.260(6)	C(1)-Cl(1)	1.75(2)	1.80(2)
Pt-P(2)	2.339(6)	C(1)-Cl(2)	1.85(2)	
Pt-C(1)	2.00(2)	C(2)-C(3)	1.48(3)	1.44(3)
Pt-C(2)	2.10(2)	C(2)-C(4)	1.40(3)	
C(1)-C(2)	1.42(3)	C(3)-N(1)	1.08(3)	1.13(3)
		C(4)-N(2)	1.19(3)	
P(1)-R _{1A} Cl	1.84(1)	P(2)-R _{2A} Cl	1.84(1)	
P(1)-R _{1B} Cl	1.83(1)	P(2)-R _{2B} Cl	1.84(1)	
P(1)-R _{1C} Cl	1.84(1)	P(2)-R _{2C} Cl	1.81(1)	

(ii). Non-bonded distances

Pt...Cl(1)	3.267(7)	P(1)...Cl(1)	4.016(10)
Pt...Cl(2)	3.304(7)	P(1)...Cl(2)	4.106(9)
Pt...C(3)	2.85(3)	P(2)...C(3)	3.90(3)
Pt...C(4)	3.06(3)	P(2)...C(4)	4.29(3)
P(1)...P(2)	3.575(8)	Cl(1)...Cl(2)	2.94(1)
P(1)...C(1)	3.34(2)	C(3)...C(4)	2.42(4)
P(2)...C(2)	3.73(2)		

TABLE 6

SELECTED INTRAMOLECULAR ANGLES (°) IN $\text{Pt}[\text{Cl}_2\text{C}=\text{C}(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$

P(1)-Pt-P(2)	102.0(2)		
C(1)-Pt-C(2)	40.6(9)		
P(1)-Pt-C(1)	103.1(7)		
P(2)-Pt-C(2)	114.3(8)		
Pt-C(1)-C(2)	73.2(1.3)	Pt-C(2)-C(3)	104.2(1.4)
Pt-C(2)-C(1)	66.2(1.2)	Pt-C(2)-C(4)	120.5(1.9)
Pt-C(1)-Cl(1)	120.7(1.2)	C(3)-C(2)-C(4)	113.9(2.4)
Pt-C(1)-Cl(2)	118.2(1.2)	C(3)-C(2)-C(1)	121.4(2.2)
Cl(1)-C(1)-Cl(2)	109.7(1.3)	C(4)-C(2)-C(1)	120.2(2.2)
Cl(1)-C(1)-C(2)	119.3(1.8)	C(2)-C(3)-N(1)	167.4(3.4)
Cl(2)-C(1)-C(2)	111.5(1.6)	C(2)-C(4)-N(2)	179.7(3.2)
Pt-P(1)-R _{1A} Cl	115.2(6)	Pt-P(2)-R _{2A} Cl	112.5(6)
Pt-P(1)-R _{1B} Cl	111.9(5)	Pt-P(2)-R _{2B} Cl	114.7(5)
Pt-P(1)-R _{1C} Cl	113.6(5)	Pt-P(2)-R _{2C} Cl	115.4(5)
R _{1A} Cl-P(1)-R _{1B} Cl	109.1(7)	R _{2A} Cl-P(2)-R _{2B} Cl	108.6(6)
R _{1A} Cl-P(1)-R _{1C} Cl	101.9(7)	R _{2A} Cl-P(2)-R _{2C} Cl	103.0(7)
R _{1B} Cl-P(1)-R _{1C} Cl	104.2(7)	R _{2B} Cl-P(2)-R _{2C} Cl	101.5(7)

the chlorine atoms and cyano groups being pushed back from the metal as shown in Figs. 1 and 2.

The two central carbon atoms of the olefin group are *not* equidistant from the metal. The Pt-C(1) distance of 2.00(2) Å is significantly shorter than the Pt-C(2) distance of 2.10(2) Å. Concomitant with these differences in bond lengths, the chlorine atoms and the cyano groups are *not* bent back equally from the Pt atom. The angle

between the C(1)–C(2) vector and the normal to the CCl₂ plane is 48.4(2.3)°, compared with a value of 69.9(3.3)° for the corresponding angle between C(2)–C(1) and C(CN)₂. Since the complements of these angles are a measure of the bending back of the substituents from the original planar configuration of the olefin, the chlorine atoms are bent back twice as much as the cyano groups. The central C(1)–C(2) bond length of 1.42(3) Å is larger than the value of 1.339(2) Å¹⁵ found in free ethylene, but its relationship to the values of 1.49(5) and 1.62(3) Å found in the analogous complexes of tetracyanoethylene (TCNE)² and tetrachloroethylene (TCLE)¹ is uncertain because of the large standard deviations.

The Pt–P(1) and Pt–P(2) bond lengths of 2.260(6) Å and 2.339(6) Å, although similar to the average values of 2.285(8) and 2.289(9) Å found in the TCLE and TCNE complexes, do show significant differences in length. Since the P(1)–Pt–P(2) and C(1)–Pt–C(2) bond angles are 102.0(2)° and 40.6(9)°, respectively, one cannot, strictly speaking, talk about *trans* groups and ligands. However, it is noteworthy that the longer Pt–P(2) bond is “*trans*” to the shorter Pt–C(1) bond.

The average C(1)–Cl bond length of 1.80(2) Å is much closer to the average C–Cl distance of 1.767(5) Å found in saturated hydrocarbons¹⁶ than the average value of 1.719(5) Å found for various substituted ethenes¹⁶. The C–Cl bond length in TCLE itself is 1.72(1) Å¹⁷. The average bond lengths of 1.42(3) and 1.13(3) Å found for the C_α–C_β and C_β–N bonds in the C(CN)₂ portion of the olefin do not differ significantly from the values of 1.441(5) and 1.134(6) Å found in free TCNE¹⁸.

Table 7 presents data on various relevant dihedral angles and vector-plane normal angles. Table 8 lists calculated least-squares planes through various atoms. The central atoms of the olefin lie strictly in the plane defined by the Pt and the two P atoms, there being virtually no tilt or twist of the olefin. The C(CN)₂ group is also planar.

In Table 9 we have collected information on this structure, and on the structures of the two analogous complexes of the olefins TCNE and TCLE.

TABLE 7
ADDITIONAL ANGLES^a

Dihedral angles (°)		Vector-plane normal angles (°)	
Pt–P(1)–P(2)	1.9(1.3)	C(1)–C(2)	91.8(1.3)
Pt–C(2)–C(1)		Pt–P(1)–P(2)	
C(1)–Cl(2)–Cl(1)	62.0(2.6) = α	C(1)–C(2)	48.4(2.3) $\equiv \beta_1$
C(2)–C(3)–C(4)		C(1)–Cl(2)–Cl(1)	
Pt–C(1)–C(2)	116.2(1.6)	C(2)–C(1)	69.9(3.3) $\equiv \beta_2$
C(1)–C(2)–Cl(1)		C(2)–C(3)–C(4)	
Pt–C(1)–C(2)	114.3(1.5)		
C(1)–C(2)–Cl(2)			
Pt–C(1)–C(2)	92.5(2.1)		
C(1)–C(2)–C(3)			
Pt–C(1)–C(2)	112.7(2.4)		
C(1)–C(2)–C(4)			

^a See preceding paper for a description of these angles.

TABLE 8

WEIGHTED LEAST-SQUARES PLANES

Plane equation: $Ax + By + Cz = D$ (in monoclinic co-ordinates).

Plane number	A	B	C	D
1	3.490	4.016	17.875	4.211
2	6.158	11.685	-9.989	4.480

DEVIATIONS FROM THE PLANES (Å)

Atom	Plane number	
	1	2
Pt	-0.0001(9)	
P(1)	0.000(6)	
P(2)	0.002(6)	
C(1)	0.038(22)	
C(2)	-0.006(21)	0.02(2)
C(3)		-0.07(3)
C(4)		0.01(3)
N(1)		0.06(3)
N(2)		-0.00(2)

DISCUSSION

The most unusual feature of the present structure is that the bond length from platinum to the carbon bearing two chlorine atoms is shorter than that to the carbon with two cyano groups. This effect is also observed in the differences between the TCNE [Pt-C=2.10(3), 2.12(3) Å] and TCLE [Pt-C=2.05(3), 2.02(3) Å] complexes (Table 9). It is commonly accepted that electron-withdrawing substituents on ethylene stabilize complexes with such metals as Pt⁰ 5,19, Pd⁰ 20, Ni⁰ 21, and Rh^I 22-24. Assuming a correlation between bond length and strength, one would expect that complexes of TCNE would have shorter platinum-carbon bond lengths than those of TCLE, since the cyano group is much more effective in withdrawing electrons than is chlorine.

For the TCNE and TCLE complexes, we can phrase a rationalization in terms of MO theory. The model^{25,26} for bonding in these compounds involves the donation of electrons from the olefin π -orbital, forming a σ -bond to the metal, and the back donation from a filled metal d -orbital to the olefin π^* -orbital, forming a π -bond. For ethylene in Zeise's salt, the π -bond and σ -bond are of nearly equal importance²⁷ about 0.3 of an electron being transferred through each bond.

This results in electroneutrality of the ethylene, and it is reasonable to assume that ethylene in Pt(H₂C=CH₂) [P(C₆H₅)₃]₂ will also be neutral, implying equal amounts of forward (σ) and back (π) bonding. Moderately effective electron withdrawing groups, such as chlorine, will lower both the π and π^* olefin orbital energies, enhancing back-bonding into the π^* -orbital and reducing the σ forward bonding from the π -orbital. Since TCLE is much more difficult to remove from Pt(olefin)-

TABLE 9

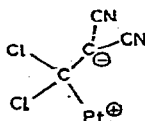
COMPARISON OF THE GEOMETRY OF SEVERAL COMPLEXES OF FORMULA BIS(TRIPHENYLPHOSPHINE)(OLEFIN)Pt(0)

	Olefin		
	Cl ₂ C=CCl ₂ ^a	Cl ₂ C=C(CN) ₂ ^b	(NC) ₂ C=C(CN) ₂ ^c
<i>Bond distances (Å)</i>			
Pt-P(1)	2.292(7) Å	2.260(6)	2.291(9)
Pt-P(2)	2.278(8)	2.339(6)	2.288(8)
Pt-C(1)	2.02(3)	2.00(2)	2.12(3)
Pt-C(2)	2.05(3)	2.10(2)	2.10(3)
C(1)-C(2)	1.62(3)	1.42(3)	1.49(5)
P(1)-Pt-P(2)	100.6(2)	102.0(2)	101.4(3)
C(1)-Pt-C(2)	47.1(1.0)	40.6(9)	41.5(1.3)
<i>Angles (°)</i>			
PtP(1)P(2)/PtC(2)C(1)	12.3(1.5)	1.9(1.3)	8.3
β ₁	47.5(3.0)	48.4(2.3)	59.7
β ₂	51.3(2.5)	69.9(3.3)	56.6
α	81.3(2.2)	62.0(2.6)	63.8
<i>Non-bonded distances (Å)</i>			
Pt...X(1)	3.267(10)	3.267(7)	3.05
Pt...X(2)	3.193(9)	3.304(7)	3.00
Pt...X(3)	3.289(9)	2.85(3)	2.95
Pt...X(4)	3.396(9)	3.06(3)	3.04
<i>Angles (°)</i>			
X(1)C(1)X(2)	115.6(1.9)	109.7(1.3)	110.2(3.7)
X(3)C(2)X(4)	105.9(1.9)	113.9(2.4)	115.7(3.4)

^a Ref. 1. ^b This work. ^c Ref. 2. Values given without errors were calculated by us from the data of ref. 2.

[P(C₆H₅)₃]₂ than is ethylene, we conclude that the increase in π-bonding more than compensates for decreased σ bonding. Very powerful electron-withdrawing groups, such as CN, will lower the π and π* olefin orbitals much further, to the point where electron donation from the π-orbital to form a σ-bond is of very little importance. There is a limit, however, to the strength of the π-bond that can be formed. We believe that this limit is reached in Pt(TCNE)[P(C₆H₅)₃]₂ and that, compared with Pt(TCLE)[P(C₆H₅)₃]₂, the increase in π back bonding cannot compensate for the loss of σ-bonding.

The use of π and π* olefin orbitals assumes that the carbon orbitals are equivalent. Since this is not the case in Pt[Cl₂C=C(CN)₂][P(C₆H₅)₃]₂ it is more convenient to rephrase the discussion above in terms of the individual carbon 2p orbitals. From this viewpoint, the carbon atoms of ethylene would be bound to platinum by a purely covalent bond, of bond order less than one. The TCLE molecule, with both ionic and covalent contributions to its bond strength, is held more tightly than either ethylene or TCNE, the carbon-platinum bonds of which are almost entirely ionic. These arguments predict, in other words, a large contribution of the resonance form:



to the ground state of the molecule. Ashley-Smith *et al.*²⁸ have postulated precisely such a structure as an intermediate in the addition of 1,2-dichloro-1,2-difluoroethylene to bis(triphenylphosphine)stilbeneplatinum.

The longer Pt-P bond *trans* to the CCl_2 group may be understood in terms of a pure σ *trans* effect, since there are no metal orbitals which interact with any olefin orbitals and the phosphorus *d*-orbitals. In compounds in which the σ *trans* effect is operative, the stronger σ donor lengthens the bond of the ligand *trans* to it^{29,30}, and the CCl_2 group is certainly a better donor than the $\text{C}(\text{CN})_2$ group. We cannot explain, however, why the platinum-phosphorus distances of the TCNE complex are the same as those in the TCLE complex.

The bending back of the ethylene substituents from the usual planar structure is caused by the increased electron density in the olefin π^* -orbital. The fact that cyano groups are bent through a smaller angle than the chlorine atoms, in spite of the presumably greater occupancy of the π^* -orbital in the TCNE complex, is presumably due to the interaction of the cyanide *p*-orbitals with the electron density of the carbon *p*-orbital.

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