Journal of Organometallic Chemistry, 70 (1974) 133–145
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THE STRUCTURE OF A METALLOCYCLOBUTANE COMPLEX, $Pt[C_3H_2(CN)_4][P(C_6H_5)_3]_2$, THE PRODUCT OF THE REACTION BETWEEN 1,1,2,2-TETRACYANOCYCLOPROPANE AND $Pt[P(C_6H_5)_3]_4$

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(Received October 2nd, 1973)

Summary

The metallocyclobutane complex $Pt[C_3H_2(CN)_4][P(C_6H_5)_3]_2$ was prepared from the reaction between 1,1,2,2-tetracyanocyclopropane and $Pt[P(C_6H_5)_3]_4$. The crystal and molecular structure of this complex has been determined from three-dimensional X-ray diffraction data. The crystal has symmetry consistent with the space group $P\bar{1}(C_i^1)$ with two molecules of the complex in a unit cell of dimensions a 11.422(5), b 17.001(8), c 10.478(5) Å, α 107.27(2), β 110.72(2), γ 82.50(2)°. The structure was refined by least-squares techniques to a conventional R index of 0.035 based on 4553 reflections above background collected using a four-circle diffractometer. The structure determination shows that $Pt[P(C_6H_5)_3]_2$ has inserted into the 1—2 carbon—carbon bond of 1,1,2,2-tetracyanocyclopropane. Comparisons are made between the structural parameters of this complex and those of other metallocyclobutanes.

Introduction

Recently, interest has been shown in the reactions of transition metals with systems containing cyclopropane rings [1-5]. Thus it has been demonstrated [2] that a variety of transition metal complexes promote ring-opening in the isomerization of a series of [1,1,0]-bicyclobutane derivatives. Insertion reactions of a transition metal into carbon—carbon bonds of substituted cyclopropanes have also been reported [3-5]. The products of these reactions are "metallocyclobutanes", and steric strain within the three-membered ring has been relieved. However, accurate structural data are not available on these metallocyclobutane complexes. The reported structural determinations of $PtCl_2(C_3H_6)(C_5H_5N)_2$, (I) [6], and $PtCl_2[C_3H_4(C_6H_5)_2](C_5H_5N)_2$, [two forms, (II) and (III), Fig. 1] [7], have been of only limited accuracy owing to decomposition of the crystals during data collection. We now report the result of an accurate structural investigation of the four-coordinate metallocyclobutane complex Pt[$C_3H_2(CN)_4$]-[$P(C_6H_5)_3$]$_2$, (IV).

Collection and reduction of X-ray data

The metallocyclobutane complex (IV) was prepared by the addition of a THF solution of 1,1,2,2-tetracyanocyclopropane to an equimolar amount of $Pt[P(C_6H_5)_3]_4$ dissolved in a minimum amount of THF. The white precipitate that formed was subsequently recrystallized from $CHCl_3$ to yield crystals suitable for X-ray examination. The preparation and spectral data have been discussed previously [8].

Preliminary precession photographs using Cu-*Kα* radiation revealed no lattice symmetry and no systematic absences, nor did a Delaunay reduction suggest any hidden symmetry. The crystal was thus assigned to the triclinic system and the subsequent successful refinement of the structure showed the space group to be $P\bar{1}$. The crystal of dimensions 0.16 × 0.07 × 0.04 mm was transferred to a Picker FACS-1 automatic diffractometer and lattice parameters were obtained as previously described [9] by hand centering of 12 reflections with Cu-*Kα* radiation (λ 1.540562 Å) in the range $28° \leqslant 2\theta \leqslant 66°$. The constants of the reduced cell at 22° are *a* 11.422(5), *b* 17.001(8), *c* 10.478(5) Å; *α* 107.27(2), *β* 110.72(2), *γ* 82.50(2)°. A density of 1.54 g · cm^{-3}, calculated for two formula

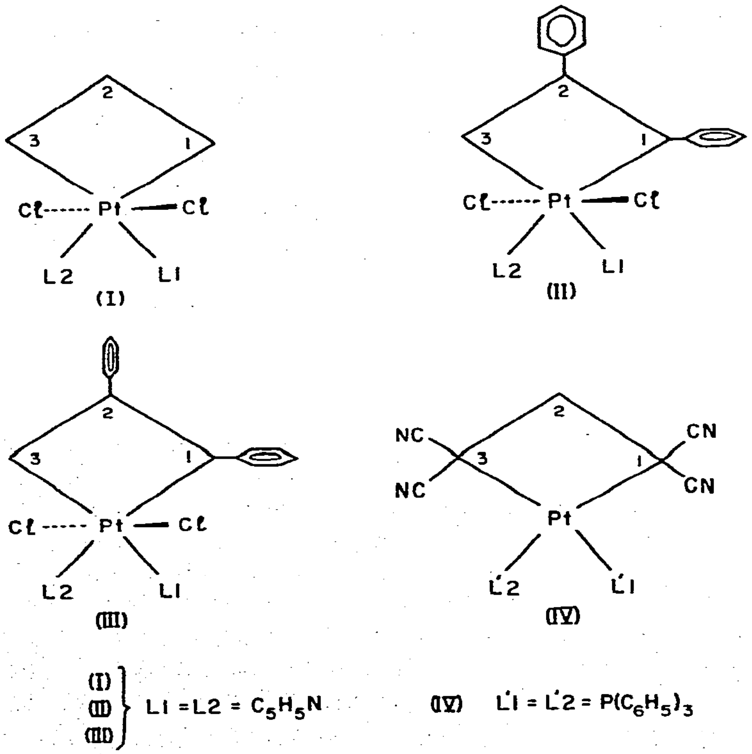

Fig. 1. Complexes derived from cyclopropanes.

units of $Pt[C_3H_2(CN)_4][P(C_6H_5)_3]_2$ per unit cell, agrees well with that of 1.56(2) $g \cdot cm^{-3}$ measured by flotation of the material in hexane/CCl_4.

Data were collected in a manner previously described [10]. A total of 5034 unique reflections was measured out to a 2θ (Cu-$K\alpha$) value of 113°, and of these 4553 obeyed the condition $F_o^2 > 3\sigma(F_o^2)$ and were used in subsequent refinements. Six standard reflections from diverse parts of reciprocal space were measured after every 100 reflections, and the intensities of these reflections remained constant within counting statistics.

The data were collected by the $\theta - 2\theta$ scan technique using Cu-$K\alpha$ radiation prefiltered with Ni foil. The scan range in 2θ was from $-0.8°$ from the $K\alpha_1$ peak to $+0.8°$ from the $K\alpha_2$ peak. The take-off angle was 3.0° and the receiving counter was positioned 32 cm from the crystal with an aperture 3.0 mm high and 5.0 mm wide. The pulse height analyzer was adjusted to admit approximately 85% of the Cu-$K\alpha$ peak. A scan rate of 2° in 2θ/min was used. Stationary-crystal, stationary-counter background counts were taken for 10 sec at each end of the 2θ scan range. Attenuators were automatically inserted if the intensity of the diffracted beam exceeded approximately 7000 counts per second during a scan. The attenuators were of Ni foil and gave attenuation factors of about 2.3. The data were processed in a manner previously described [9,10] to yield values of F_o^2 and $\sigma(F_o^2)$. A value of 0.04 for p was used in the estimation of standard deviations.

Solution and refinement of the structure

An unsharpened, three-dimensional Patterson function was computed* and interpreted to give the coordinates of the platinum atom. The remaining non-hydrogen atoms were readily located by the usual combination of Fourier and least-squares techniques. Throughout the refinement the function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where the weight, w, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for all non-hydrogen atoms were taken from the usual tabulation [11], while those for H were from the calculations of Stewart et al. [12]. The effects of anomalous dispersion were included in F_c [13]. In preparation for an absorption correction, the data crystal was measured and its faces were identified by optical means. The fourteen crystal faces were (010), (001), (110), $(1\bar{1}0)$, $(01\bar{1})$, $(11\bar{1})$, $(02\bar{1})$ and their respective Friedel pairs. Based on a calculated linear absorption coefficient of 53.86 cm^{-1} the transmission factors were found to vary between 0.34 and 0.68.

The trial structure was refined by a least squares procedure in which the phenyl rings were constrained to D_{6h} symmetry and treated as rigid groups ($C—C = 1.390$ Å) with individual isotropic thermal parameters. This initial isotropic refinement, based on the inner 2500 data, converged to values of R_1 and

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* In addition to various local programs for the CDC 6400, local modifications of the following programs were employed: Zalkin's FORDAP Fourier Program, the AGNOST absorption program, Johnson's ORTEP II thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program. Our least-squares program, NUCLS, in its non-group form, closely resembles the Busing and Levy ORFLS program.

TABLE 1

POSITIONAL, THERMAL AND GROUP PARAMETERS FOR $Pt\{C_3H_2(CN)_2\}[P(C_6H_5)_3]_2$

Atom	x	y	z	$10^4\beta_{11}$ [a]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Pt	0.15866(2) [b]	−0.23190(1)	0.04618(2)	44.5(3)	22.2(1)	69.5(4)	−1.2(1)	1.5(2)	8.9(1)
P(1)	0.3077(1)	−0.14934(9)	0.2339(2)	62(1)	25.3(6)	69(2)	−1.6(7)	18(1)	9.2(8)
P(2)	0.2862(1)	−0.34619(9)	0.0106(2)	61(1)	23.9(6)	85(2)	−0.2(7)	21(1)	11.3(9)
C(1)	−0.0003(5)	−0.1528(4)	0.0608(6)	5[illegible](6)	29(3)	94(8)	−6(3)	21(5)	6(4)
C(2)	−0.0727(6)	−0.1824(4)	−0.0997(7)	5[illegible](6)	36(3)	114(9)	5(3)	4(6)	13(4)
C(3)	−0.0014(6)	−0.2676(4)	−0.1399(7)	6[illegible](6)	28(3)	109(9)	0(3)	20(6)	13(4)
C(4)	0.0331(6)	−0.2768(4)	−0.2619(7)	8[illegible](7)	35(3)	90(9)	2(4)	−3(6)	11(4)
C(5)	−0.0674(6)	−0.3379(5)	−0.1527(8)	64(7)	40(3)	143(10)	−2(4)	20(7)	9(5)
C(6)	0.0111(5)	−0.0641(4)	0.1166(7)	5[illegible](6)	36(3)	94(8)	9(3)	22(5)	20(4)
C(7)	−0.0500(6)	−0.1858(4)	0.1424(8)	67(6)	36(3)	152(11)	−1(4)	40(7)	8(5)
N(1)	0.0194(5)	0.0059(4)	0.1635(6)	98([illegible])	32(3)	105(7)	5(3)	20(5)	13(4)
N(2)	−0.0890(7)	−0.2143(5)	0.2053(9)	153(9)	66(4)	259(14)	−18(5)	124(10)	36(6)
N(3)	0.0642(7)	−0.2809(5)	−0.3583(7)	149(5)	62(4)	108(9)	4(5)	28(7)	27(5)
N(4)	−0.1207(7)	−0.3912(5)	−0.1603(9)	105(8)	45(3)	311(15)	−16(4)	68(9)	25(6)
H(1) [c]	−0.068(6)	−0.154(4)	−0.170(7)						
H(2) [c]	−0.164(6)	−0.186(4)	−0.121(7)						

Group [d]	x_c	y_c	z_c	δ	ϵ	η
A	0.3747(2)	−0.0064(2)	0.1288(3)	−1.461(3)	−2.477(2)	−2.590(3)
B	0.5872(3)	−0.2121(2)	0.3880(3)	2.347(7)	−1.897(3)	2.659(7)
C	0.1975(3)	−0.0648(2)	0.4869(3)	−0.232(3)	3.101(2)	1.992(3)
D	0.3866(3)	−0.3926(2)	0.3078(3)	1.519(3)	−2.789(3)	2.057(3)
E	0.4893(3)	−0.3257(2)	−0.1237(3)	0.563(3)	3.067(3)	−0.756(3)
F	0.1509(3)	−0.5109(2)	−0.2145(3)	2.369(6)	−2.169(3)	−1.324(6)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2\beta_{12}\cdot h\cdot k+2\beta_{13}\cdot h\cdot l+2\beta_{23}\cdot k\cdot l)]$. [b] Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant figures. [c] This hydrogen atom is attached to C(2) and was located by a difference Fourier synthesis and subsequently the atomic coordinates were refined with a fixed isotropic temperature factor, B 4.2 Å^2. [d] x_c, y_c, z_c are the fractional coordinates of the ring center; δ, ϵ and η (in radians) have been defined in ref. 30. Groups A-F are phenyl rings.

R_2 of 0.054 and 0.077, respectively, where $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w \cdot F_o^2]^{1/2}$. The positions of the 30 phenyl hydrogen atoms were idealized on the assumption that C—H = 0.95 Å, and their contributions were added in a fixed manner to subsequent structure factor calculations. After a cycle of anisotropic refinement the positions of the hydrogen atoms of the tetracyanocyclopropane moiety were located in a difference Fourier synthesis. These hydrogen atoms were assigned a fixed isotropic temperature factor of 4.2 Å^2 (1 Å^2 greater than the C atom to which they are attached) and their positional parameters were allowed to refine in a final cycle of anisotropic refinement. This cycle reduced the values of R_1 and R_2 to 0.035 and 0.048, respec-

TABLE 2

DERIVED PARAMETERS FOR RING ATOMS

Ring atom	Carbon			B(Å^2)	Hydrogen			B(Å^2)
	x	y	z		x	y	z	
A_1[a]	0.3448(3)[b]	−0.0677(2)	0.1751(4)	2.6(1)				
A_2	0.2711(3)	−0.0552(2)	0.0439(5)	3.1(1)	0.200[c]	−0.088	−0.014	3.8
A_3	0.3010(4)	0.0062(3)	−0.0024(3)	4.0(1)	0.250	0.016	−0.091	3.8
A_4	0.4046(4)	0.0550(2)	0.0824(4)	4.2(1)	0.424	0.098	0.052	3.8
A_5	0.4783(3)	0.0424(2)	0.2136(4)	4.1(1)	0.548	0.076	0.272	3.8
A_6	0.4484(3)	−0.0190(3)	0.2599(3)	3.4(1)	0.498	−0.028	0.349	3.8
B_1	0.4650(3)	−0.1870(3)	0.3212(4)	2.7(1)				
B_2	0.5520(4)	[illegible]	0.2498(3)	3.6(1)	0.528	−0.201	0.155	4.4
B_3	0.6742(3)	−0.2302(3)	0.3166(5)	4.5(1)	0.723	[illegible]	0.287	4.4
B_4	0.7004(5)	−0.2276(3)	0.4516(5)	5.3(2)	0.782	−0.255	0.500	4.4
B_5	0.6224(4)	−0.2192(3)	0.5262(3)	5.0(2)	0.647	−0.224	0.620	4.4
B_6	0.5002(4)	−0.1941(3)	0.4594(4)	3.8(1)	0.442	−0.182	0.509	4.4
C_1	0.2485(4)	−0.0997(2)	0.3788(4)	2.8(1)				
C_2	0.1969(4)	−0.1501(2)	0.4280(5)	4.4(1)	0.196	−0.208	0.387	4.5
C_3	0.1460(5)	−0.1151(3)	0.5361(5)	5.1(2)	0.112	−0.150	0.570	4.5
C_4	0.1466(5)	−0.0298(3)	0.5950(4)	5.3(2)	0.113	−0.006	0.670	4.5
C_5	0.1981(5)	0.0205(2)	0.5459(5)	4.7(1)	0.199	0.079	0.588	4.5
C_6	0.2490(4)	−0.0144(2)	0.4377(4)	3.7(1)	0.283	0.021	0.405	4.5
D_1	0.3498(4)	−0.3735(3)	0.1781(4)	3.2(1)				
D_2	0.4744(3)	−0.3961(3)	0.2411(5)	4.1(1)	0.534	−0.398	0.196	5.2
D_3	0.5112(3)	−0.4152(3)	0.3709(5)	5.4(2)	0.597	−0.430	0.414	5.2
D_4	0.4233(5)	−0.4117(4)	0.4375(4)	6.3(2)	0.450	−0.424	0.527	5.2
D_5	0.2988(4)	−0.3890(3)	0.3744(5)	5.8(2)	0.240	−0.386	0.421	5.2
D_6	0.2620(3)	−0.3699(3)	0.2447(5)	4.6(1)	0.177	−0.354	0.203	5.2
E_1	0.4053(3)	−0.3351(2)	−0.0598(4)	2.9(1)				
E_2	0.5077(4)	−0.3899(2)	−0.0600(5)	4.3(1)	0.520	−0.434	−0.017	4.6
E_3	0.5917(4)	−0.3806(3)	−0.1238(5)	5.4(2)	0.661	−0.418	−0.124	4.6
E_4	0.5734(4)	−0.3164(3)	−0.1875(5)	5.4(2)	0.631	−0.310	−0.231	4.6
E_5	0.4710(4)	−0.2616(3)	−0.1874(5)	4.7(1)	0.459	−0.218	−0.231	4.6
E_6	0.3870(4)	−0.2709(2)	−0.1235(5)	3.7(1)	0.318	−0.234	−0.123	4.6
F_1	0.2099(4)	−0.4400(2)	−0.1161(4)	3.3(1)				
F_2	0.1976(5)	−0.4550(3)	−0.2588(4)	4.7(1)	0.230	−0.418	−0.289	5.4
F_3	0.1386(5)	−0.5264(3)	−0.3572(3)	5.9(2)	0.129	−0.537	−0.455	5.4
F_4	0.0920(5)	−0.5818(3)	−0.3129(5)	6.0(2)	0.050	−0.629	−0.381	5.4
F_5	0.1043(5)	−0.5663(3)	−0.1702(5)	5.9(2)	0.072	−0.604	−0.141	5.4
F_6	0.1633(5)	−0.4954(3)	−0.0718(4)	4.6(1)	0.173	−0.486	0.025	5.4

[a] Ring atoms are numbered sequentially, with A_1, B_1, C_1 attached to P(1) and D_1, E_1, F_1 attached to P(2). [b] The estimated standard deviations are derived from those of the group parameters. [c] Hydrogen atom A_2 is attached to carbon A_2, hydrogen A_3 is attached to carbon A_3, etc.

tively, and led to the final parameters given in Table 1. The derived positions for the ring carbon atoms as well as the idealized positions of the phenyl hydrogen atoms are given in Table 2. An analysis of $\Sigma w(|F_o|-|F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices indicated no unusual trends and provided no evidence for extinction effects. The error in an observation of unit weight is 1.89 e. The maximum density on a final difference Fourier map is 0.82 electrons/Å^3, approximately 16% of the height of a carbon atom in this structure. The final values of the structure amplitudes are tabulated as $10 \times |F_o|$ and $10 \times |F_c|$ (in electrons) for those reflections used in the refinement*.

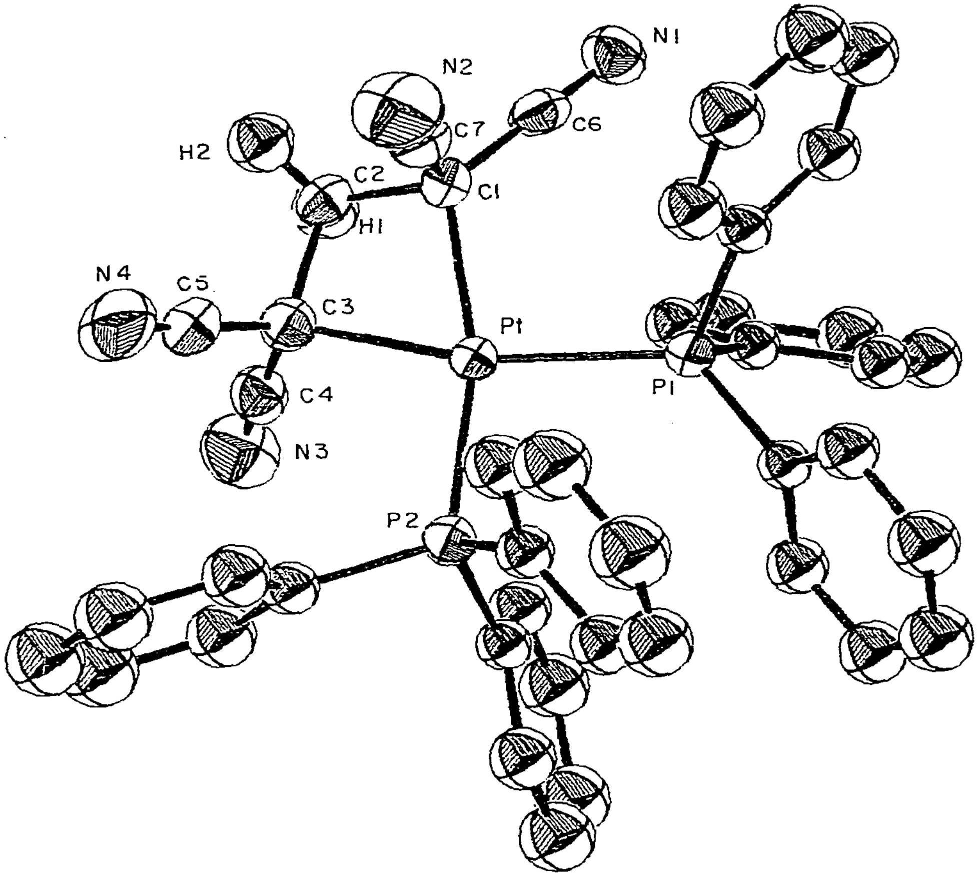

Fig.2. A drawing of the $Pt[C_3H_2(CN)_4][P(C_6H_5)_3]_2$ molecule. Hydrogen atoms of the phenyl rings have been omitted. The 50% probability vibrational ellipsoids are shown.

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* See NAPS document no. 02283 for 32 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies up to 30 pages. 15c for each additional page. Make checks payable to Microfiche Publications.

Description and discussion of the structure

Figure 2 presents a drawing of the $Pt[C_3H_2(CN)_4][P(C_6H_5)_3]_2$ molecule and indicates the numbering scheme. The vibrational thermal ellipsoids at their 50% probability level are also displayed in this figure and the root-mean-square amplitudes of vibration are presented in Table 3. These vibrational data appear to be reasonable; as expected the greatest thermal motion is shown by the cyano nitrogen atoms. From the positional parameters in Table 1 and the correlation matrix, the relevant interatomic distances, bond angles, and their standard deviations were calculated and are presented in Table 4.

The crystal structure consists of individual monomeric molecules, each of which is one asymmetric unit. The stereo drawing of two complete molecules in a unit cell (Fig. 3) represents a view along x. All intermolecular contacts are normal, the shortest distance being 2.62(7) Å between N(1) and H(1) in adjacent molecules.

Although previous structural investigations [6,7] on other complexes derived from cyclopropanes are of only limited accuracy it is still of interest to make comparisons between the six-coordinate complexes (I), (II) and (III) and the four-coordinate complex (IV) that we now report. These complexes are illustrated in Fig. 1. Molecule (I) is the unsubstituted cyclopropane complex [6], while (II) and (III) are independent molecules found in the unit cell of $PtCl_2$-$[C_3H_4(C_6H_5)_2](C_5H_5N)_2$ [7]. Complex (III) differs from (II) in the conformation of the phenyl ring bonded to C(2). The plane of the phenyl ring is perpendicular to the plane of the cyclopropane ring in (III). Tables 5 and 6 contain selected intramolecular internuclear distances, bond angles, dihedral angles, and displacements of atoms from planes that are useful in comparing the structural features of the four molecules. The atom nomenclature in (I), (II) and (III) has been made consistent with that of (IV).

The parameters listed in Table 6 [planes (i) and (iii)] indicate that for the octahedral complexes (I), (II) and (III) the platinum atom and the four equatorial ligands C(1), C(3), L(1), L(2) are essentially coplanar. However complex

(continued on p. 142)

TABLE 3

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min.	Inter.	Max.
Pt	0.1630(5)	0.1717(5)	0.1852(5)
P(1)	0.173(2)	0.178(2)	0.188(2)
P(2)	0.178(2)	0.188(2)	0.203(2)
C(1)	0.170(9)	0.194(9)	0.224(8)
C(2)	0.166(10)	0.217(9)	0.266(9)
C(3)	0.186(9)	0.195(9)	0.233(9)
C(4)	0.178(10)	0.212(10)	0.274(9)
C(5)	0.192(10)	0.227(10)	0.280(9)
C(6)	0.162(10)	0.207(9)	0.230(10)
C(7)	0.192(10)	0.216(10)	0.277(9)
N(1)	0.201(9)	0.213(8)	0.264(8)
N(2)	0.200(10)	0.307(9)	0.362(9)
N(3)	0.217(9)	0.282(9)	0.313(9)
N(4)	0.210(10)	0.268(9)	0.383(9)

TABLE 4

BOND DISTANCES AND ANGLES

Bond distances (Å)		
Pt—P(1)	2.314(2)	
Pt—P(2)	2.291(2)	
Pt—C(1)	2.137(6)	2.138(6)[a]
Pt—C(3)	2.139(6)	
C(1)—C(2)	1.545(9)	
C(3)—C(2)	1.584(9)	
C(1)—C(3)	2.404(9)	
C(1)—C(6)	1.452(9)	1.441(10)
C(1)—C(7)	1.441(10)	
C(3)—C(4)	1.428(10)	
C(3)—C(5)	1.443(10)	
C(6)—N(1)	1.147(8)	1.147(14)
C(7)—N(2)	1.150(9)	
C(4)—N(3)	1.164(9)	
C(5)—N(4)	1.125(9)	
C(2)—H(1)	1.02(6)	
C(2)—H(2)	0.99(7)	
P(1)—C(A_1)	1.825(5)	1.823(8)
P(1)—C(B_1)	1.832(3)	
P(1)—C(C_1)	1.814(5)	
P(2)—C(D_1)	1.814(5)	
P(2)—C(E_1)	1.821(5)	
P(2)—C(F_1)	1.831(4)	

Bond angles (°)		
P(1)—Pt—P(2)	96.99(6)	
C(1)—Pt—C(3)	68.4(2)	
P(1)—Pt—C(1)	97.1(2)	
P(2)—Pt—C(3)	99.8(2)	
P(1)—Pt—C(3)	160.2(2)	
P(2)—Pt—C(1)	162.9(2)	
Pt—C(1)—C(2)	93.5(4)	
Pt—C(3)—C(2)	92.3(4)	
C(1)—C(2)—C(3)	100.4(5)	
C(6)—C(1)—C(7)	111.0(6)	
C(4)—C(3)—C(5)	111.9(4)	
C(6)—C(1)—Pt	121.3(4)	
C(6)—C(1)—C(2)	114.6(5)	
C(7)—C(1)—Pt	103.2(4)	
C(7)—C(1)—C(2)	111.8(6)	
C(4)—C(3)—Pt	109.0(4)	
C(4)—C(3)—C(2)	112.1(6)	
C(5)—C(3)—Pt	116.7(5)	
C(5)—C(3)—C(2)	113.4(6)	
H(1)—C(2)—H(2)	104.2(51)	
H(2)—C(2)—C(1)	112.6(37)	
H(2)—C(2)—C(3)	115.0(38)	
H(1)—C(2)—C(1)	122.3(36)	
H(1)—C(2)—C(3)	102.3(38)	
C(1)—C(6)—N(1)	178.3(7)	177.8(8)
C(1)—C(7)—N(2)	178.0(8)	
C(3)—C(4)—N(3)	176.9(8)	
C(3)—C(5)—N(4)	178.0(8)	
C(A_1)—P(1)—C(B_1)	101.0(2)	105(2)
C(A_1)—P(1)—C(C_1)	107.1(2)	
C(B_1)—P(1)—C(C_1)	103.9(2)	
C(D_1)—P(2)—C(E_1)	113.4(2)	
C(D_1)—P(2)—C(F_1)	103.7(2)	
C(E_1)—P(2)—C(F_1)	101.7(2)	

[a] These are averaged quantities. The estimated standard deviation in parentheses is the larger of an individual standard deviation or of the standard deviation of a single observation as calculated from the mean.

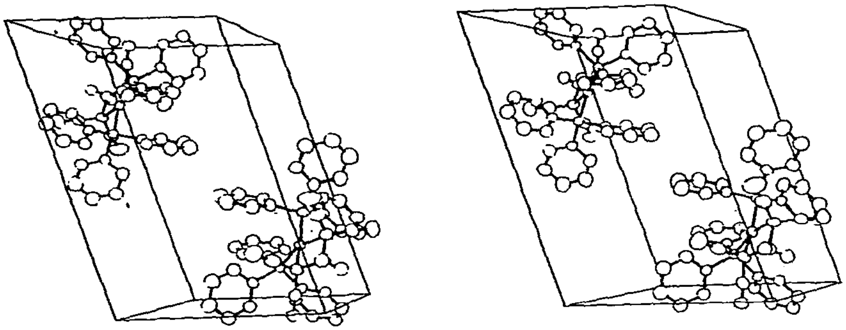

Fig.3. A stereoscopic drawing of two molecules of $Pt[C_3H_2(CN)_4][P(C_6H_5)_3]_2$ whose central metal atoms all lie within the same unit cell.

TABLE 5

COMPARISON OF INTRAMOLECULAR DISTANCES, BOND ANGLES, DIHEDRAL ANGLES[a] AND CONFORMATION ANGLES[a]

	(I)	(II)	(III)	(IV)
Intramolecular distances (Å)				
Pt—C(1)	2.04(5)	2.06(3)	2.05(3)	2.137(6)
Pt—C(2)	2.69(4)	2.60(4)	2.62(3)	2.712(6)
Pt—C(3)	2.19(5)	2.11(5)	2.17(3)	2.139(6)
C(1)—C(2)	1.48(8)	1.59(7)	1.59(4)	1.545(9)
C(1)—C(3)	2.55(10)	2.39(7)	2.60(4)	2.404(9)
C(2)—C(3)	1.82(9)	1.48(5)	1.71(4)	1.584(9)
Pt—L(1)	2.25(3)	2.20(4)	2.33(3)	
Pt—L(2)	2.11(3)	2.15(3)	2.16(3)	
Pt—L′(1)				2.314(2)
Pt—L′(2)				2.291(2)
Bond angles (°)				
C(1)—Pt—C(3)	74(2)	70(2)	76(1)	68.4(2)
C(1)—C(2)—C(3)	101(4)	102(3)	104(2)	100.4(5)
Pt—C(1)—C(2)	99(4)	90(2)	91(2)	93.5(4)
Pt—C(3)—C(2)	84(3)	91(3)	84(2)	92.3(4)
L(1)—Pt—L(2)	89(1)	82(1)	92(1)	
L′(1)—Pt—L′(2)				96.99(6)
Dihedral angles[b] (°)				
C(1)—Pt—C(3) L(2)—Pt—L(1)	1(1)	4(1)	3(2)	18.0(2)
C(3)—Pt—C(1) C(1)—C(2)—C(3)	12(5)	28(3)	22(2)	24.4(4)
C(1)—C(2)—C(3) L(2)—L(1)—Pt	13(4)	28(2)	21(4)	30.4(4)
Conformation angles[c] (°)				
Pt—C(1)—C(2)—C(3)	10(4)	23(2)	18(3)	20.1(5)
C(1)—C(2)—C(3)—Pt	−9(4)	−23(2)	−17(3)	−20.0(5)
C(2)—C(3)—Pt—C(1)	7(3)	18(2)	13(3)	15.2(4)
C(3)—Pt—C(1)—C(2)	−9(3)	−17(2)	−14(3)	−15.6(4)

[a] These parameters were recalculated for complexes (I), (II) and (III) using standard deviations presented in the original papers, and hence correlation effects have been ignored. [b] The unsigned acute angles are given. [c] The conformation angle of a chain of atoms 1—2—3—4 is positive if, when looking from 2 to 3, a clockwise motion of atom 1 would superimpose it on atom 4.

TABLE 6

COMPARISON OF DISPLACEMENTS (Å) FROM PLANES

	(I)	(II)	(III)	(IV)
(i). Plane defined by L(1), Pt, L(2), [or L′(1), Pt, L′(2)]				
C(1)	0.00(6)	−0.09(4)	−0.12(6)	−0.356(6)
C(2)	0.24(7)	0.44(4)	0.30(6)	0.408(8)
C(3)	0.03(4)	0.07(4)	0.01(6)	0.386(7)
(ii). Plane defined by C(1), Pt, C(3)				
C(2)	0.22(9)	0.46(5)	0.39(8)	0.41(1)
(iii). Least-squares plane defined by C(1), C(3), L(1), L(2), [or C(1), C(3), L′(1), L′(2)]				
C(1)	−0.01(6)	−0.05(3)	−0.03(5)	−0.348(6)
C(3)	0.00(4)	0.05(3)	0.04(5)	0.380(6)
L(1) (or L′(1))	0.00(3)	−0.02(2)	−0.02(4)	0.012(1)
L(2) (or L′(2))	0.00(3)	0.02(2)	0.03(5)	−0.010(1)
Pt	0.008	0.006	0.026	0.000
C(2)	0.218	0.459	0.372	0.410

(IV) is severely distorted from a square-planar arrangement, such that the dihedral angle between planes C(1)—Pt—C(3) and L(2)—Pt—L(1) is 18.0(2)°. The related four-coordinate complex, Pt(TCNE)[P(C_6H_5)$_3$]$_2$, is also perturbed from a square-planar arrangement [14], the dihedral angle between planes C(1)—Pt—C(2), P(1)—Pt—P(2) being 8.3°. The coplanarity of the atoms in the equatorial plane of the octahedral complexes (I), (II) and (III) may arise from the influence of non-bonding interactions with the axial ligands inhibiting distortions from a square-planar arrangement.

All of the four complexes possess a puckered metallocyclobutane ring (Tables 5 and 6). The degree of puckering is least in the unsubstituted complex, (I), and this may be understood in terms of the minimization in this complex of non-bonding 1,2- and 1,3-substituent repulsions [15]. The extent of puckering in the metallocyclobutane ring for complexes (II), (III) and (IV) is of the same order as reported for other substituted cyclobutanes [16]. Fig. 4 illustrates the conformation of the metallocyclobutane ring in the tetracyano-substituted complex, (IV), and also reveals the distortion from a square-planar arrangement of atoms in the inner coördination sphere. The difference between the two independent platinum—phosphorus distances [2.291(2) and 2.314(2) Å] is unusual, and these bonds are apparently lengthened over the analogous TCNE complex [14], Pt[$C_2(CN)_4$][P(C_6H_5)$_3$]$_2$, which exhibits an average Pt—P distance of 2.290 Å. It is of interest to note that asymmetry of the platinum—phosphorus bonds has been reported [17] for the fumaronitrile complex, Pt[$C_2(CN)_2$]-[P(C_6H_5)$_3$]$_2$, [Pt—P bond distances, 2.277(5) and 2.296(4) Å]. The P—C distances and the C—P—C angles have mean values of 1.82 Å and 105°, which are nearly identical with the values found for the triphenylphosphine ligand [18].

The platinum atom is bonded to C(1) and C(3), the carbon atoms bearing the cyano substituents. The two independent platinum—carbon distances are equal [2.137(6) and 2.139(6) Å]. It is interesting to note that a structural investigation [19] of 1,1,2,2-tetracyanocyclopropane reveals that the 1—2 bond is apparently lengthened by the strong electron-withdrawing cyano substituents,

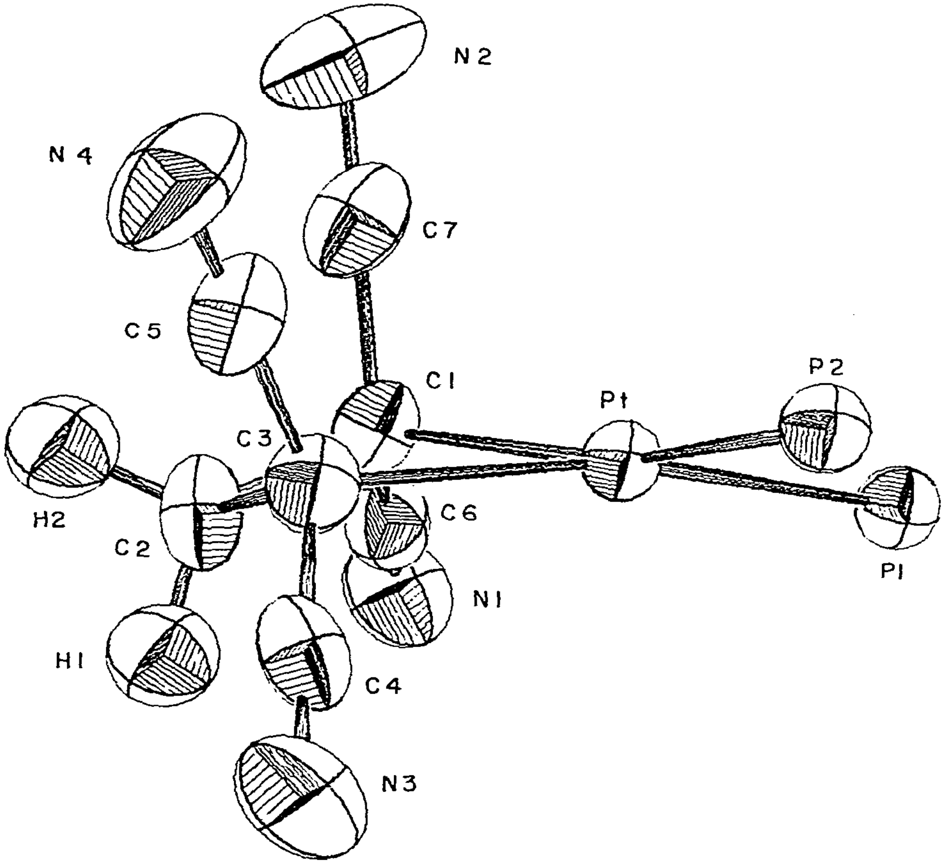

Fig.4. The conformation of the metallocyclobutane ring in the molecule $Pt[C_3H_2(CN)_4][P(C_6H_5)_3]_2$.

[1—2 bond length 1.561(4) Å compared with an average value of 1.503(4) Å for 1—3 and 2—3 bonds]. The presence of a positive charge on the substituent-bearing carbon atoms of tetracyanocyclopropane has been proposed on the basis of ESCA measurements and theoretical calculations [20]. Thus the formation of the observed metallocyclobutane product may be regarded as having proceeded via nucleophilic attack of Pt^0 at this site of least electron density. This proposition gains some support from the observation that, under the same experimental conditions, $Pt[P(C_6H_5)_3]_4$ does not react with 1,2-dicyanocyclopropane [8].

The average value of 1.565 Å for the C(1)—C(2), C(2)—C(3) bond lengths in (IV) signifies an appreciable lengthening over the analogous bond distances in tetracyanocyclopropane [19], [1.501(4) and 1.506(4) Å]. Such lengthening of the carbon—carbon bonds is not surprising, as bond distances may be expected to increase with the relief of forces within the three-membered ring. For example the carbon—carbon bond distances in cyclobutane [21] and cyclopropane [22] are 1.56(2) and 1.524(14) Å, respectively, and a similar trend is shown in the bond lengths of 1,2,3,4-tetracyanocyclobutane [23] and 1,2,3-tricyanocyclopropane [24] [1.561(3) and 1.518(3) Å].

The exocyclic C—C and C≡N bonds are normal, the average bond distances being 1.441(10) and 1.147(14) Å, respectively. The average C—C≡N bond angle of 177.8(8)° is not significantly different from 180°. The cyano groups are bent away from the metal such that the angles α, β, β' defined in ref. 25 have values 19.1(4)°, 81.6(5)° and 81.4(4)°, respectively. These angles have been used by Stalick and Ibers to describe the nonplanarity of coordinated tetracyanoethylene.

The exocyclic NC—C—CN bond angles of 111.0(6)° and 111.9(4)° are significantly smaller than the analogous bond angles in tetracyanocyclopropane [114.7(3)° and 116.2(2)°], and may reflect a rehybridization of orbitals associated with C(1) and C(3) upon forming the metallocyclobutane. In particular the H—C—H bond angle of 121.4(30)° in tetracyanocyclopropane [19] suggests sp^2 hybridization at this methylene carbon center, in accordance with the Walsh [26] and the Randić—Maksić modification [27] of the Coulson—Moffitt [28] bonding schemes for cyclopropane rings [29]. However, the H(1)—C(2)—H(2) bond angle of 104.2(51)° in complex (IV) indicates an increase in *p*-orbital contribution to the hybrid orbitals interacting with these hydrogens, and overall implies a reorganization of the bonding scheme of the cyclopropane skeleton upon metallation. A similar trend in exocyclic bond angles may be observed in the molecules 1,2,3-tricyanocyclopropane [24] and 1,2,3,4-tetracyanocyclobutane [23]. The former complex possesses a NC—C—H bond angle of 116.2° while the average exocyclic bond angle in the cyclobutane is 111.1°.

These observations lend themselves to the conclusion that the bonding scheme in the metallocyclobutane is of the same nature as that in cyclobutanes. McQuillin [4] and McGinnety [7] have interpreted the bonding scheme in complexes (II) and (III) as a synergic interaction between available metal orbitals of the correct symmetry and the molecular orbitals of the cyclopropane moiety as obtained from the Walsh description [26]. This model does not readily explain the puckering observed, but it is supported by the observation that cyclopropanes are liberated from complexes (I), (II) and (III) on treatment with base, and rationalizes the general proton deshielding that is observed in the NMR spectrum of complexes of this type [4,6]. It is of interest to note that 1,1,2,2-tetracyanocyclopropane was not liberated from (IV) under a variety of conditions employed, and NMR spectra revealed that the chemical shift of the methylene protons of (IV) is not altered on varying the basicity of the phosphine, nor upon arsine substitution [8].

It seems generally true that the bonding of a substituted trimethylene moiety to a metal cannot be depicted in simple terms as four two-center, two-electron σ-bonds, nor as a π-type of interaction. Rather, the true description of the bonding in a particular molecule is intermediate between these two extremes and is influenced by the nature of the trimethylene substituent groups. Thus if the initial step in the cleavage of a cyclopropane carbon—carbon bond is considered as an overlap between metal orbitals of the correct symmetry and Walsh molecular orbitals of the cyclopropane moiety, (involving a σ-donor component from the lowest cyclopropane orbital, together with π-back donation into an antibonding orbital, Fig. 5), then cyano substituents at C(1) and C(3) will promote back donation and produce effective σ-character in the Pt—C(1) and Pt—C(3) bonds of the metallocyclobutane product (IV).

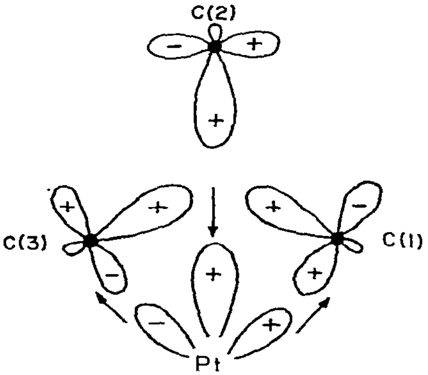

Fig.5. Proposed interaction of cyclopropane and metal, leading to metal insertion.

Acknowledgements

This work was supported in part by the U.S. National Science Foundation. M.G. thanks the C.N.R. (Roma) for partial financial support. The authors thank Dr. J.A. McGinnety for providing a preprint of his paper.

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