

Metallocyclobutanes. Preparation and Structural Characterization of the Products of Insertion of $\text{Pt}(\text{P}(\text{C}_6\text{H}_5)_3)_2$ into 1,1,2,2-Tetracyano-3-phenylcyclopropane and 1-Carboethoxy-1,2,2-tricyano-*trans*-3-phenylcyclopropane

Jayaraman Rajaram and James A. Ibers*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received May 20, 1977

Abstract: The compound $\text{Pt}(\text{C}_2\text{H}_4)(\text{P}(\text{C}_6\text{H}_5)_3)_2$ reacts smoothly in THF with the activated cyclopropanes 1,1,2,2-tetracyano-3-phenylcyclopropane or 1-carboethoxy-1,2,2-tricyano-*trans*-3-phenylcyclopropane to form the corresponding $-\text{Pt}(\text{PC}_6\text{H}_5)_3)_2$ insertion product by breaking the bond possessing the largest number of cyano substituents. These metallocyclobutanes have been characterized by x-ray diffraction methods. The compound $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_4][\text{P}(\text{C}_6\text{H}_5)_3)_2$ crystallizes with two molecules in space group $C_2^2-P2_1$ of the monoclinic system in a cell of dimensions $a = 11.272(2)$, $b = 17.209(2)$, $c = 11.598(2)$ Å, $\beta = 112.57(1)^\circ$. A total of 210 variables has been refined from 4132 observations by conventional least-squares methods to an R index on F_o of 0.029. The compound $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_3(\text{COOC}_2\text{H}_5)][\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot x\text{CHCl}_3$ ($x \approx 0.8$) crystallizes with four formula units in space group $C_2h^3-P2_1/c$ of the monoclinic system in a cell of dimensions $a = 12.844(2)$, $b = 12.498(3)$, $c = 30.406(4)$ Å, $\beta = 90.67(1)^\circ$. A total of 276 variables has been refined from 4235 observations to an R index of 0.056. Comparisons are made between the structural parameters of these complexes and those of other platinum-containing metallocyclobutanes.

Introduction

Recently, there has been considerable interest in the reactions of transition metal complexes with strained alkane ring systems. One such reaction that has been studied is the insertion of a transition metal into carbon-carbon bonds of substituted cyclopropanes.¹⁻⁵ The products formed from these reactions are metallocyclobutanes—the relief of ring strain produced on ring opening has been claimed to be the major driving force for these reactions. Very recently, the ring opening of a substituted cyclobutane by platinum(0) has also been reported.⁶ It is reasonable to assume that these metallocycloalkanes are important intermediates in various transition metal promoted isomerizations of strained ring systems. Accurate molecular structure determinations of these metallocyclobutanes are hence of interest. Chart I (I-IV) sketches the platinacyclobutane complexes whose structures have been reported earlier. Structure determinations of the formally Pt(IV) compounds I,⁷ II, and III⁸ (II and III being two forms of the same compound, Chart I) have been of limited accuracy owing to crystal decomposition during data collection. An accurate structure determination of the four-coordinate platinacyclobutane, IV, is available.⁹ In this work, we report the structures of two four-coordinate platinacyclobutanes (Chart I, V and VI) prepared by the reactions of $\text{Pt}(\text{C}_2\text{H}_4)-[\text{P}(\text{C}_6\text{H}_5)_3)_2$ with 1,1,2,2-tetracyano-3-phenylcyclopropane (Chart II (a)) and with 1-carboethoxy-1,2,2-tricyano-*trans*-3-phenylcyclopropane (Chart II (b)). These structures were studied in order to determine substituent effects on the conformation of the metallocyclobutane ring system. The ultimate aim of this work is to determine the stereochemistry of the insertion of transition metals into carbon-carbon bonds of chiral cyclopropanes.

Experimental Section

The cyclopropanes (Chart II) were prepared by methods described by Kim and Hart.¹⁰

The compounds V and VI were prepared by stirring equimolar quantities of $\text{Pt}(\text{C}_2\text{H}_4)[\text{P}(\text{C}_6\text{H}_5)_3)_2$ and the corresponding cyclopropane in THF, similar to the method used for the preparation of $\text{Pt}[\text{C}_3(\text{CH}_3)_2(\text{CN})_4][\text{P}(\text{C}_6\text{H}_5)_3)_2$.¹¹

Compound V was recrystallized from benzene/hexane. Anal. Calcd for $\text{C}_{49}\text{H}_{36}\text{N}_4\text{P}_2\text{Pt}$: C, 62.75; H, 3.84; N, 5.98. Found: C, 62.93; H, 3.73; N, 5.86. Decomposition point: 262 °C. Infrared spectrum: $\nu(\text{C}\equiv\text{N})$ 2215 cm^{-1} (m). (For Chart II (a), $\nu(\text{C}\equiv\text{N})$ is at 2240 cm^{-1} .) Crystals suitable for x-ray work were grown by vapor diffusion of pentane into a benzene solution.

Compound VI was recrystallized from $\text{CHCl}_3/\text{MeOH}$. Anal. of unrecrystallized product. Calcd for $\text{C}_{51}\text{H}_{41}\text{N}_3\text{O}_2\text{P}_2\text{Pt}$: C, 62.19; H, 4.17; N, 4.27. Found: C, 61.83; H, 4.60; N, 4.12. Anal. of product recrystallized from $\text{CHCl}_3/\text{MeOH}$. Calcd for $\text{C}_{51}\text{H}_{41}\text{N}_3\text{O}_2\text{P}_2\text{Pt} \cdot 1.0 \text{CHCl}_3$: C, 56.55; H, 3.81; N, 3.81. Found: C, 56.10; H, 3.77; N, 3.86. Decomposition point: 204 °C. Infrared spectrum: $\nu(\text{C}\equiv\text{N})$ 2208 cm^{-1} (m), $\nu(\text{C}=\text{O})$ 1693 cm^{-1} (s). (For Chart II (b): $\nu(\text{C}\equiv\text{N})$ 2245 cm^{-1} (w), $\nu(\text{C}=\text{O})$ 1751 cm^{-1} (vs)). Crystals suitable for x-ray work were grown from a $\text{CHCl}_3/\text{MeOH}$ solution.

Crystal Structure A (Compound V). Details on crystal data, intensity collection, and refinement are given in Table I. Data were collected on a FACS-I diffractometer using methods previously described.¹² The data were processed¹³ using a value of p of 0.03. The structure was solved from a three-dimensional, origin-removed Patterson function.¹⁴ Refinement proceeded by methods standard in this laboratory.¹⁵ Because $P2_1$ is a polar space group it was necessary to establish the correct enantiomeric structure for the selected crystal. After isotropic refinement of the nonhydrogen atoms and the group carbon atoms the conventional R and R_w indices on F_o for the enantiomer initially chosen arbitrarily were 0.0553 and 0.0762, respectively; those for the other enantiomer on refinement were 0.0644 and 0.0891, respectively. An examination of 104 of the 287 Friedel pairs for which the calculated difference was expected to be greater than 5% indicated that the first enantiomer correctly led to the predicted direction in 103 cases. There is no doubt that the correct enantiomer has been selected. Refinement then continued along standard lines. Before the final cycle of least-squares refinement the fixed contributions of the 36 hydrogen atoms were added, based on idealized positions ($\text{C}-\text{H} = 0.95$ Å). No attempt was made to refine the unique H atom on the metallocyclic ring. An analysis of $\Sigma w(|F_o| - |F_c|)^2$ vs. $|F_o|$, setting angles, and Miller indices revealed no unusual trends. The maximum electron density in the final difference Fourier map is 0.7 (1) $\text{e}/\text{Å}^3$. Table II(a) presents the final parameters and Table III(a) the derived positions of the ring carbon atoms. A tabulation of $10|F_o|$ vs. $10|F_c|$ is available.¹⁶

Crystal Structure B (Compound VI). Details on this structure determination are also presented in Table I. Data collection in this instance was complicated by crystal decomposition. Collection of in-

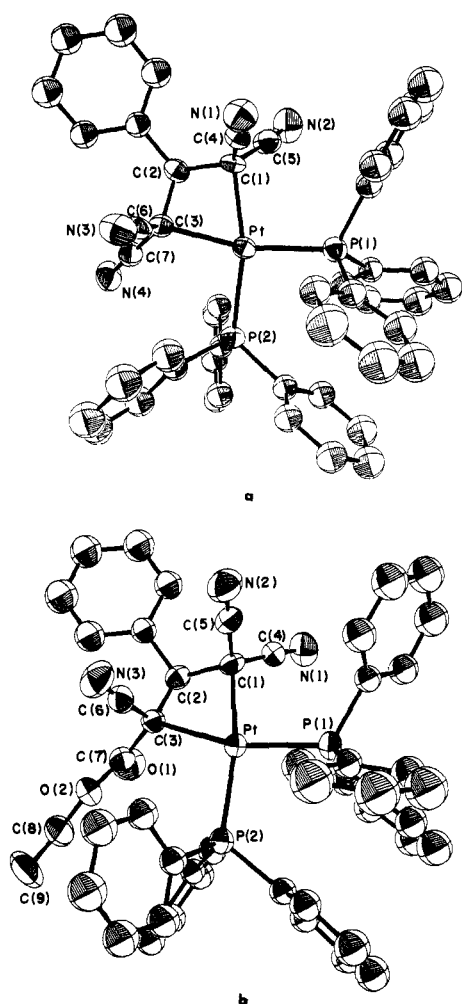


Figure 1. (a) A drawing of the $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_4][\text{P}(\text{C}_6\text{H}_5)_3]_2$ molecule. Hydrogen atoms have been omitted. The 50% probability ellipsoids are shown. (b) A drawing of the $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_3(\text{COOEt})][\text{P}(\text{C}_6\text{H}_5)_3]_2$ molecule. Hydrogen atoms have been omitted. The 50% probability ellipsoids are shown.

tensity data on crystal 1 was terminated at $2\theta = 75^\circ$ since the six standard reflections had decreased an average of 10%. A second crystal was employed for data collection in the region $75 \leq 2\theta \leq 101^\circ$. Data collection was again terminated when this second crystal showed about a 15% drop in the intensities of the standard reflections. After absorption correction, approximate decomposition corrections were applied to the two data sets, based on the changes of the standard reflections with x-ray exposure. The two data sets were brought to an approximately common scale and merged. Separate scale factors were employed in ensuing calculations. The structure was solved from a Patterson function and was refined by standard procedures. In the course of the refinement the Cl atoms of the CHCl_3 solvate molecule showed very high thermal motion, with isotropic B values averaging around 25 \AA^2 . In the final cycle of refinement the occupancy factor of the CHCl_3 molecule was included as a variable. This occupancy factor converged to a value of 0.78 (1). It is probable that problems with decomposition of the two data crystals arose from slow loss of solvate molecules. Also included in this last cycle were the fixed contributions from the 42 hydrogen atoms whose positions had been idealized ($\text{C-H} = 0.95 \text{ \AA}$). An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices indicated substantially poorer agreement at low scattering angle. This is to be expected if the scattering model for the solvate molecule is inadequate. Similarly, the highest feature on the final difference Fourier map is a peak of height 2.0 (2) $e/\text{\AA}^3$ in the vicinity of the solvate molecule. Table II(b) presents the final parameters and Table III(b) the derived positions of the ring carbon atoms. A tabulation of $10|F_o|$ vs. $10|F_c|$ is available.¹⁶

Chart I

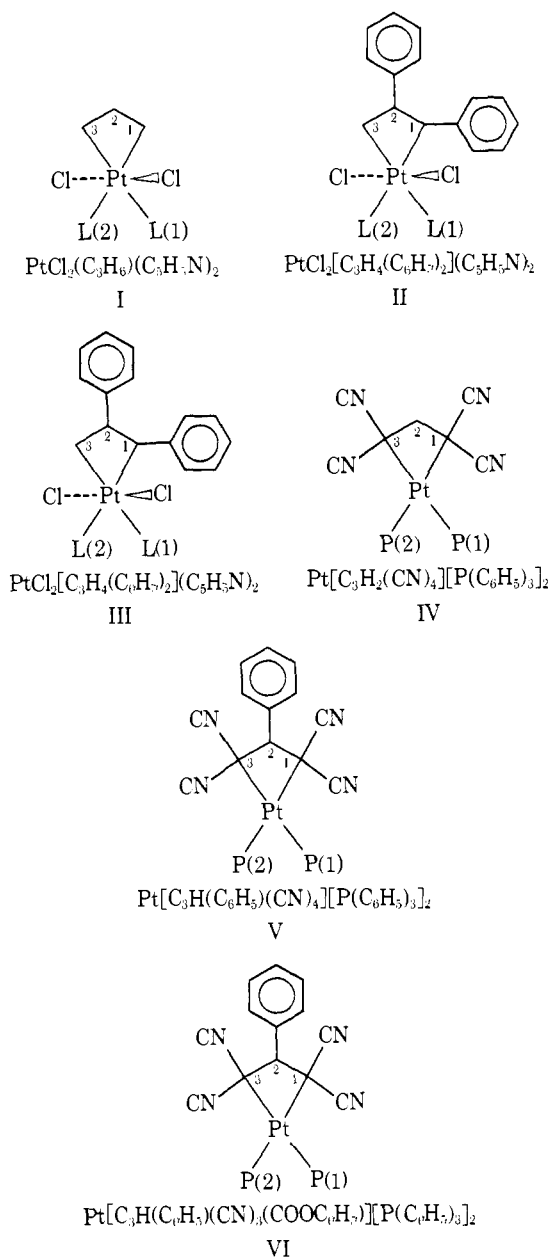
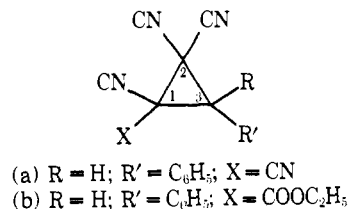


Chart II



Description of the Structures

Overall views of the molecules V and VI are presented in Figures 1(a) and 1(b), respectively. The vibrational ellipsoids at their 50% probability level are displayed in these figures and the corresponding root-mean-square amplitudes of vibration are given in Tables IV(a) and IV(b).¹⁶ The vibrational data are reasonable with the cyano nitrogen atoms and the ester group atoms (in molecule VI) showing the largest thermal motion, apart from the solvent chloroform atoms in crystal structure B. A selection of bond distances, nonbonded contacts, and angles, together with standard deviations, is given in Table V.

Table I. Summary of Crystal Data, Intensity Collection, and Refinement

	Structure A	Structure B
Compd	Pt[C ₃ H(C ₆ H ₅)(CN) ₄][P(C ₆ H ₅) ₃] ₂	Pt[C ₃ H(C ₆ H ₅)(CN) ₃ (COOC ₂ H ₅)]- [P(C ₆ H ₅) ₃] ₂ -CHCl ₃ ^a
Formula weight	C ₄₉ H ₃₆ N ₄ P ₂ Pt 937.9 amu	C ₅₂ H ₄₂ Cl ₃ N ₃ O ₂ P ₂ Pt 1104.3 amu
<i>a</i>	11.272 (2) Å	12.844 (2) Å
<i>b</i>	17.209 (2) Å	12.498 (3) Å
<i>c</i>	11.598 (2) Å	30.406 (4) Å
β	112.57 (1)°	90.67 (1)°
Volume	2077.6 Å ³	4880.3 Å ³
Z	2	4
Density	1.499 g cm ⁻³ (calcd) 1.51 (2) g cm ⁻³ (obsd)	1.502 g cm ⁻³ (calcd) 1.52 (2) g cm ⁻³ (obsd)
Space group	C ₂ ² -P2 ₁	C _{2h} ⁵ -P2 ₁ /c
Crystal dimensions	0.2 × 0.5 × 0.3 mm	(1) ^b 0.10 × 0.45 × 0.15 mm (2) 0.12 × 0.50 × 0.22 mm
Crystal shape	Lath-shaped crystal with seven faces—two faces of the pinacoid form {100}, two of the pinacoid form {101}, two of the spheroid form {323}, and an end face $\bar{2}32$	(1) Flat crystal with well-formed faces, ten in number, of the forms {102}, {100}, and {011} (2) Same as (1)
Crystal volume	0.00526 mm ³	(1) 0.00316 mm ³ (2) 0.00523 mm ³
Temp	24 ± 2 °C	24 ± 1 °C
Radiation	Cu K α ₁ (λ 1.540562 Å) prefiltered with 1 mil of Ni foil	Cu K α ₁ (λ 1.540562 Å) prefiltered with 1 mil of Ni foil
μ	74.07 cm ⁻¹	79.42 cm ⁻¹
Transmission factors	0.216–0.670	(1) 0.382–0.613 (2) 0.188–0.589
Receiving aperture	5.0 × 4.9 mm; 33 cm from crystal	(1) 5.6 × 5.9 mm; 32 cm from crystal (2) 5.1 × 5.1 mm; 32 cm from crystal
Take-off angle	4.8°	(1) 3.2° (2) 3.3°
Scan rate	2.0°/min in 2 θ	2.0°/min in 2 θ
Scan range	1.1° below K α ₁ to 1.0° above K α ₂	(1) 0.9° below K α ₁ to 0.9° above K α ₂ (2) 1.0° below K α ₁ to 1.0° above K α ₂
Background	10 s single rescan for observations with $I < 3\sigma(I)$	(1) 10 s two rescans for observation with $I < 3\sigma(I)$ (2) Same as for (1)
2 θ limits	3.5–160°	(1) 5.0–75° (2) 75–101°
Observations	$\pm h, \pm k, l$ 2 $\theta < 45^\circ$ $\pm h, k, l$ 2 $\theta \geq 45^\circ$	$\pm h, -k, l$
Total no. of observations	4767	5569
Final no. of variables	210	276
Unique data with $F_o^2 > 3\sigma(F_o^2)$	4132	4235
<i>R</i> (on <i>F</i> , F_o^2)	0.029	0.056
$R_w > 3\sigma(F_o^2)$	0.038	0.088
Error in observation of unit weight	1.89 electrons	2.90 electrons

^a The average CHCl₃ content in the data crystals is 0.78 (1) mol per mol of Pt from the least-squares refinement. ^b (1) and (2) refer to the data for two different crystals used in the solution of structure B.

No crystallographic symmetry is imposed on the discretely packed molecules of V or VI. Figures 2(a) and 2(b) depict stereoscopic views of the contents of the unit cells with two molecules of V (structure A) and four molecules of VI along with solvent (structure B), respectively. All intermolecular contacts are normal with the shortest H...H contacts being 2.24 and 2.35 Å in structures A and B, respectively. Also a short

N...H distance of 2.47 Å is observed in structure A and a C...H contact of 2.6 Å in structure B.

Two different views of the coordination spheres of molecules V and VI are shown in Figures 3(a), 4(a), 3(b), and 4(b), respectively. The substituents on these molecules are normal; there are no unusual features in the cyano groups nor in the ester group.

Table IIa. Positional and Thermal Parameters for the Nongroup Atoms of Pt[C₃H(C₆H₅)(CN)₄][P(C₆H₅)₃]₂

ATOM	X ^A	Y	Z	811 ^B	822	833	812	813	823
PT	0.175510(18)	1/4	0.254518(19)	48.56(18)	22.82(9)	61.18(18)	-1.40(19)	15.48(13)	1.99(20)
P(1)	0.23545(16)	0.29453(12)	0.45618(16)	63.5(13)	27.97(71)	66.7(14)	-2.01(80)	13.8(11)	-2.44(80)
P(2)	-0.00200(15)	0.33026(10)	0.16460(15)	54.2(12)	21.48(60)	71.0(13)	-0.81(68)	17.4(110)	0.37(71)
C(1)	0.30964(56)	0.15656(40)	0.28899(61)	52.4(48)	19.9(24)	70.5(53)	7.4(26)	13.9(41)	6.2(28)
C(2)	0.24158(62)	0.12428(47)	0.15409(62)	59.1(55)	29.8(30)	69.9(56)	-1.1(32)	15.1(45)	3.2(32)
C(3)	0.17293(57)	0.19825(42)	0.08396(60)	50.7(48)	27.2(28)	68.6(54)	0.8(28)	19.1(42)	0.8(29)
C(4)	0.43907(63)	0.18777(48)	0.31850(64)	57.7(56)	32.4(30)	64.8(57)	5.3(32)	9.9(44)	-1.5(32)
N(1)	0.53770(67)	0.21117(52)	0.33852(75)	78.6(66)	48.1(33)	122.5(85)	-7.7(39)	37.4(61)	-7.8(45)
C(5)	0.30122(87)	0.10337(56)	0.38298(84)	93.5(79)	30.9(34)	96.1(81)	8.7(42)	28.8(63)	0.1(41)
N(2)	0.28794(92)	0.05626(53)	0.44508(77)	166.(11)	40.0(38)	114.4(81)	-13.6(52)	57.9(79)	1.4(44)
C(6)	0.25172(51)	0.24909(82)	0.04121(57)	57.8(42)	39.3(29)	83.5(52)	16.0(59)	25.8(40)	20.2(65)
N(3)	0.31420(64)	0.28837(50)	0.00989(76)	83.8(61)	50.4(33)	142.2(85)	3.5(38)	56.0(62)	25.0(44)
C(7)	0.04944(65)	0.18230(50)	-0.01569(66)	65.5(60)	36.7(33)	70.5(59)	3.1(34)	23.7(49)	-1.4(34)
N(4)	-0.04890(57)	0.17026(52)	-0.09131(59)	71.4(51)	60.6(40)	77.8(55)	-2.8(37)	13.5(43)	-10.8(38)

^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: $\text{EXP}[-(811h^2 + 822k^2 + 833l^2 + 2812hk + 2813hl + 2823kl)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS $\times 10^4$.

Table IIb. Positional and Thermal Parameters for the Nongroup Atoms of Pt[C₃H(C₆H₅)(CN)₃(COOC₂H₅)][P(C₆H₅)₃]₂·0.8CHCl₃

ATOM	X	Y	Z	811	822	833	812	813	823
PT	0.213512(46)	0.214497(51)	0.143191(19)	39.25(68)	41.69(75)	7.67(12)	-2.69(44)	-1.35(13)	-0.35(18)
CL(1)	0.4130(10)	0.0629(11)	0.38626(51)	213.(14)	231.(17)	54.5(36)	51.(13)	15.4(56)	-5.5(61)
CL(2)	0.2948(15)	0.2242(14)	0.41668(67)	294.(23)	297.(24)	68.6(50)	75.(19)	-25.9(82)	-56.9(88)
CL(3)	0.1954(14)	0.0367(15)	0.40531(57)	380.(26)	412.(27)	54.4(37)	-181.(22)	78.4(81)	-77.7(82)
P(1)	0.13501(29)	0.13416(34)	0.08325(12)	47.4(29)	55.1(34)	7.85(50)	-3.4(25)	-1.76(91)	-3.5(11)
P(2)	0.32639(29)	0.07161(32)	0.15767(12)	41.0(28)	47.6(31)	8.89(52)	-5.1(24)	-0.34(90)	-0.1(10)
C(1)	0.1149(11)	0.3541(11)	0.14593(45)	53.(12)	32.(11)	8.6(20)	4.8(95)	1.3(36)	-1.4(40)
C(2)	0.1546(11)	0.3805(12)	0.19323(45)	55.(12)	44.(12)	8.3(19)	0.0(97)	2.5(36)	-1.5(39)
C(3)	0.2602(11)	0.3277(12)	0.19523(44)	56.(12)	44.(12)	6.5(18)	3.3(98)	-1.5(36)	0.0(37)
C(4)	0.0036(14)	0.3303(13)	0.14522(51)	62.(14)	53.(13)	10.9(23)	4.(11)	-7.6(44)	-0.9(42)
N(1)	-0.0824(12)	0.3075(12)	0.14603(48)	51.(11)	101.(15)	15.7(22)	9.(11)	1.4(39)	-9.6(45)
C(5)	0.1426(13)	0.4309(14)	0.11334(58)	72.(14)	46.(14)	10.9(25)	-3.(12)	-1.8(46)	-1.5(52)
N(2)	0.1694(14)	0.4902(13)	0.08816(53)	125.(17)	69.(14)	13.7(24)	-18.(13)	-1.7(49)	3.6(48)
C(6)	0.3395(14)	0.3961(14)	0.17569(55)	59.(14)	60.(15)	10.9(24)	8.(12)	-5.4(46)	-5.2(48)
N(3)	0.3987(12)	0.4490(12)	0.15854(55)	78.(14)	72.(14)	19.5(28)	-27.(11)	4.6(48)	1.5(49)
C(7)	0.2902(14)	0.2877(14)	0.23974(63)	63.(15)	55.(14)	15.3(29)	13.(13)	-6.5(52)	-7.8(56)
O(1)	0.2276(11)	0.2696(11)	0.26917(40)	120.(13)	97.(13)	10.9(17)	3.(10)	0.6(38)	3.8(38)
O(2)	0.39116(93)	0.26642(93)	0.24378(40)	76.(10)	69.(10)	16.9(19)	1.8(82)	-16.7(33)	-0.1(36)
C(8)	0.4254(17)	0.2226(17)	0.28727(66)	144.(21)	83.(20)	18.5(31)	-7.(17)	-31.8(64)	9.0(65)
C(9)	0.5390(18)	0.1930(19)	0.28415(95)	123.(20)	123.(25)	50.5(60)	-31.(17)	-56.6(90)	37.2(94)
C(10)	0.2839(42)	0.1278(38)	0.3844(15)	434.(72)	227.(52)	59.4(94)	127.(51)	111.(23)	-9.(19)

A comparative listing of selected intramolecular bond distances, bond angles, dihedral angles, and displacements of atoms from planes for the molecules I-VI (Chart 1) is shown in Tables VI and VII. Consistency has been maintained in the atom nomenclature for all the molecules listed.

A survey of the parameters listed in Table VII [planes (i) and (iii)] indicates that in the six-coordinate complexes I, II, and III, the platinum atom and the four equatorial ligands C(1), C(2), L(1), and L(2) are essentially coplanar. However, a severe tetrahedral distortion is observed in complex IV, with the dihedral angle between the planes C(1)-Pt-C(3) and L(2)-Pt-L(1) being 18.0(2)°. Complexes V and VI have dihedral angles of 10.5(2) and 6.4(5)°, respectively. As can be seen, the twist is significant but not as severe as in IV. The related four-coordinate complex, Pt[C₂(CN)₄][P(C₆H₅)₃]₂, is also perturbed from coplanarity with a corresponding dihedral angle of 8.3°. ¹⁷ This dihedral angle in the metallocyclopentane complex Pt[C₄H₃(CN)₄(OC₂H₅)][P(C₆H₅)₃]₂ has been found to be only 1.5°. ⁶ As no significant trends can be culled from these observations, we believe that the deviations from coplanarity require little energy and occur at least in part to lessen nonbonded contacts. ⁸ The coplanarity of the atoms in the equatorial plane of the complexes I, II, and III may arise from the influence of nonbonding interactions with the axial ligands; these ligands may inhibit distortions from a square-

planar arrangement. The angle between the normal to the P(1)-Pt-P(2) plane and the C(1)-C(3) vector is 79.5(2) and 84.2(5)° in complexes V and VI, respectively. These values are almost exactly complementary to the P(1)-Pt-P(2)/C(1)-Pt-C(3) dihedral angles. ¹⁸ In comparing the displacements of the atoms from planes (i) and (iii) in Table VII, we see a similarity between complexes IV and V in that atoms C(1) and C(3) are displaced by nearly equivalent amounts below and above the planes. However, in complex VI the displacement of atom C(3) above plane (i) is much smaller than that of atom C(1) below this plane. This may be caused by the presence of the ethyl ester group bonded to atom C(3). An inspection of plane (ii) in Table VII also reveals a slight pyramidal distortion in complex VI, where the Pt atom is 0.042 Å above this plane.

As observed in complex IV, both V and VI show differences between the Pt-P(1) and Pt-P(2) bond distances. Also, these distances are larger than the average Pt-P distance of 2.290 Å in Pt[C₂(CN)₄][P(C₆H₅)₃]₂. ¹⁷ Note that the observation of Pt-P bond distances of 2.33 Å in V and VI is in disagreement with the correlation that has been drawn between metallocycloalkane ring size and Pt-P distances. ⁶ In addition to ring size substituents on the cycloalkane rings also appear to play a role. The P(1)-Pt-P(2) angles in IV and V are nearly the same (96.99(6) and 97.15(6)°) whereas in VI this angle is 94.6

Table IIIa. Derived Parameters for the Rigid Group Atoms of $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_4][\text{P}(\text{C}_6\text{H}_5)_3]_2$

ATOM	X	Y	Z	B·A ²	ATOM	X	Y	Z	B·A ²
C11	0.26619(58)	0.39819(29)	0.45805(56)	3.99(13)	C44	-0.08145(56)	0.53537(28)	0.38397(51)	5.16(17)
C12	0.24095(61)	0.45117(39)	0.53679(54)	5.12(18)	C45	-0.01435(54)	0.54839(23)	0.30669(52)	4.58(16)
C13	0.27624(72)	0.52891(36)	0.53727(64)	6.50(24)	C46	0.00876(46)	0.48697(29)	0.23961(43)	3.92(13)
C14	0.33676(76)	0.55365(31)	0.45901(75)	6.83(26)	C51	-0.00244(50)	0.37745(33)	0.02258(42)	3.60(12)
C15	0.36201(71)	0.50066(41)	0.38028(65)	7.35(28)	C52	-0.11360(41)	0.38531(37)	-0.08506(51)	4.52(16)
C16	0.32672(64)	0.42293(37)	0.37979(55)	4.45(19)	C53	-0.11081(50)	0.42846(42)	-0.18580(44)	5.35(20)
C21	0.12401(38)	0.27537(31)	0.53104(40)	3.38(11)	C54	0.00314(65)	0.46375(41)	-0.17891(52)	5.97(22)
C22	0.14975(41)	0.29788(34)	0.65389(41)	4.60(15)	C55	0.11429(51)	0.45589(41)	-0.07126(62)	5.92(22)
C23	0.05916(52)	0.28444(44)	0.70646(36)	5.50(19)	C56	0.11151(42)	0.41274(40)	0.02948(47)	4.90(17)
C24	-0.05717(46)	0.24847(46)	0.63623(47)	5.33(15)	C61	-0.14871(33)	0.27387(23)	0.12158(43)	3.15(11)
C25	-0.08291(38)	0.22596(39)	0.51342(46)	4.98(19)	C62	-0.14261(34)	0.19376(24)	0.14141(45)	3.62(13)
C26	0.00768(43)	0.23940(33)	0.46084(33)	3.96(13)	C63	-0.25487(46)	0.15164(20)	0.11979(54)	4.63(16)
C31	0.38777(35)	0.25870(37)	0.57271(39)	3.55(9)	C64	-0.37323(36)	0.18962(27)	0.07835(51)	4.75(17)
C32	0.50316(47)	0.29559(32)	0.58844(48)	4.80(16)	C65	-0.37933(32)	0.26973(27)	0.05853(48)	4.32(15)
C33	0.61808(36)	0.26933(38)	0.67939(55)	5.08(18)	C66	-0.26708(42)	0.31186(19)	0.08015(49)	4.16(14)
C34	0.61762(44)	0.20617(40)	0.75461(53)	5.99(22)	C71	0.32362(48)	0.07659(31)	0.10039(45)	3.41(11)
C35	0.50223(59)	0.16928(34)	0.73888(55)	5.63(20)	C72	0.42218(54)	0.02954(37)	0.17921(34)	4.78(17)
C36	0.38730(44)	0.19554(36)	0.64793(50)	4.59(16)	C73	0.49256(51)	-0.01702(36)	0.12994(50)	5.47(19)
C41	-0.03523(46)	0.41253(25)	0.24982(41)	3.23(11)	C74	0.46439(54)	-0.01653(35)	0.00185(53)	4.92(17)
C42	-0.10232(49)	0.39951(25)	0.32710(49)	4.00(13)	C75	0.36582(57)	0.03053(38)	-0.07698(36)	5.00(17)
C43	-0.12543(52)	0.46093(33)	0.39418(48)	5.09(17)	C76	0.29544(47)	0.07708(33)	-0.02770(42)	4.06(14)

RIGID GROUP PARAMETERS

GROUP	X _C ^A	Y _C	Z _C	DELTA ^B	EPSILON	ETA
RING1	0.30148(42)	0.47592(29)	0.45853(42)	-2.0694(86)	2.0050(43)	-2.8883(89)
RING2	0.03342(32)	0.26192(24)	0.58365(31)	2.1684(51)	2.4043(28)	1.3252(52)
RING3	0.50269(34)	0.23243(26)	0.66366(33)	2.5306(38)	-2.6260(36)	2.6642(40)
RING4	-0.0584(31)	0.47395(22)	0.31690(31)	-0.6550(40)	2.4743(29)	2.2122(40)
RING5	0.00035(39)	0.42060(24)	-0.07816(37)	-1.3720(42)	-2.9943(34)	-2.1150(41)
RING6	-0.26047(30)	0.23175(19)	0.09997(28)	0.5675(25)	3.0703(32)	2.9719(30)
RING7	0.39400(35)	0.03003(24)	0.05112(34)	1.0156(63)	2.2685(29)	-1.7837(60)

^AX_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. ^BTHE RIGID GROUP ORIENTATION ANGLES DELTA, EP-SILON, AND ETARADIANS) HAVE BEEN DEFINED PREVIOUSLY: S. J. LA PLACA AND J. A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

Table IIIb. Derived Parameters for the Rigid Group Atoms of $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_3(\text{COOC}_2\text{H}_5)][\text{P}(\text{C}_6\text{H}_5)_3]_2 \cdot 0.8\text{CHCl}_3$

ATOM	X	Y	Z	B·A ²	ATOM	X	Y	Z	B·A ²
C11	0.03908(71)	0.21028(84)	0.05232(32)	3.30(30)	C44	0.29514(88)	-0.26304(67)	0.09161(35)	5.19(40)
C12	-0.06714(78)	0.18720(76)	0.05325(34)	4.31(36)	C45	0.24473(81)	-0.24248(73)	0.13111(35)	4.90(40)
C13	-0.13691(59)	0.24699(96)	0.02776(40)	5.72(45)	C46	0.25201(80)	-0.14150(85)	0.15045(27)	4.27(35)
C14	-0.10047(86)	0.32988(92)	0.00134(37)	5.94(46)	C51	0.31331(74)	0.03020(82)	0.21541(26)	3.12(32)
C15	0.00575(96)	0.35296(83)	0.00042(36)	5.80(44)	C52	0.21351(63)	0.03340(85)	0.23298(32)	4.18(36)
C16	0.07552(64)	0.29316(95)	0.02591(37)	4.94(40)	C53	0.19449(61)	-0.01322(94)	0.27379(33)	4.48(39)
C21	0.22605(74)	0.10649(91)	0.03889(31)	3.49(32)	C54	0.27526(83)	-0.06303(92)	0.29703(27)	5.09(41)
C22	0.32610(84)	0.14963(90)	0.04158(33)	4.91(38)	C55	0.37506(70)	-0.06623(87)	0.27946(32)	4.65(38)
C23	0.39633(67)	0.1323(11)	0.00766(42)	6.75(50)	C56	0.39408(56)	-0.01961(87)	0.23865(32)	3.80(33)
C24	0.36652(91)	0.0719(11)	-0.02894(35)	6.90(51)	C61	0.46434(58)	0.09795(81)	0.14784(34)	3.27(32)
C25	0.2665(10)	0.0287(10)	-0.03163(32)	6.71(52)	C62	0.49470(72)	0.20131(70)	0.13634(35)	3.90(34)
C26	0.19624(71)	0.04604(93)	0.00229(38)	4.84(40)	C63	0.59950(82)	0.22396(69)	0.12919(37)	5.02(39)
C31	0.06162(74)	0.01684(76)	0.10093(33)	3.21(31)	C64	0.67394(58)	0.14325(95)	0.13354(39)	5.60(43)
C32	0.05247(85)	-0.07883(91)	0.07757(29)	4.93(40)	C65	0.64358(73)	0.03989(81)	0.14503(38)	5.08(41)
C33	-0.01196(98)	-0.16013(74)	0.09298(39)	6.46(49)	C66	0.53878(83)	0.01724(63)	0.15218(37)	4.42(37)
C34	-0.06723(89)	-0.14577(85)	0.13176(41)	6.38(48)	C71	0.14429(81)	0.49596(67)	0.20816(34)	3.38(32)
C35	-0.05808(85)	-0.0501(10)	0.15512(31)	5.43(44)	C72	0.05847(73)	0.55569(88)	0.19401(31)	4.29(36)
C36	0.00635(85)	0.03121(75)	0.13971(32)	4.05(35)	C73	0.04150(73)	0.65767(85)	0.21115(38)	5.42(42)
C41	0.30971(79)	-0.06107(65)	0.13029(31)	3.26(31)	C74	0.11035(94)	0.69991(71)	0.24244(38)	5.66(43)
C42	0.36012(78)	-0.08163(76)	0.09079(32)	4.15(36)	C75	0.19616(83)	0.64018(94)	0.25659(34)	6.04(45)
C43	0.35283(86)	-0.18261(88)	0.07145(28)	5.36(43)	C76	0.21313(69)	0.53820(88)	0.23945(36)	4.88(40)

RIGID GROUP PARAMETERS

GROUP	X _C	Y _C	Z _C	DELTA	EPSILON	ETA
RING1	-0.03069(59)	0.27008(60)	0.02683(23)	-0.9449(71)	2.7808(68)	-2.5158(73)
RING2	0.29629(62)	0.08918(62)	0.00497(25)	2.2309(86)	2.6338(69)	-2.1165(86)
RING3	-0.00280(56)	-0.06446(64)	0.11634(25)	0.407(10)	-2.2391(69)	2.555(11)
RING4	0.30242(50)	-0.16206(60)	0.11095(22)	2.0651(95)	-2.2820(65)	-2.441(10)
RING5	0.29429(53)	-0.01642(54)	0.25622(22)	-1.8491(65)	-3.0815(56)	1.1044(68)
RING6	0.56914(56)	0.12060(61)	0.14069(21)	-2.9003(60)	-2.9437(67)	-2.9702(67)
RING7	0.12732(55)	0.59794(62)	0.22530(23)	-1.6804(78)	-2.5446(68)	2.6704(81)

Table V. Metrical Details for the Two Structure Determinations

	Structure B	Structure A		Structure B	Structure A
Distances, Å					
Pt-P(1)	2.303 (4)	2.302 (2)	P(1)-C11	1.811 (10)	1.816 (5)
Pt-P(2)	2.339 (4)	2.332 (2)	P(1)-C21	1.829 (10)	1.811 (6)
Pt-C(1)	2.158 (14)	2.137 (6)	P(1)-C31	1.827 (10)	1.837 (4)
Pt-C(3)	2.200 (14)	2.159 (6)	P(2)-C41	1.867 (9)	1.846 (5)
C(1)-C(2)	1.556 (19)	1.557 (9)	P(2)-C51	1.840 (9)	1.835 (6)
C(2)-C(3)	1.509 (19)	1.548 (10)	P(2)-C61	1.830 (9)	1.815 (4)
C(1)-C(3)	2.403 (20)	2.394 (9)			
C(1)-C(4)	1.459 (22)	1.467 (9)	C(2)-C71	1.519 (17)	1.536 (10)
C(1)-C(5)	1.428 (23)	1.454 (11)			
C(3)-C(6)	1.461 (23)	1.462 (11)	Cl(1)-C(10)	1.85 (5)	
C(3)-C(7)	1.489 (22)	1.454 (9)	Cl(2)-C(10)	1.56 (4)	
C(4)-N(1)	1.142 (19)	1.120 (10)	Cl(3)-C(10)	1.73 (4)	
C(5)-N(2)	1.122 (20)	1.132 (12)	Cl(1)-Cl(2)	2.69 (2)	
C(6)-N(3)	1.138 (20)	1.132 (11)	Cl(2)-Cl(3)	2.69 (2)	
C(7)-N(4)		1.138 (9)	Cl(3)-Cl(1)	2.88 (2)	
C(7)-O(1)	1.23 (2)				
C(7)-O(2)	1.328 (19)				
O(2)-C(8)	1.49 (2)				
C(8)-C(9)	1.51 (3)				
Bond Angles, deg					
P(1)-Pt-P(2)	94.6 (1)	97.15 (6)	C11-P(1)-Pt	118.1 (4)	108.6 (2)
C(1)-Pt-C(3)	66.9 (5)	67.7 (2)	C21-P(1)-Pt	112.8 (4)	116.8 (15)
P(1)-Pt-C(1)	97.5 (4)	98.6 (2)	C31-P(1)-Pt	109.9 (4)	117.6 (2)
P(2)-Pt-C(3)	101.1 (4)	97.3 (2)	C41-P(2)-Pt	121.8 (3)	122.18 (14)
P(1)-Pt-C(3)	166.6 (4)	164.4 (2)	C51-P(2)-Pt	109.3 (4)	111.8 (2)
P(2)-Pt-C(1)	164.3 (4)	163.1 (2)	C61-P(2)-Pt	115.5 (5)	110.03 (14)
Pt-C(1)-C(2)	91.2 (8)	92.3 (4)	C11-P(1)-C21	98.8 (5)	109.7 (3)
Pt-C(3)-C(2)	90.8 (8)	91.7 (4)	C21-P(1)-C31	102.9 (5)	102.1 (2)
			C31-P(1)-C11	113.7 (5)	101.6 (3)
C(1)-C(2)-C(3)	103.2 (11)	100.9 (6)	C41-P(2)-C51	99.5 (5)	102.1 (2)
			C51-P(2)-C61	107.8 (5)	107.6 (2)
			C61-P(2)-C41	101.1 (5)	101.9 (2)
C(4)-C(1)-C(5)	112.2 (13)	113.6 (6)	C71-C(2)-C(1)	116.7 (11)	117.2 (5)
C(4)-C(1)-C(2)	111.6 (12)	115.3 (6)	C71-C(2)-C(3)	119.0 (11)	118.9 (6)
C(5)-C(1)-C(2)	114.6 (13)	112.3 (6)			
C(4)-C(1)-Pt	114.2 (10)	109.7 (5)			
C(5)-C(1)-Pt	111.4 (10)	111.6 (5)			
C(6)-C(3)-C(7)	113.1 (14)	111.4 (6)	N(1)-C(4)-C(1)	176.6 (17)	178.5 (8)
C(6)-C(3)-C(2)	111.0 (13)	115.1 (6)	N(2)-C(5)-C(1)	176.6 (20)	172.1 (10)
C(7)-C(3)-C(2)	114.0 (12)	113.3 (6)	N(3)-C(6)-C(3)	176.6 (18)	178.9 (2)
C(6)-C(3)-Pt	105.6 (9)	105.5 (6)	N(4)-C(7)-C(3)		178.0 (7)
C(7)-C(3)-Pt	120.2 (10)	118.6 (4)			
C(3)-C(7)-O(1)	123.9 (16)				
C(3)-C(7)-O(2)	113.1 (16)				
O(1)-C(7)-O(2)	122.8 (17)				
C(7)-O(2)-C(8)	115.6 (15)				
O(2)-C(8)-C(9)	108.0 (18)				
Dihedral Angle					
C(1)-Pt-C(3)	6.4 (5)	10.5 (2)	C(1)-Pt-C(3)	7.1 (9)	11.5 (5)
P(2)-Pt-P(1)			C72-C71-C76		
C(3)-Pt-C(1)	29.7 (13)	28.6 (6)	C(1)-C(2)-C(3)	35.3 (14)	39.7 (8)
C(1)-C(2)-C(3)			C72-C71-C76		
C(1)-C(2)-C(3)					
P(2)-Pt-P(1)	33.0 (11)	30.6 (4)			
Conformation Angles, deg					
Pt-C(1)-C(2)-C(3)	24.6 (11)	23.6 (4)			
C(1)-C(2)-C(3)-Pt	-24.1 (10)	-23.3 (4)			
C(2)-C(3)-Pt-C(1)	18.2 (8)	17.8 (4)			
C(3)-Pt-C(1)-C(2)	-17.6 (8)	-17.7 (4)			
Displacements from Planes, Å					
(i) Plane Defined by P(1), Pt, P(2)					
C(1)	-0.209 (14)	-0.224 (7)			
C(2)	-0.594 (15)	-0.474 (8)			
C(3)	0.032 (15)	0.213 (7)			
(ii) Plane Defined by C(1), Pt, C(3)					
C(2)	0.47 (2)	0.27 (1)			

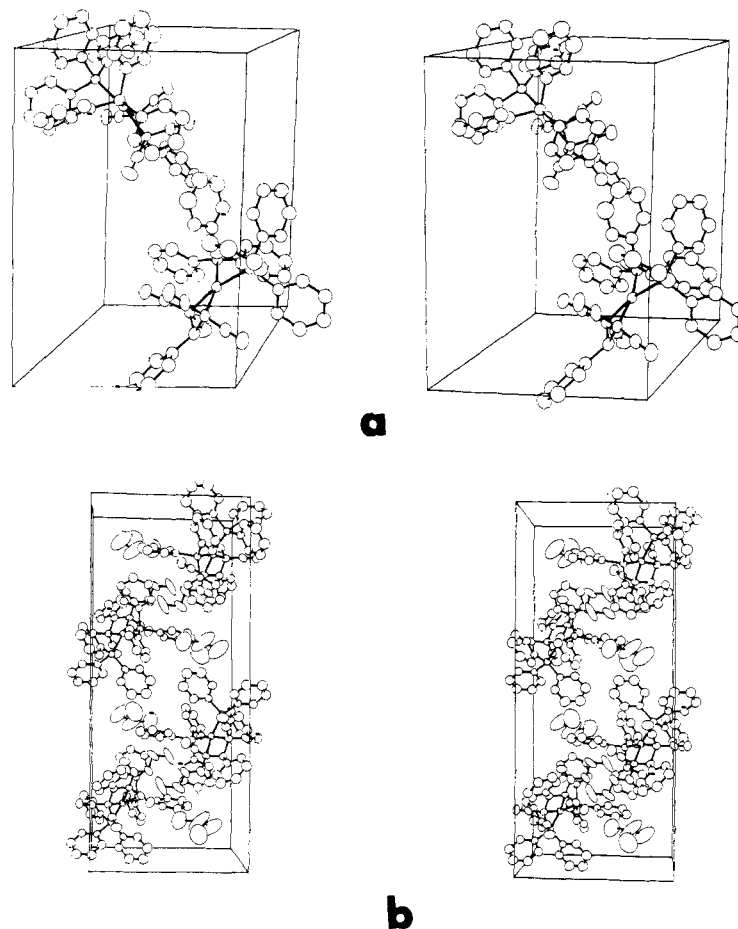


Figure 2. (a) A stereoscopic drawing of the contents of a unit cell of $\text{Pt}(\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_4)[\text{P}(\text{C}_6\text{H}_5)_3]_2$. Hydrogen atoms have been omitted for the sake of clarity. The other atoms are drawn at their 50% probability levels. The x axis goes from left to right, y from bottom to top, and z comes out of the paper. (b) A stereoscopic drawing of the contents of a unit cell of $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_3(\text{COOEt})][\text{P}(\text{C}_6\text{H}_5)_3]_2$. Hydrogen atoms have been omitted for the sake of clarity. The other atoms are drawn at their 50% probability levels. The x axis goes from left to right, y comes out of the paper, and the z axis goes from bottom to top.

(1)°. The average P–C distances for the triphenylphosphine ligands in V and VI are normal (1.834 and 1.827 Å) and the average C–P–C angles are 104.0 and 104.2°, respectively.

Metallocyclobutane Ring Comparisons

All six complexes listed in Tables VI and VII possess the expected puckered metallocyclobutane ring. The degree of puckering is least in the unsubstituted complex I, and this may be understood in terms of a minimum 1,2 and 1,3 substituent nonbonding interaction. Cyclobutane itself, with a dihedral angle of $30 \pm 6^\circ$, is puckered and the barrier to inversion is low (1.4 kcal/mol).¹⁹ Figures 4(a) and 4(b) depict the nature of the metallocyclobutane puckering in complexes V and VI, respectively. The range of puckering angles observed in the structures of various substituted cyclobutanes reported earlier is from about 20 to 35°. As seen from Table V, the extent of puckering for the complexes II–VI lies in this same range. Also, as would be expected from the number of substituents, a larger degree of puckering is observed for V and VI (28.6 (6) and 29.7 (13)°) than for IV (24.4 (4)°).

The Pt atom is bonded to atoms C(1) and C(3). A slight difference is observed in these two independent Pt–C bond distances for V (2.137 (6) and 2.159 (6)), and a larger difference (2.158 (14) and 2.200 (14)) for VI. These differences are not significant. However, it is of interest that the shorter Pt–C bonds are always trans to the longer Pt–P bonds in V and VI. The C(1)–Pt–C(3) angles are not significantly different for the complexes IV, V, and VI (68.4 (2), 67.7 (2), and 66.9 (5)°), these values being smaller than those for complexes I, II, and

III (Table VI). However, the limited accuracy of the crystal structures for I, II, and III makes legitimate comparisons impossible. The presence of the ethyl ester group bonded to atom C(3) in complex VI most probably accounts for the larger P(1)–Pt–C(3) and P(2)–Pt–C(3) angles observed for VI compared with those in IV and V.

The C(1)–C(2) and C(2)–C(3) distances in V (1.557 (9) and 1.548 (10) Å) are equal and are similar to those observed in a large number of substituted cyclobutanes.¹⁹ Differences are observed in these two bond lengths in IV and VI. Though differences have been observed in the corresponding bond lengths in some substituted cyclobutanes, they are usually more pronounced in the planar, centrosymmetric molecules and have been attributed to steric forces.¹⁹ With the exception of the short C(2)–C(3) distance of 1.509 Å in VI, all these bond lengths are considerably longer than the corresponding ones in tetracyanocyclopropane²⁰ (1.501 (4) and 1.506 (4) Å) and in 1,1,2,2-tetracyano-3-*o*-methoxyphenylcyclopropane (Chart II (a) where $\text{R}' = \text{o-CH}_3\text{OC}_6\text{H}_4$, 1.528 (3) and 1.527 (3) Å).²¹ This is to be expected on the basis of ring expansion and the consequent relief of strain. For example, the bond distances in cyclobutane and cyclopropane are 1.56 (2)²² and 1.524 (14) Å,²³ respectively, and a similar trend is seen in the bond lengths of 1,2,3,4-tetracyanocyclobutane²⁴ and 1,2,3-tricyanocyclopropane²⁵ (1.561 (3) and 1.518 (3) Å).

The angles within the ring for puckered cyclobutane systems are usually about 88°. The Pt–C(1)–C(2) and Pt–C(3)–C(2) angles for the metallocyclobutanes IV, V, and VI are found to be larger than this value. This observation along with the angle

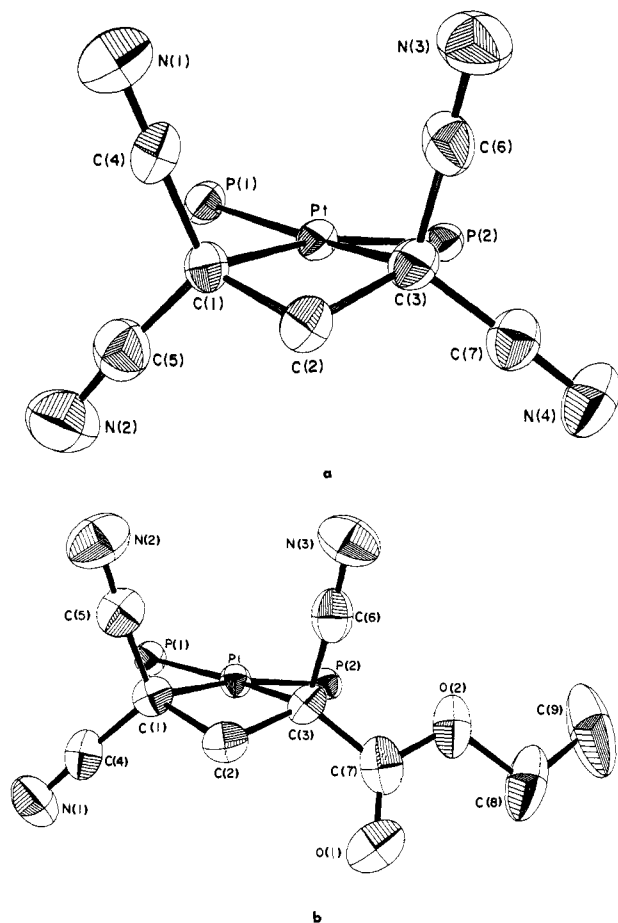


Figure 3. Another view of the coordination sphere of (a) $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_4][\text{P}(\text{C}_6\text{H}_5)_3]_2$ and (b) $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_3(\text{COOEt})][\text{P}(\text{C}_6\text{H}_5)_3]_2$ highlighting the twists (see text).

$\text{C}(1)-\text{C}(2)-\text{C}(3)$ of around 100° and $\text{C}(1)-\text{Pt}-\text{C}(3)$ angle of about 68° makes for a larger $\text{C}(1)\cdots\text{C}(3)$ distance in these metalocyclobutanes than in the cyclobutanes. Hence, although a large number of observations made above lead us to suggest a bonding scheme for the metalocyclobutanes similar to that used for cyclobutanes,⁸ the differences in geometry between these systems should be borne in mind. The bonding scheme in complexes II and III⁸ has been interpreted 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 The orbitals of the correct symmetry in the cyclopropanes are antibonding, consistent with bond scission. This model does not readily explain the puckering observed, but is supported by the observation that cyclopropanes are liberated from complexes I, II, and III on treatment with base.^{4,7} Under a variety of conditions, 1,1,2,2-tetracyanocyclopropane was not liberated from IV,¹¹ suggesting that cyano-substituted metalocyclobutanes have a greater stability. This can be rationalized, as has been done earlier,⁹ by suggesting that the cyano groups on atoms C(1) and C(3) promote π -back-donation into corresponding antibonding orbitals of the cyclopropane. The above model suggests that the Pt-C bonds possess both σ and π character. The $\text{C}(1)-\text{Pt}-\text{C}(3)$ angle of about 68° in compounds IV, V, and VI is consistent with some bending of the bonds in these ring systems. The larger Pt-C(1)-C(2), Pt-C(3)-C(2), and C(1)-C(2)-C(3) angles compared with the analogous angles in cyclobutane suggests that the C atoms possess greater sp^3 character in the metalocycles. These angles, as well as the $\text{C}(1)-\text{Pt}-\text{C}(3)$ angle and the puckering angle, appear to be

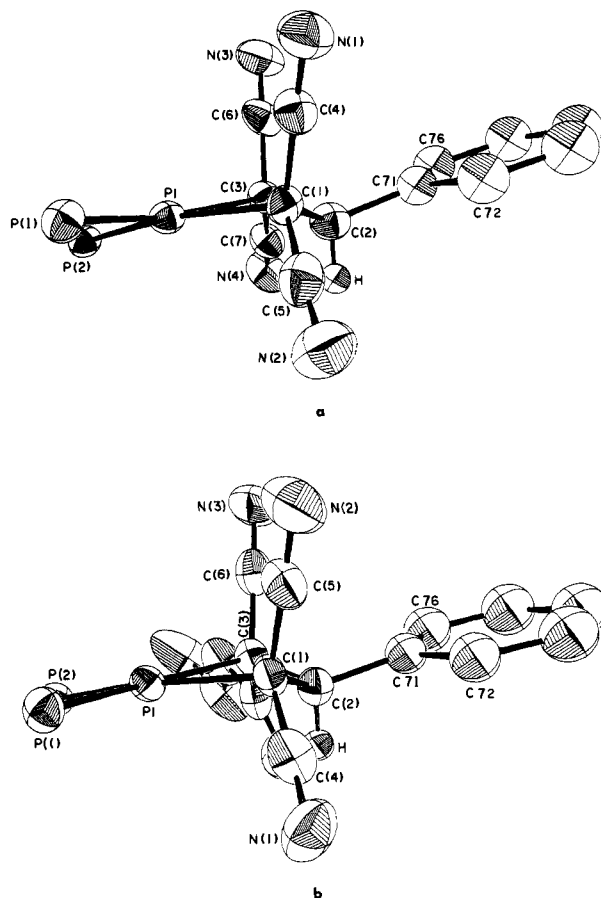


Figure 4. The conformation of the metalocyclobutane ring in (a) $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_4][\text{P}(\text{C}_6\text{H}_5)_3]_2$ and (b) $\text{Pt}[\text{C}_3\text{H}(\text{C}_6\text{H}_5)(\text{CN})_3(\text{COOEt})][\text{P}(\text{C}_6\text{H}_5)_3]_2$.

relatively insensitive to the nature of the substituents on the metalocycle. From these observations we conclude that the strain involved in the metalocyclobutane ring system is smaller than that in cyclobutane.

The phenyl ring substituent on atom C(2) is arranged in an equatorial position in complexes V and VI (Figure 4) which provides for smaller nonbonded interactions. In bromocyclobutane, which has been found to have a puckering angle of 29° , the bromine atom takes an equatorial conformation.²⁷ It is interesting that complexes V and VI have a similar arrangement of the phenyl ring substituent on the metalocyclobutane ring (Figures 1 and 4), i.e., the plane of the phenyl ring lies nearly parallel to the $\text{C}(1)-\text{Pt}-\text{C}(3)$ plane on the metalocyclobutane. The corresponding dihedral angles between the phenyl ring plane and the $\text{C}(1)-\text{Pt}-\text{C}(3)$ plane in V and VI are $11.5(5)$ and $7.1(9)^\circ$, respectively. This arrangement is about the same as that found for the phenyl group bonded to atom C(2) in molecule II (Chart I). The dihedral angles between the $\text{C}(1)-\text{C}(2)-\text{C}(3)$ plane and the plane of the phenyl ring are $39.7(8)$ and $35.3(14)^\circ$ in compounds V and VI, respectively. These values are smaller than that of 56° found for the corresponding 3-*o*-methoxyphenyl compound.²¹ One expects the greatest amount of π overlap when the phenyl ring plane is perpendicular to the cycloalkane ring system. This is the arrangement observed in molecule III, and as II and III are found in the same unit cell, it is assumed that there is only a low energy barrier to rotation of the phenyl ring. The rather confusing experimental results and theoretical rationalizations on halogen and phenyl substitution effects on cyclopropane rings, an area closely related to the present discussion, have been reviewed recently.²⁸

Table VI. Comparisons of Geometries of Platinacyclobutanes

	I ^a	II	III	IV	V	VI
Intramolecular Distances, Å						
Pt-C(1)	2.04 (5)	2.06 (3)	2.05 (3)	2.137 (6)	2.137 (6)	2.158 (14)
Pt...C(2)	2.69 (4)	2.60 (4)	2.62 (3)	2.712 (6)	2.694 (6)	2.687 (14)
Pt-C(3)	2.19 (5)	2.11 (5)	2.17 (3)	2.139 (6)	2.159 (6)	2.200 (14)
C(1)-C(2)	1.48 (8)	1.59 (7)	1.59 (4)	1.545 (9)	1.557 (9)	1.556 (19)
C(2)-C(3)	1.82 (9)	1.48 (5)	1.71 (4)	1.584 (9)	1.548 (10)	1.509 (19)
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-P(1)				2.314 (2)	2.302 (2)	2.303 (4)
Pt-P(2)				2.291 (2)	2.332 (2)	2.339 (4)
C(1)...C(3)	2.55 (10)	2.39 (7)	2.60 (4)	2.404 (9)	2.394 (9)	2.403 (20)
Bond Angles, deg						
C(1)-Pt-C(3)	74 (2)	70 (2)	76 (1)	68.4 (2)	67.7 (2)	66.9 (5)
C(1)-C(2)-C(3)	101 (4)	102 (3)	104 (2)	100.4 (5)	100.9 (6)	103.2 (11)
Pt-C(1)-C(2)	99 (4)	90 (2)	91 (2)	93.5 (4)	92.3 (4)	91.2 (8)
Pt-C(3)-C(2)	84 (3)	91 (3)	84 (2)	92.3 (4)	91.7 (4)	90.8 (8)
L(1)-Pt-L(2)	89 (1)	82 (1)	92 (1)			
P(1)-Pt-P(2)				96.99 (4)	97.15 (6)	94.6 (1)
Conformation Angles, deg						
Pt-C(1)-C(2)-C(3)	10 (4)	23 (2)	18 (3)	20.1 (5)	23.6 (4)	24.6 (11)
C(1)-C(2)-C(3)-Pt	-9 (4)	-23 (2)	-17 (3)	-20.0 (5)	-23.3 (4)	-24.1 (10)
C(2)-C(3)-Pt-C(1)	7 (3)	18 (2)	13 (3)	15.2 (4)	17.8 (4)	18.2 (8)
C(3)-Pt-C(1)-C(2)	-9 (3)	-17 (2)	-14 (3)	-15.6 (4)	-17.7 (4)	-17.6 (8)
Dihedral Angles, deg						
C(1)-Pt-C(3) } L(2)-Pt-L(1) }	1 (1)	4 (1)	3 (2)	18.0 (2)	10.5 (2)	6.4 (5)
C(3)-Pt-C(1) } C(1)-C(2)-C(3) }	12 (5)	28 (3)	22 (2)	24.4 (4)	28.6 (6)	29.7 (13)
C(1)-C(2)-C(3) } L(2)-L(1)-Pt }	13 (4)	28 (2)	21 (4)	30.4 (4)	30.6 (4)	33.0 (11)
Displacements from Planes, Å						
(i) Plane Defined by L(1), Pt, L(2) [or P(1), Pt, P(2)]						
C(1)	0.00 (6)	-0.09 (4)	-0.12 (6)	-0.356 (6)	-0.224 (7)	-0.209 (12)
C(2)	0.24 (7)	0.44 (4)	0.30 (6)	0.408 (8)	-0.474 (8)	-0.594 (15)
C(3)	0.03 (4)	0.07 (4)	0.01 (6)	0.386 (7)	0.213 (7)	0.032 (15)
(ii) Plane Defined by C(1), Pt, C(3)						
C(2)	0.22 (9)	0.46 (5)	0.39 (8)	0.41 (1)	0.47 (1)	0.47 (2)
(iii) Weighted, Least-Squares Plane Defined by C(1), C(3), L(1), L(2)						
C(1)	-0.01 (6)	-0.05 (3)	-0.03 (5)	-0.348 (6)	-0.214 (7)	-0.115 (14)
C(3)	0.00 (4)	0.05 (3)	0.04 (5)	0.380 (6)	0.207 (7)	0.121 (14)
L(1)	0.00 (3)	-0.02 (2)	-0.02 (4)	0.012 (1)	0.013 (2)	0.005 (4)
L(2)	0.00 (3)	0.02 (2)	0.03 (5)	0.010 (1)	-0.009 (2)	-0.006 (4)
Pt	0.008	0.006	0.026	0.000	0.002	0.042
C(2)	0.218	0.459	0.376	0.410	-0.473	-0.482

^a Notation of Chart I.

The conformation angles shown in Table VI clearly indicate the similarity in the nature of puckering, also reflecting the corresponding magnitudes of puckering in the six complexes listed. Relief of ring strain and the attack by platinum(0) on the positively charged carbon atom (possessing the electron-withdrawing cyano groups)¹³ have both been suggested as being possible driving forces for the insertion reaction. This has been prompted by the observation of the insertion of platinum(0) into a tetracyanocyclobutane derivative.⁶ That both these factors are of importance is seen from the observation that tetracyanocyclopropane is more reactive than the tetracyanocyclobutane.⁶ Though we have not conducted any kinetic studies, there appear to be no significant differences in the rates of formation of IV, V, and VI. Preliminary studies performed by us indicate that a straightforward insertion does not seem to occur with a 1,1,2,2-tetracyanocyclohexane de-

rivative. Attempts are being made to characterize the reaction products.

Acknowledgments. This research was kindly supported by the National Science Foundation. We are indebted to Matthey-Bishop Inc. for the loan of platinum used in this study.

Supplementary Material Available: A listing of structure amplitudes for both complexes and Table IV, the root-mean-square amplitudes of vibration (32 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970); F. J. McQuillan and K. G. Powell, *J. Chem. Soc., Dalton Trans.*, 2129 (1972).
- (2) P. G. Gassman and F. J. Williams, *J. Am. Chem. Soc.*, **94**, 7733 (1972); P. G. Gassman and R. R. Reitz, *J. Organomet. Chem.*, **52**, C51 (1973).
- (3) R. M. Moriarty, K. Chen, C. Yeh, J. Flippen, and J. Karle, *J. Am. Chem. Soc.*,

- 94, 8944 (1972); M. Lenarda, R. Ros, M. Graziani, and U. Belluco, *J. Organomet. Chem.*, **46**, C29 (1972); R. Aumann, *ibid.*, **47**, C29 (1973).
- (4) F. J. McQuillin and K. G. Powell, *J. Chem. Soc., Dalton Trans.*, 2123 (1972).
- (5) C. F. H. Tipper, *J. Chem. Soc.*, 2045 (1955).
- (6) R. Ros, M. Lenarda, N. B. Pahor, M. Calligaris, P. Delise, L. Randaccio, and M. Graziani, *J. Chem. Soc., Dalton Trans.*, 1937 (1976).
- (7) R. D. Gillard, M. Keeton, R. Mason, M. F. Pilbrow, and D. R. Russell, *J. Organomet. Chem.*, **33**, 247 (1971).
- (8) J. A. McGinnety, *J. Organomet. Chem.*, **59**, 429 (1973).
- (9) D. J. Yarrow, J. A. Ibers, M. Lenarda, and M. Graziani, *J. Organomet. Chem.*, **70**, 133 (1974).
- (10) Y. C. Kim and H. Hart, *J. Chem. Soc. C*, 2409 (1969); Y. C. Kim and H. Hart, *Tetrahedron*, 3869 (1969).
- (11) M. Lenarda, R. Ros, M. Graziani, and U. Belluco, *J. Organomet. Chem.*, **65**, 407 (1974).
- (12) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
- (13) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).
- (14) Computer programs for the CDC 6400 and CDC 7600 computers used in this work include local versions of Zalkin's FORDP Fourier summation program, the Busing-Lévy ORFFE error function program, and the absorption program AGNOST. Our least-squares program, NUCLS, in its nongroup form closely resembles the Busing-Lévy ORFLS program. The diffractometer was run under the Vanderbilt Disk System: P. G. Lenher, *J. Appl. Crystallogr.*, **8**, 568 (1975).
- (15) See, for example, M. Cowie, B. L. Haymore, and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 7608 (1976).
- (16) See paragraph at end of paper regarding supplementary material.
- (17) G. Bombieri, E. Forsellini, C. Pannattoni, R. Graziani, and R. Gandoli, *J. Chem. Soc. A*, 1313 (1970).
- (18) S. D. Ittel and J. A. Ibers, *Adv. Organomet. Chem.*, **14**, 33 (1976).
- (19) F. A. Cotton and B. A. Frenz, *Tetrahedron*, **30**, 1587 (1974).
- (20) Y. Wang and G. D. Stucky, *Acta Crystallogr., Sect. B*, **29**, 1255 (1973).
- (21) K. Venkatesam, J. Rajaram, and R. Usha, to be published.
- (22) D. Bastiansen and O. Hassel, *Tidsskr. Kjemi, Bergves. Metall.*, **6**, 71 (1946).
- (23) G. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953).
- (24) B. Greenberg and B. Post, *Acta Crystallogr., Sect. B*, **24**, 918 (1968).
- (25) A. Hartman and F. L. Hirshfield, *Acta Crystallogr.*, **20**, 80 (1966).
- (26) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).
- (27) W. G. Rothschild and B. P. Dailey, *J. Chem. Phys.*, **36**, 2931 (1962).
- (28) M. E. Jason and J. A. Ibers, *J. Am. Chem. Soc.*, **99**, 6012 (1977).

Stereochemistry of Oxidative Addition of Benzyl- α -*d* Chloride and Bromide to Tris(triethylphosphine)palladium(0). Direct Observation of Optical Activity in a Carbon-Palladium σ -Bonded Complex

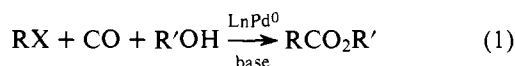
Y. Becker and J. K. Stille*

Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52242. Received June 15, 1977

Abstract: The absolute configurations of the products of oxidative addition of optically active benzyl- α -*d* chloride (**1a**) and bromide (**1b**) to tris(triethylphosphine)palladium(0) (**6**) were determined using carbonylation and cleavage with Cl_2/MeOH to produce the corresponding methyl esters. In both cases inversion of configuration at carbon was observed; higher optical yields were obtained with benzyl chloride. Neither a nucleophilic exchange mechanism in the neutral benzyl complex nor a σ - π rearrangement in the cationic intermediate (*S*)-(+)-PhCHDPd(PEt₃)₂⁺ is responsible for the observed loss of stereochemistry.

Introduction

The catalytic carboalkoxypalladation of various organic halides



can be carried out under very mild conditions.¹ The key step in the reaction is the oxidative addition of the organic halide to the zerovalent palladium phosphine complex. Since this step also determines the stereospecificity of the reaction, a study of the stereochemistry and the mechanism of the oxidative addition reaction was undertaken.

Optically active benzyl- α -*d* chloride (**1a**) and α -phenethyl bromide (**2**) react with carbonyl tris(triphenylphosphine)palladium(0) **3** with *complete* inversion of configuration at the asymmetric carbon.² The reaction of **1** with tetrakis(triphenylphosphine)palladium(0) (**4**) gave an isolable benzyl complex but only 74% net inversion of configuration at carbon was observed. However, when carbon monoxide was present during the oxidative addition, 100% net inversion of configuration on carbon was again realized. In the presence of carbon monoxide, the stereospecificity of the addition of **2** to **4** was found to be essentially the same as in the direct oxidative addition to **3**. When no carbon monoxide was present, facile β -hydride

elimination predominated. The predominance of inversion of configuration at carbon is more consistent with a concerted oxidative addition mechanism than with the generation of radical intermediates.

In contrast to these results, CIDNP was observed during the oxidative addition of benzyl bromide to tris(triethylphosphine)platinum(0) (**5**) and isopropyl iodide to tris(triethylphosphine)palladium(0) (**6**). On the other hand, no CIDNP signals were detected in the addition of benzyl chloride to **5**.^{3b} Therefore, it was suggested that free-radical processes are involved in the oxidative addition of certain alkyl halides to d¹⁰ zerovalent metal phosphine complexes, while with others an S_N2-type mechanism operates. In the present study we have tested these ideas using two model compounds, a chiral benzyl chloride and a bromide, as stereochemical probes in the oxidative addition to **6**.

Results and Discussion

Reactions and Product Characterization. Benzyl chloride and bromide react extremely rapidly with **6**⁴ under very mild conditions; the stoichiometry of both reactions was found to be consistent with eq 2 and 3.

The products were isolated either by direct crystallization in the benzyl chloride case or by column chromatography in