and could well perform these functions in the biological environment.

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Registry No. Cu(SUra)$_2$Cl·DMF, 60525-67-9.

Supplementary Material Available: Listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Diiodo(butane-1,4-diyl)bis(dimethylphenylphosphine)platinum(IV)[1]

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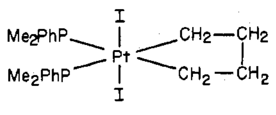
The Pt complex $C_{20}H_{30}P_2I_2Pt$ crystallizes in the monoclinic space group $C2/c$ with a = 15.286 Å, b = 9.709 Å, c = 17.036 Å, β = 107.49°, d_{calcd} = 2.15 g/cm^3 for Z = 4. X-ray diffraction intensity data were collected by an automated diffractometer using graphite-monochromated Mo Kα radiation. For 1575 reflections with $F^2 > 3\sigma(F^2)$, R_1 = 0.035 and R_2 = 0.044. The six-coordinate Pt atom is at the center of a distorted octahedron; the six neighbors of Pt are two phosphorus atoms at 2.418 (3) Å, two iodine atoms at 2.641 (1) Å, and two carbon atoms from the butanediyl ligand at 2.15 (1) Å. The complex has a crystallographic twofold axis that passes through the Pt atom.

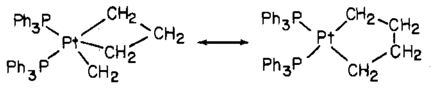
Introduction

In this paper we report the structure of a cyclic organoplatinum(IV) complex



Metallocyclic complexes of this general form have been postulated as intermediates in several transition metal complex catalyzed reactions. For example, they may be implicated in the isomerization of strained-ring carbocyclic compounds, in olefin metathesis, and in cycloaddition reactions of olefins. There is therefore a need for more information about the chemical properties and structures of these compounds.

It has previously been shown that the similar platinum(II) complex $[Pt(CH_2)_4(PPh_3)_2]$ has high thermal stability and decomposes to give mostly but-1-ene at 120 °C in dichloromethane.[2] The structure of the complex[3] is of particular interest in that it shows an unsymmetrical puckering of the $Pt(CH_2)_4$ ring. This puckering was considered to be the result of a contribution to the bonding from the canonical form I.



I II

The platinum(IV) complex $[PtI_2(CH_2)_4(PMe_2Ph)_2]$ has no vacant stereochemical position and is already an 18-electron complex. Thus a canonical form analogous to I can play no

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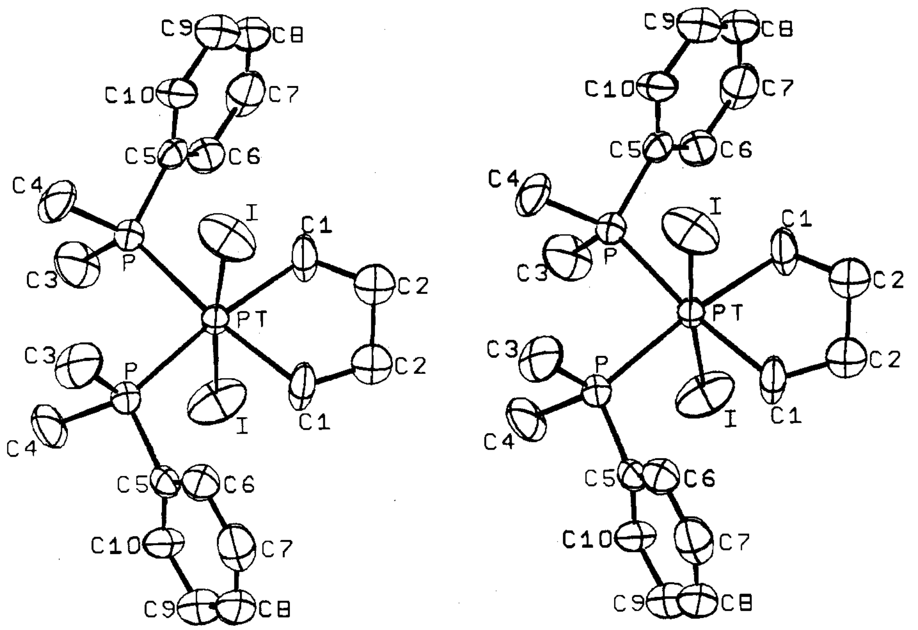


Figure 1. Stereogram of the molecular structure. Only one form of the disorder in C(2) is shown.

part in the bonding, and a symmetrical $Pt(CH_2)_4$ ring is predicted. It was therefore considered desirable to compare the structures of the Pt(II) and Pt(IV) complexes.

Experimental Section

The complex was isolated as orange-red crystals by reaction of (butane-1,4-diyl)bis(dimethylphenylphosphine)platinum(II) (prepared from *cis*-$PtCl_2(PMe_2Ph)_2$ and 1,4-dilithiobutane) with iodine. Suitable crystals were obtained by recrystallization from dichloromethane–methanol, mp 214 °C dec.

The Pt complex is air stable, and a small crystal was glued with epoxy to a Pyrex glass fiber for the x-ray work. Preliminary Weissenberg photography showed the crystal to be monoclinic in space group *Cc* or *C*2/*c*; a successful structure determination was accomplished in *C*2/*c*. The crystal was mounted on a Picker FACS-I automated diffractometer equipped with a graphite monochromator and molybdenum tube. The cell dimensions were obtained by a least-squares refinement procedure from the angular positions of 12 manually centered reflections for which $K\alpha_1$ peaks were resolved. The space group and cell dimensions are given in Table I with some other details of the experiment. ω scans at several low-angle reflections showed widths at half-peak height of 0.1°. A total of 4676 scans were measured and later averaged to give a set of 2150 unique reflections. Three standard reflections were measured after each 100th scan to monitor for crystal decay, instrumental stability, and crystal alignment. After about 1 week of irradiation, the standards exhibited about a 38% decay in intensity. A correction was made assuming all the reflections changed in a similar manner.

Absorption corrections were calculated using an analytical integration.[4] The crystal shape was described by eight surface planes. Azimuthal scans of integrated intensities were performed for eight different reflections in as diverse a region of reciprocal space as the instrument would allow, and the dimensions of the crystal were adjusted to fit these scans. The data were processed, averaged, and given estimated standard deviations using formulas presented in the supplementary material. The factor $p = 0.05$ was used in the calculation of $\sigma(F^2)$.

The Patterson function revealed the positions of the platinum, iodine, and phosphorus atoms. The subsequent electron density Fourier calculated from the phases of the partial structure gave the positions of all of the carbon atoms. The structure was refined by full-matrix least squares where the function $\sum w(|F_o| - |F_c|)^2$ was minimized. After the application of anisotropic temperature factors to all of the atoms, the central carbon atom of the butane ligand, C(2), was observed to suffer rather severe anisotropy. A ΔF Fourier calculated with only platinum and iodine in the structure showed two peaks that suggested disorder. C(2) was reintroduced into the least-squares calculation as two isotropic atoms, which were given occupancies of one-third atom in one position and two-thirds atom in the second position as suggested by the peak heights in the ΔF Fourier. Least-squares refinements were performed to convergence; i.e., the largest shift of any parameter was less than 2.4% of its estimated standard deviation. No correction for extinction was indicated, and none was made.

Table I. Summary of Crystal Data and Intensity Collection

Compd	$[(CH_3)_2(C_6H_5)P]_2I_2Pt(CH_2CH_2CH_2CH_2)$
Formula wt	781.307
a	15.286 (6) Å
b	9.709 (4) Å
c	17.036 (6) Å
β	107.49 (5)°
V	2412 Å^3
Z	4
Density (calcd)	2.152 g/cm^3
Space group	$C_{2h}{}^6$-$C2/c$
Crystal shape and size	Prism with 8 faces: 100, $\bar{1}00$, 110, $\bar{1}\bar{1}0$, $1\bar{1}0$, $\bar{1}10$, $\bar{1}01$, $10\bar{1}$; 0.06 mm × 0.11 mm × 0.14 mm
Crystal vol	0.001 24 mm^3
Temp	23 °C
Radiation	Mo $K\alpha_1$ (λ 0.709 26 Å), monochromated from (002) face of mosaic graphite
Transmission factors	0.42–0.65
μ	81 cm^{-1}
Data collection method	θ-2θ scan (1°/min along 2θ)
Scan range	0.75° below $K\alpha_1$ to 0.75 above $K\alpha_2$
Background counts	4 s, background offset from scan limits by 0.5°
2θ limits	5.0–50.0°
Final no. of variables	113
Unique data used ($F_o{}^2 > 3\sigma(F_o{}^2)$)	1575

A ΔF Fourier showed 50 peaks that were greater than 0.5 e/Å^3; the largest was 2 e/Å^3. Although some of these could be interpreted as hydrogen atoms, most could not. No attempt was made to refine the hydrogen atoms.

The final *R* factors are as follows: $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.035$ for the 1575 data where $F^2 > 3\sigma(F^2)$ and 0.054 for all 2150 data; $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2} = 0.044$. The goodness of fit was 1.23.

Final positional and thermal parameters are given in Table II, and distances and angles are listed in Tables III and IV.

Discussion

The neutral molecular complex consists of a Pt atom at the center of a distorted octahedron, as shown in Figure 1. Platinum, on a twofold axis, is bonded to two phosphorus, two

Table II. Atomic Parameters and Standard Deviations[a]

Atom	B_{11}, Å^2	B_{22}, Å^2	B_{33}, Å^2	B_{12}, Å^2	B_{13}, Å^2	B_{23}, Å^2
Pt	2.70 (2)	2.00 (2)	2.38 (2)	0	0.53 (2)	0
I	6.39 (5)	9.49 (6)	5.05 (4)	−2.66 (4)	3.31 (4)	−0.22 (4)
P	3.0 (1)	2.4 (1)	4.3 (1)	0.08 (8)	0.5 (1)	0.10 (8)
C(1)	6.4 (6)	1.8 (4)	4.8 (5)	−0.3 (4)	−1.3 (5)	0.4 (3)
C(2)1	4.6 (3)					
C(2)2	4.3 (6)					
C(3)	6.1 (7)	6.1 (6)	6.8 (8)	−1.2 (5)	1.3 (6)	3.8 (5)
C(4)	5.3 (7)	3.8 (5)	9.1 (9)	1.6 (4)	0.2 (6)	−3.1 (5)
C(5)	2.9 (4)	2.5 (4)	3.5 (4)	0.5 (3)	−0.0 (3)	0.4 (3)
C(6)	3.7 (5)	3.9 (5)	3.9 (5)	0.2 (4)	0.7 (4)	0.2 (4)
C(7)	6.1 (7)	4.1 (5)	4.2 (5)	1.0 (5)	−0.7 (5)	−0.6 (4)
C(8)	3.4 (5)	4.5 (5)	6.0 (7)	−0.1 (4)	−0.1 (5)	0.5 (5)
C(9)	3.6 (5)	5.6 (6)	5.8 (6)	−0.2 (4)	0.8 (5)	−0.2 (5)
C(10)	2.5 (4)	4.9 (6)	5.8 (6)	−0.2 (3)	1.0 (4)	0.5 (4)

Atom	x	y	z	Atom	x	y	z
Pt	0	0.027 52 (5)	0.250	C(4)	0.1424 (9)	−0.279 (1)	0.2813 (9)
I	0.101 50 (6)	0.040 3 (1)	0.149 20 (5)	C(5)	0.2101 (6)	−0.0599 (8)	0.3969 (6)
P	0.104 5 (2)	−0.138 3 (2)	0.335 0 (2)	C(6)	0.2112 (7)	0.005 (1)	0.4702 (6)
C(1)	0.082 4 (9)	0.194 1 (9)	0.316 6 (7)	C(7)	0.2920 (9)	0.077 (1)	0.5152 (7)
C(2)1	0.051 (1)	0.326 (2)	0.267 (1)	C(8)	0.3671 (8)	0.081 (1)	0.4866 (8)
C(2)2	0.015 (3)	0.327 (3)	0.299 (2)	C(9)	0.3668 (8)	0.015 (1)	0.4152 (8)
C(3)	0.067 (1)	−0.232 (1)	0.411 8 (9)	C(10)	0.2869 (7)	−0.057 (1)	0.3694 (7)

[a] The temperature factor has the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$. C(2)1 and C(2)2 represent the disordered sites of C(2); the site occupancies are $^2/_3$ and $^1/_3$ atom, respectively. The disordered atoms have isotropic thermal parameters.

Table III. Interatomic Distances (Å)[a]

Pt-2C(1)	2.15 (1)	C(2)1-C(2)1	1.49 (4)[b]
Pt-2P	2.418 (3)	C(2)2-C(2)2	1.60 (7)[b]
Pt-2I	2.641 (1)	C(5)-C(6)	1.40 (2)
P-C(3)	1.82 (1)	C(5)-C(10)	1.39 (2)
P-C(4)	1.83 (1)	C(6)-C(7)	1.42 (2)
P-C(5)	1.81 (1)	C(7)-C(8)	1.38 (2)
C(1)-C(2)1	1.54 (2)[b]	C(8)-C(9)	1.37 (2)
C(1)-C(2)2	1.62 (4)[b]	C(9)-C(10)	1.42 (2)

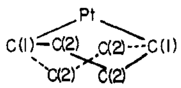
[a] Uncorrected for thermal motion. [b] C(2)1 and C(2)2 represent the two sites of the C(2) atoms; the distance between the two refined positions is 0.9 Å.

Table IV. Selected Angles (deg)

I-Pt-I	174.63 (5)	C(4)-P-C(5)	104.1 (5)
I-Pt-P	90.55 (5)	Pt-C(1)-C(2)1	107.4 (9)
I-Pt-P	93.03 (7)	Pt-C(1)-C(2)2	105.4 (13)
I-Pt-C(1)	86.7 (4)	C(1)-C(2)1-C(2)1	80.6 (5)
I-Pt-C(1)	89.3 (4)	C(1)-C(2)2-C(2)2	81.6 (9)
P-Pt-P	96.6 (2)	P-C(5)-C(6)	118.7 (8)
P-Pt-C(1)	90.5 (3)	P-C(5)-C(10)	120.6 (8)
P-Pt-C(1)	173.0 (3)	C(6)-C(5)-C(10)	120.6 (9)
C(1)-Pt-C(1)	82.6 (5)	C(5)-C(6)-C(7)	118.5 (11)
Pt-P-C(3)	118.1 (5)	C(6)-C(7)-C(8)	120.4 (11)
Pt-P-C(4)	116.6 (5)	C(7)-C(8)-C(9)	121.2 (11)
Pt-P-C(5)	112.5 (3)	C(8)-C(9)-C(10)	119.3 (12)
C(3)-P-C(4)	101.5 (7)	C(9)-C(10)-C(5)	120.0 (11)
C(3)-P-C(5)	102.2 (6)		

iodine, and two carbon atoms. The maximum distortion from an ideal octahedron is in the C(1)–Pt–C(1) angle of 82.6°, which is a result of the closed ring made with the butanediyl ligand.

The disorder observed in the butanediyl ligand is a result of the two central carbon atoms alternating between the two forms indicated schematically as



This puckering of the ring relieves the crowding of the hydrogen atoms on adjacent carbon atoms, and the two conformations are equivalent as far as the immediate neighbors of platinum are concerned. They are not equivalent when one considers the relation to the phenyl rings or the neighboring molecules. The Fourier patterns indicated a predominance of one form over the other of about 2:1. Upon refinement of least squares using the indicated occupancy factors, the resulting isotropic thermal parameters are statistically equal. The dominant form is presented in Figure 1. The anisotropy of the thermal parameters of C(1) is probably more representative of a minor disorder than a large thermal effect. Any disorder in C(2) would be expected to carry over to C(1) and possibly to other parts of the structure nearby. The disorder does not seriously affect the gross geometrical interpretation but does make the bond distances and angles in the region of the disorder less reliable. Interpretation of thermal parameters for the atoms adjacent to the disorder is ambiguous as it is not possible to separate out the disorder effects from the thermal effects. For the puckering of the ring we detect no lack of symmetry with respect to the platinum atom, in contrast to the result reported for the Pt(II) complex.[3] By virtue of the twofold axis, each configuration is found to be exactly symmetrical, and the Pt–C(2) distances in the two forms, 3.00 and 3.02 Å, are equal within the experimental precision. But, because of the disorder, one cannot exclude the possibility of a mixture of slightly unsymmetrical configurations.

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Registry No. $[(CH_3)_2(C_6H_5)P]_2I_2Pt(CH_2CH_2CH_2CH_2)$, 59991-49-0.

Supplementary Material Available: Data processing formulas and a table of observed structure factors (9 pages). Ordering information is given on any current masthead page.

References and Notes

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