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The Crystal Structure of o-(Diphenylphosphino)phenyl-cis-1,2-dicarbomethoxyethenyltriphenylphosphineplatinum.

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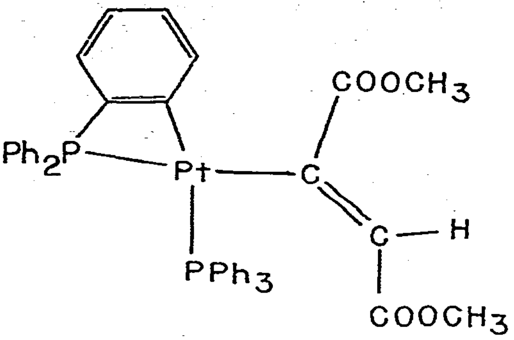
Summary The structure of o-(diphenylphosphino)phenyl-cis-1,2-dicarbomethoxyethenyltriphenylphosphineplatinum, (Ph_3P)-$[Ph_2P(C_6H_4)]Pt$-cis-$(CO_2MeC{=}CHCO_2Me)$, has been determined by single crystal X-ray diffraction methods. The crystals are triclinic, space group $P\bar{1}$, two molecules per unit cell with dimensions $a = 12.560(1)$, $b = 13.600(1)$, $c = 11.452(1)$ Å, $\alpha = 110.01(1)$, $\beta = 97.58(1)$, and $\gamma = 91.03(1)°$. A calculated density of 1.57 g cm^{-3} for two formula units per cell is consistent with the measured value of 1.56(2) g cm^{-3}. The coordination about the platinum atom is square-planar with the two phosphine ligands oriented cis with respect to one another. The σ-bonded vinyl group also possesses cis stereochemistry. The geometry of the four-atom metallocyclic ring in this compound is compared to those of metallocyclobutene and platinacyclobutane complexes. The average Pt-P bond length is 2.330(2) Å and the observed Pt-C bond lengths are 2.059(8) and 2.026(8) Å. These bond lengths are discussed in terms of the trans-influence. Full-matrix least-squares refinement has yielded R = 0.047 (0.048 for weighted R) based on the 5208 reflections whose intensities are significantly above background ($I_{net} \geq 10$ counts s^{-1}).

Introduction

During an examination of the thermal stability of dicarbomethoxyacetylenebis(triphenylphosphine)platinum, Clark and Hine [1] isolated a product formulated as



I

resulting from internal metalation. The detailed stereochemical assignment for I was based upon the observed IR and NMR spectra.

Although metalation reactions of transition metal complexes have been known for some time [2-4], the mechanism of the reaction yielding I is unusual. These reactions normally proceed via oxidative-addition of an aryl C-H bond to the metal atom followed by elimination of the resultant hydride in the form of H_2, as part of an alkane, or as part of a more complex species. In the reaction forming I, insertion of the alkyne ligand into the Pt-H bond subsequent to the oxidative-addition step is required.

Molecular structure studies of orthometalation products have predominantly involved complexes containing five- or six-atom chelate rings. Perego and coworkers [5,6] have reported structures of two iridium complexes containing four-atom rings analogous to that propcsed for I. In order to confirm the identity of I and to allow an unambiguous assignment of the stereochemistry of the molecule, a single crystal X-ray diffraction investigation was initiated.

Experimental

A sample of the title compound was kindly supplied by Professor H. C. Clark and was recrystallized from a 2:1 mixture of ethanol and methylene chloride before use. The colorless data crystal was mounted with [121] parallel to the phi axis of the goniometer. X-ray studies were performed using a Diano-XRD 700 diffractometer equipped with a single crystal orienter using Cu Kα radiation at ambient room temperature (∿21°C).

Intensity weighted plots of the reciprocal lattice revealed only triclinic diffraction symmetry ($\bar{1}$). No higher symmetry was revealed by a reduced cell calculation. Lattice parameters listed in Table 1 were obtained by least-squares refinement of 66 independent reflections with $K\alpha_1$ and $K\alpha_2$ well resolved.

The mosaic character of the crystal was determined by inspection of ω scans (5° take off angle and 0.05° receiving slit) for several reflections. The scans revealed peaks that were single, narrow (< .5° wide), and symmetrical, indicating suitable quality for the stationary-crystal, stationary-counter technique of data collection (5° take off angle and 1° receiving slit) using balanced Ross filters. During data collection the crystal was frequently aligned and the intensities of 6 standard reflections were monitored. Only random variations in intensities were noted thus no correction for crystal decomposition was required.

The intensities were corrected for absorption as a function of crystal shape [7] with correction factors ranging from 2.86 to 4.97. Additional corrections for Lorentz and polarization

Table 1. Experimental Summary

Crystal Data for $C_{42}H_{36}O_4P_2Pt$

Formula Weight 861.79

a = 12.560(1) Å

b = 13.600(1) Å

c = 11.452(1) Å

α = 110.01(1)°

β = 97.58(1)°

γ = 91.03(1)°

d_{calcd} = 1.57 g cm^{-3}

d_{measd} = 1.56(2) g cm^{-3}
(flotation, aqueous $AgNO_3$)

Triclinic

Systematic absences: none

Space group $P\bar{1}$ (No. 2)

Z = 2

F(000) = 856 e

λ_{Cu}: $K\alpha_1$, 1.54051 Å;
$K\alpha_2$, 1.54433 Å

Data Collection

Crystal Dimensions: ~0.09 x 0.10 x 0.14 mm

$\mu(CuK\bar{\alpha})$ = 85.33 cm^{-1}

5390 symmetry independent reflections for $6° < 2\theta \leq 120°$.
(5208 reflections with $I_{net} \geq 10$ counts s^{-1})

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effects, and for α_1-α_2 splitting [8] were applied. Standard deviations in the observed structure factor amplitudes, $\sigma(|F_o|)$, were calculated on the basis of counting statistics [9].

The positions of the platinum and the two phosphorus atoms were determined by interpretation of a three-dimensional Patterson map. A subsequent electron density calculation revealed the positions of all remaining nonhydrogen atoms of the structure. The five nonmetalated phenyl rings were treated as rigid groups with idealized geometry (120° bond angles, C-C distances 1.397 Å, C-H distances 0.95 Å) in the least-squares calculations, with each carbon atom assigned a variable isotropic temperature factor. The isotropic temperature factor of each hydrogen atom was constrained to 6.0 $Å^2$. Least-squares refinement employing isotropic temperature factors for the non-group atoms converged at

$$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| = .057 \quad \text{and}$$

$$R_2 = [\Sigma(\omega||F_o|-|F_c||^2)/\Sigma\omega(|F_o|)^2]^{\frac{1}{2}} = .096,$$

where $\omega = \sigma^{-2}(|F_o|)$. The function minimized in the least-squares calculation was $\Sigma\omega(|F_o|-|F_c|)^2$. A difference electron density map calculated at this point contained peaks in reasonable positions for the remaining eleven hydrogen atoms of the structure. These hydrogen atoms were included in all subsequent least-squares calculations at their idealized positions with B = 6.0 $Å^2$. Additional least-squares refinement of this model varying the overall scale factor, an isotropic extinction parameter (6.1(5) x 10^{-6} e^{-2})[10], the positional and anisotropic thermal parameters of the nineteen nonhydrogen, nongroup atoms, six orientational and positional parameters for each of the rigid groups, and the isotropic thermal parameters of the nonhydrogen atoms of the phenyl rings served to complete refinement at R_1 = 0.047 and R_2 = 0.048.* A final difference electron density map contained a number of peaks in the order of 1.0 e $Å^{-3}$ in the vicinity

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*The table of structure factors has been deposited as NAPS Document No. 03157 (26 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number, remitting $6.50 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications.

Table 2. Fractional Atomic Coordinates and Thermal Parameters (x10^4) for the Nongroup Atoms of $C_{42}H_{36}O_4P_2Pt$.[a]

	x	y	z	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Pt[b]	30325(3)	24536(3)	25098(3)	3262(21)	3501(22)	3428(21)	300(13)	696(13)	1257(15)
P(1)	1836(2)	2992(2)	1149(2)	354(11)	446(12)	414(12)	16(9)	59(9)	181(10)
P(2)	4726(1)	2635(2)	1958(2)	347(10)	405(12)	352(11)	31(9)	70(8)	116(9)
O(1)	992(5)	500(5)	1719(5)	892(48)	671(45)	510(39)	-172(36)	- 80(35)	183(34)
O(2)	1774(5)	431(5)	3553(6)	847(47)	560(42)	897(49)	- 72(35)	-132(38)	412(39)
O(3)	- 137(5)	1624(5)	4319(6)	920(53)	757(51)	884(53)	-271(42)	362(42)	67(42)
O(4)	113(6)	3293(5)	5620(7)	1079(58)	686(49)	1051(58)	- 13(42)	709(48)	70(43)
C(1)	1823(6)	2074(6)	3319(7)	445(45)	444(49)	416(46)	22(38)	36(37)	214(40)
C(2)	1458(6)	925(7)	2764(8)	471(50)	581(59)	607(59)	2(43)	121(44)	320(50)
C(3)	1443(9)	- 670(9)	3069(12)	1135(97)	744(82)	1605(122)	-108(70)	-340(86)	744(86)
C(4)	1327(6)	2729(7)	4203(7)	439(48)	680(62)	437(49)	- 17(43)	131(39)	180(45)
C(5)	366(7)	2468(8)	4685(8)	661(62)	645(66)	494(56)	- 71(52)	194(47)	103(50)
C(6)	- 837(11)	3111(10)	6134(14)	1747(138)	1055(109)	2114(159)	192(96)	1610(128)	255(105)
C(7)	4221(6)	2021(6)	3621(7)	551(51)	390(47)	319(42)	43(39)	3(37)	23(36)
C(8)	5182(6)	2138(6)	3191(7)	397(44)	535(53)	356(44)	126(38)	39(35)	110(39)
C(9)	6178(7)	1909(8)	3702(8)	522(55)	884(75)	495(55)	139(50)	- 9(43)	241(53)
C(10)	6183(8)	1532(8)	4679(9)	652(66)	1080(90)	622(66)	262(61)	- 19(53)	369(64)

C(11)	5252(8)	1406(8)	5123(8)	875(75)	903(79)	423(53)	247(62)	75(51)	317(53)
C(12)	4252(7)	1633(7)	4615(7)	709(60)	625(61)	435(50)	146(48)	173(44)	261(46)
H(3A)	738	- 776	2611	6.00[c]					
H(3B)	1928	-1042	2526	6.00					
H(3C)	1450	- 924	3746	6.00					
H(4)	1621	3439	4560	6.00					
H(6A)	-1106	2400	5736	6.00					
H(6B)	- 643	3242	7019	6.00					
H(6C)	-1369	3562	6020	6.00					
H(9)	6827	1998	3393	6.00					
H(10)	6844	1362	5044	6.00					
H(11)	5272	1150	5806	6.00					
H(12)	3603	1543	4926	6.00					

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[a] Numbers in parentheses are the estimated standard deviations in the units of the last digit. The temperature factor expression for the nonhydrogen atoms is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}h\ell a^*c^*\cos\beta^* + 2U_{23}k\ell b^*c^*\cos\alpha^*)]$. For the hydrogen atoms the temperature factor expression is $\exp[-U_{11}(\sin\theta/\lambda)^2]$.

[b] Positional and thermal parameters for the Pt atom are presented x 10^5.

[c] Thermal parameters for the hydrogen atoms are presented x 1.

Table 3. Group Parameters[a]

Group	x_o	y_o	z_o	ϕ	θ	ρ
PH(1)	0.1772(4)	0.2132(4)	-0.0488(4)	-0.121(9)	-1.942(3)	-1.612(9)
PH(2)	0.2126(4)	0.4335(3)	0.1227(5)	2.923(3)	3.116(3)	2.525(3)
PH(3)	0.0434(3)	0.3042(4)	0.1425(5)	-1.542(4)	2.772(3)	-0.819(4)
PH(4)	0.5463(4)	0.3885(3)	0.2316(5)	2.668(3)	2.963(3)	1.665(3)
PH(5)	0.5067(4)	0.1821(4)	0.0468(4)	0.741(9)	-1.916(3)	-1.673(9)

Derived phenyl group C atoms[b]					Derived phenyl group H atoms[b,c]			
Atom	x	y	z	B(Å^2)	Atom	x	y	z
				PH(1)				
C(37)	1772(4)	2132(4)	-488(4)	3.6(2)	H(38)	1881(6)	3215(3)	-1348(7)
C(38)	1817(4)	2485(3)	-1493(5)	4.7(2)	H(39)	1798(7)	2002(6)	-3394(5)
C(39)	1768(5)	1763(5)	-2711(4)	5.6(2)	H(40)	1641(7)	197(6)	-3752(4)
C(40)	1674(5)	688(4)	-2924(4)	6.1(2)	H(41)	1565(7)	- 396(3)	-2064(8)
C(41)	1629(4)	335(3)	-1919(5)	5.7(2)	H(42)	1648(6)	817(6)	- 18(6)
C(42)	1678(4)	1057(4)	- 701(5)	4.7(2)				
				PH(2)				
C(31)	2126(4)	4336(3)	1227(5)	3.6(2)	H(32)	3463(5)	4615(6)	2553(6)
C(32)	3020(4)	4918(4)	2046(5)	4.7(2)	H(33)	3872(5)	6342(6)	2679(7)
C(33)	3263(4)	5946(4)	2122(5)	5.9(2)	H(34)	2778(7)	7091(4)	1428(8)
C(34)	2612(5)	6392(3)	1377(6)	6.0(2)	H(35)	1275(6)	6113(6)	51(7)
C(35)	1718(4)	5810(4)	557(5)	5.7(2)	H(36)	867(5)	4385(6)	- 76(6)
C(36)	1475(4)	4781(4)	482(5)	4.9(2)				

Table 3 - continued

Derived phenyl group C atoms					Derived phenyl group H atoms[b]			
Atom	x	y	z	$B(\AA^2)$	Atom	x	y	x
PH(3)								
C(13)	434(3)	3042(4)	1425(5)	3.9(2)	H(14)	- 133(7)	1619(5)	116(6)
C(14)	- 328(5)	2210(4)	763(5)	5.0(2)	H(15)	-1894(5)	1683(5)	602(7)
C(15)	-1376(4)	2248(4)	1052(5)	6.3(2)	H(16)	-2375(4)	3143(7)	2200(8)
C(16)	-1662(4)	3118(5)	2004(6)	6.5(2)	H(17)	-1096(7)	4540(5)	3313(6)
C(17)	- 901(5)	3949(4)	2666(5)	6.6(2)	H(18)	666(6)	4476(5)	2827(7)
C(18)	148(4)	3911(4)	2376(5)	5.2(2)				
PH(4)								
C(19)	5463(4)	3885(3)	2316(5)	3.7(2)	H(20)	5549(7)	4280(7)	4218(6)
C(20)	5718(4)	4524(5)	3576(4)	5.2(2)	H(21)	6397(7)	5958(6)	4750(5)
C(21)	6223(5)	5523(4)	3893(4)	6.8(3)	H(22)	6817(7)	6563(4)	3164(9)
C(22)	6473(5)	5883(4)	2949(6)	7.1(3)	H(23)	6387(7)	5488(7)	1047(7)
C(23)	6217(5)	5244(5)	1689(5)	6.5(2)	H(24)	5539(6)	3809(6)	515(4)
C(24)	5712(4)	4244(4)	1372(4)	4.7(2)				
PH(5)								
C(25)	5067(4)	1821(4)	468(4)	3.2(2)	H(26)	3952(5)	2396(5)	- 555(7)
C(26)	4508(4)	1924(4)	- 617(5)	5.0(2)	H(27)	4384(6)	1402(6)	-2533(5)
C(27)	4765(4)	1332(4)	-1795(4)	5.8(2)	H(28)	5756(6)	235(6)	-2687(4)
C(28)	5581(4)	637(4)	-1887(4)	5.2(2)	H(29)	6696(5)	62(5)	- 863(7)
C(29)	6141(4)	534(4)	- 801(5)	4.7(2)	H(30)	6264(5)	1056(6)	1115(5)
C(30)	5884(4)	1126(4)	376(4)	4.0(2)				

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[a] A description of these group parameters is provided in Reference 14. Angular coordinates are in radians. The internal coordinate system of each phenyl ring was defined as follows: the ring was defined to be in the *xy* plane with atom C(1)- bound to a phosphorus atom- at the origin, vector C(6)-C(2) coincident with positive *x* axis, and vector C(1)-C(4) parallel to the positive *y* axis.

[b] Positional parameters of the rigid group atoms are presented x 10^4.

[c] Hydrogen atoms were assigned isotropic thermal parameters, $B = 6.0\ \AA^2$.

of the platinum and the phosphorus atoms. Smaller peaks (0.3 to 0.8 e $Å^{-3}$) were located near the five rigid phenyl groups or near the methyl substituents.

Scattering factors for the platinum, phosphorus, carbon, and oxygen atoms were taken from Cromer and Waber [11]. The anomalous dispersion corrections for the platinum and the phosphorus atoms were included [12]. Scattering factors for the hydrogen atoms were taken from Stewart, Davidson, and Simpson [13].

Discussion

The final atomic parameters of I are given in Table 2. The parameters associated with the five phenyl rings treated as rigid groups are given in Table 3. Table 4 contains equations for selected least-squares planes. Figure 1 presents a stereoscopic view of the molecule and indicates the atom labeling scheme used. Each hydrogen atom is numbered according to the carbon atom to which it is bonded. The methyl hydrogen atoms attached to C(i) are labeled H(iA), H(iB), and H(iC). Bond lengths and bond angles are displayed in Figures 2 and 3 respectively. Figure 4 presents a stereoscopic view of the molecular packing.

The structure is monomeric and reveals a slightly distorted square-planar geometry about the platinum atom. Plane A, defined by Pt, C(1), and C(4), and the plane containing Pt, P(1), and P(2), plane B, intersect to form an angle of 80.51°, which is comparable to the angle between the PtP_2 and $PtCO_2$ planes in <u>trans</u>-$Pt(COOEt)_2(PPh_3)_2$, 80.8° [15]. The P(1)-Pt-P(2) angle in this structure agrees favorably with the values observed in other <u>cis</u>-triphenylphosphine complexes. Plane C, the plane of the four-atom metalated ring, and the plane of

Table 4. Selected Least-Squares Planes[a]

Plane	Atoms defining the plane	$A(\times 10^4)$	$B(\times 10^4)$	$C(\times 10^4)$	$D(\times 10^4)$	dev^b (Å)
A	Pt,C(1),C(4)	5798	- 4022	7086	-29033	-
B	Pt,P(1),P(2)	138	7852	6518	-35662	-
C	Pt,P(2),C(8),C(7)	144	7576	6526	-35689	0.008
D	C(7),C(8),C(9),C(10),C(11),C(12)	334	7562	6535	-36704	0.003

[a] The equations of the planes are of the form: $A\underline{p} + B\underline{q} + C\underline{r} + D = 0$. $\underline{p}$, $\underline{q}$ and $\underline{r}$ are the Cartesian coordinates (Å) relative to the crystallographic directions a, $c^* \times a$, and c^*.

[b] Average out of plane deviation.

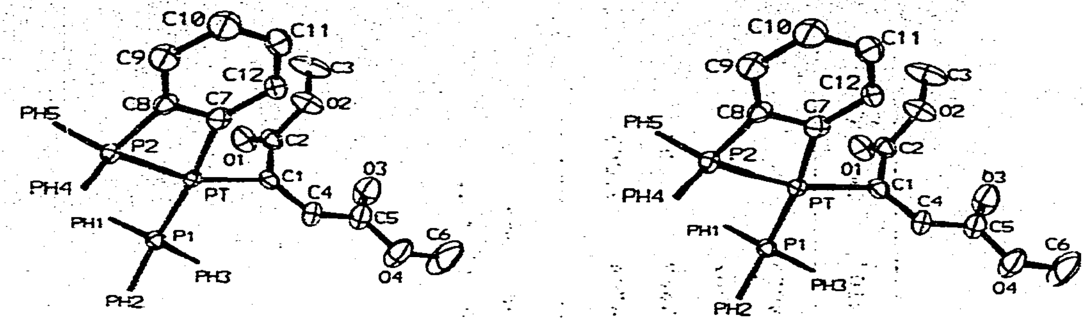


Figure 1. A stereoscopic view of the molecule illustrating the atom-numbering scheme employed. Ellipsoids of 30% probability are shown.

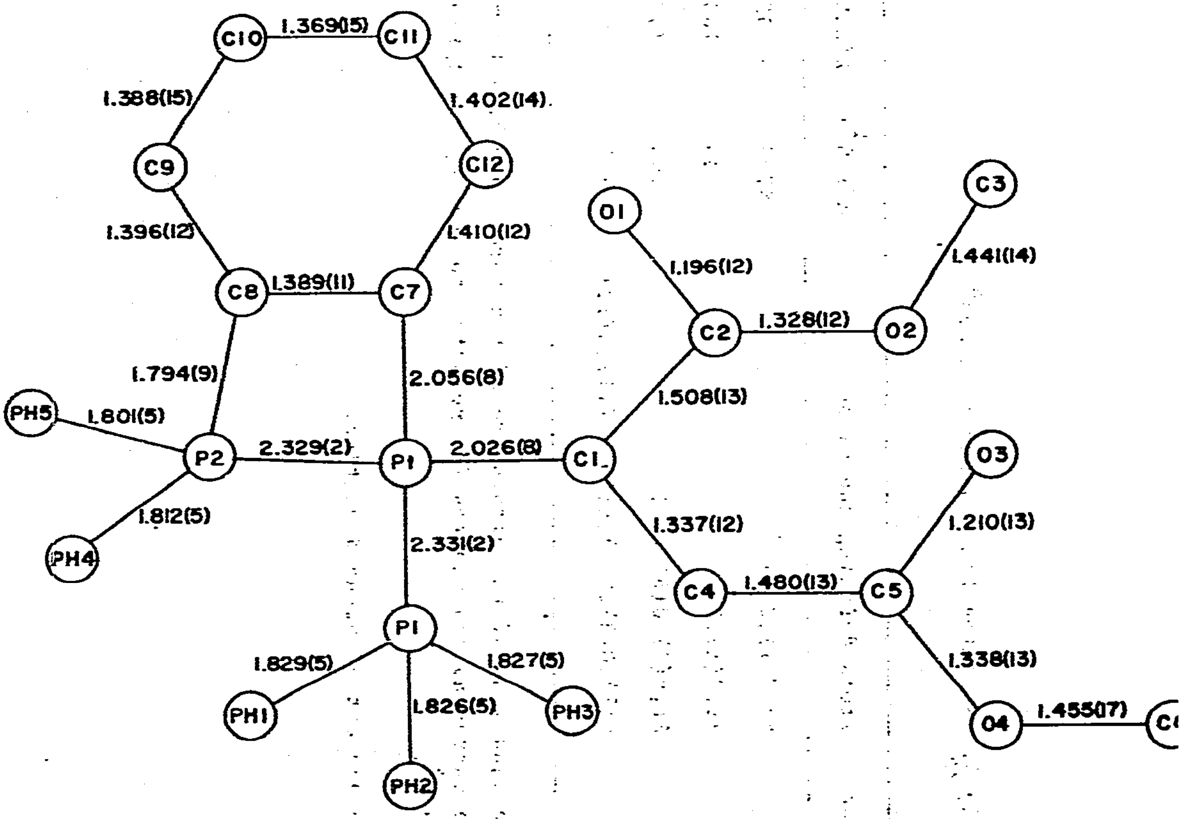
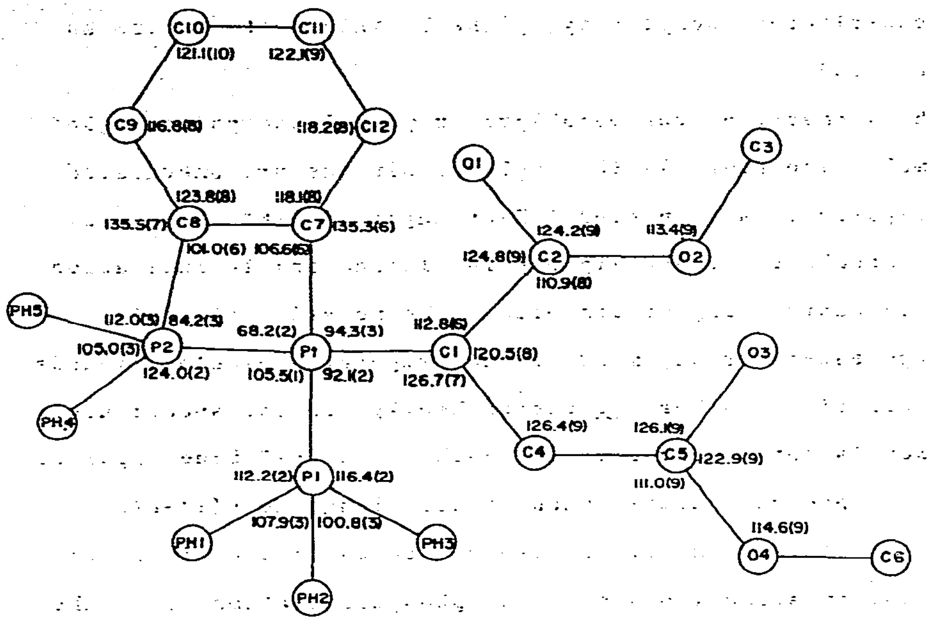


Figure 2. Bond distances. The estimated standard deviation given in parentheses refers to the last decimal place.



ANGLES NOT SHOWN

C1	Pt	P2	162.2(2)
C7	Pt	P1	173.7(2)
PH1	P1	PH3	104.3(3)
PH2	P1	Pt	114.1(2)
PH4	P2	C8	107.3(3)
PH5	P2	Pt	121.3(2)

Figure 3. Bond angles. The estimated standard deviation given in parentheses refers to the last decimal place.

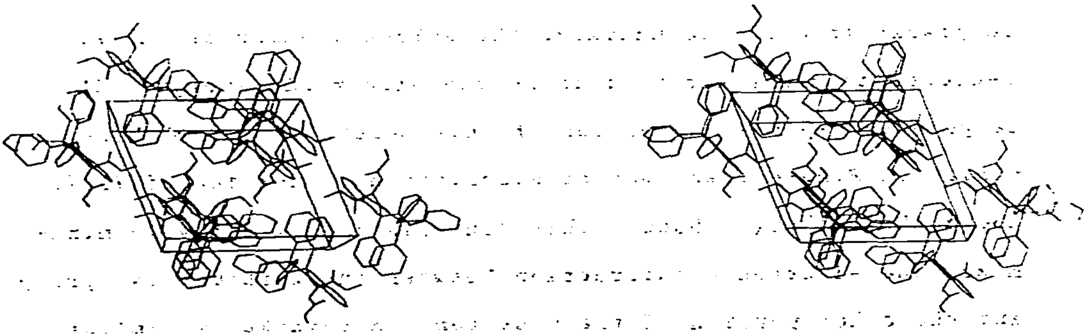


Figure 4. A stereoscopic view of the molecular packing with the unit cell outlined. The *b* axis is horizontal, the *c* axis is vertical, and the *a* axis points toward the reader.

the disubstituted phenyl ring, plane D, intersect to form an angle of 1.09°.

The geometry of the monohapto triphenyl phosphine ligand is normal. The Pt-P(2)-C(8) angle within the orthometalated ring compares to an expected C-P-Pt angle of 116° [16] in a normal, monohapto triphenylphosphine ligand and is indicative of the extensive ring strain within the metallocyclic ring. The "egg-beater" arrangement of the triphenylphosphine ligands characteristic of other <u>cis</u>-bistriphenylphosphine substituted complexes is not observed in I. Rather, the P-C bonds approximately eclipse one another when viewed along the P(1)-P(2) direction. This geometry is also reflected in the distances of the carbon atoms (bonded to the phosphorus atoms) from the PtP_2 plane, plane B. Pertinent out-of-plane displacements for the groups PH(1), PH(5), PH(2), PH(4), and PH(3) are +1.53, +1.42, -1.42, -1.44 and -0.13 Å, respectively; C(8) is +0.19 Å out of plane B.

The stereochemistry of the σ-bonded vinyl group was unexpected in that the observed <u>cis</u> stereochemistry is the exact opposite of that predicted by Clark and Hine [1]. The distinct lack of planarity of this ligand is also unusual. Simple valence-bond arguments would require that the entire ligand be planar in order to maximize the delocalization of the six π-electrons and thereby minimize the electronic energy. The large out-of-plane distortion of this moiety is clearly revealed in Figure 1 and may be described as a torsion of 75.72° about the C(1)-C(2) bond. This conformation effectively minimizes the electronic interaction between one carbomethoxy group and the other portion of the π-system. A remarkably similar lack of planarity for a <u>trans</u>-1,2-dicarbomethoxyethenyl ligand

[17] has been observed as a consequence of an intramolecular hydrogen bond involving the ketonic oxygen atom of one ester group. Presumably, this lack of planarity of the vinyl ligand in I produces spectroscopic features which lead to the erroneous assignment of its stereochemistry.

A comparison of the geometry of the four-atom ring in I to the geometries of the metallocyclobutene rings in $\mathrm{IrHP(Ph)_2(C_6H_4)_2P(Ph)_3}$(II) [5], $\mathrm{Ir(C_2H_4)_2P(Ph)_2(C_6H_4)P(Ph)_3 \cdot 1.5\ C_6H_5CH_3}$-(IIIa) [6], $\mathrm{Ir(CO)_2P(Ph)_2C_6H_4P(Ph)_3 \cdot THF}$(IIIb) [6], $\mathrm{\overline{PtC(Ph){=}C(Ph)C}{=}O[P(Ph)_3]_2}$(IV) [18], and $\mathrm{Fe_3(CO)_8(Ph)_2PC_4(CF_3)_2P(Ph)_2}$(V) [19] is presented in Table 5. As a result of the differences in covalent radii the M-X and C-X distances are consistently longer and the angle β, centering on atom X, is smaller when atom X is phosphorus. The geometry of I is strikingly similar to that of the bis(orthometalated) iridium complex (II).

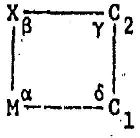
Detailed tabulations of the representative geometries of products from insertion of platinum into cyclopropane rings have appeared [20]. Whereas the four-atom rings within the platinacyclobutane complexes are puckered, the metallocyclobutene rings described in Table 5 are virtually flat. The C(7)-C(8) aromatic bond length in I is 0.17 Å shorter than the average carbon-carbon single-bond length of the platinacyclobutane complexes. The X-Pt-C and X-C-C angles for I and those for the platinacyclobutane rings are similar however the remaining two angles within the four-atom rings are drastically different. The Pt-X-C angle within I is approximately 18° larger and the Pt-C-C angle is approximately 14° smaller than the related angles within the platinacyclobutane complexes.

The average Pt-P bond length, 2.330(2) Å, observed in I is 0.082 Å longer than the average Pt-P bond length in $\mathrm{Pt[P(CH_3)_3]_2Cl_2}$ [21] where each phosphine ligand is opposite a weakly <u>trans</u>-labelizing ligand. Based on the Cruickshank

Table 5. Comparison of Intramolecular Distances and Bond Angles[a] within Metallocyclobutene Complexes

	I[b]	II[c]	III[d] (a,b)	IV[e]	V[f]
Intramolecular distances (Å)					
M-C_1	2.056(8)	2.063(11), 2.085(10)	2.07(1), 2.11(1)	2.09(4)	1.96(1)
C_1-C_2	1.389(11)	1.40(2), 1.39(2)		1.31(8)	1.74(1)
C_2-X	1.794(9)	1.807(16), 1.816(10)		1.45(7)	1.53(2)
M-X	2.329(2)	2.396(4), 2.362(3)		2.08(6)	2.02(1)
Bond Angles (°)					
α	68.2(2)	67.1(3), 67.8(2)		62	
β	84.2(3)	83.8(3), 84.1(2)		97	
γ	101.0(6)	100.3(7), 101.0(5)	101.2, 101.9	100	
δ	106.6(6)	108.6(6), 107.1(5)		101	

[a] Ring labeling scheme:



[b] M=Pt, X=P; [c] M=Ir, X=P; [d] M=Ir, X=P; [e] M=Pt, X=C; [f] M=Fe, X=C.

criteria [22] this difference, $\Delta\ell/\sigma\ell = 11.7$, is highly significant. The Pt-C(1) bond length in I is virtually identical to the Pt-C (styryl) bond length, 2.022(8) Å, in *trans*-bromo (*trans*-styryl) bis(triphenylphosphine)platinum(II) [23]. The lengthening of the Pt-C(7) bond results from the strain within the metallocyclic ring. Thus the Pt-P and Pt-C bond lengths in I are consistent with the σ-bonded, sp^2 hybridized carbon atoms' exerting a stronger *trans*-influence than the triphenylphosphine ligands, as predicted by Appleton, Clark and Manzer [24].

The shortest non bonded contact distance, H(27)···H(11), is 2.26(1) Å. The shortest non-bonded contact distance involving two nonhydrogen atoms, O(3)···C(41) is 3.41(1) Å. Thus no intermolecular contact distances significantly shorter than the sum of the respective van der Waals radii are observed.

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