

THE MOLECULAR STRUCTURE OF A THREE-COORDINATE PALLADIUM(II)-STYRENE COMPLEX $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PEt}_3)(\text{styrene})]\text{BF}_4$

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Summary

The molecular structure of a three-coordinate palladium(II)-styrene complex, $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PEt}_3)(\text{styrene})]\text{BF}_4$ has been determined by means of X-ray diffraction. The crystal belongs to the monoclinic system, space group $P2_1/c$, with four formula units in a cell of dimensions: a 10.229(3), b 11.262(3), c 18.760(5) Å and β 103.77(2)°. The structure was solved by the heavy atom method, and refined by the least-squares procedure to $R = 0.050$ for 3635 observed reflections. The palladium atom is surrounded by the cyclopentadienyl group, the triethylphosphine ligand and the olefinic bond of styrene in the cationic complex. In the palladium–styrene bonding, the olefinic bond is inclined by 77.3° to the coordination plane defined by the Pd and P atoms and the center of the cyclopentadienyl ring (Pd–C(1) 2.176(6), Pd–C(2) 2.234(5) and C(1)–C(2) 1.369(8) Å).

Introduction

The olefin-palladium(II) complexes have not been so widely studied in spite of their importance in various synthetic reactions as starting materials and intermediates. It is, of course, important to clarify the coordination geometry of the olefin to the metal atom in order to realize the nature of the metal–olefin bonds. Few reports are now available, however, for both the X-ray molecular structures and preparations of palladium-olefin complexes, especially those containing monoolefins. Recently, stable cationic palladium(II) complexes containing various olefins of the type, $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{olefin})]\text{X}$ ($\text{R} = \text{Et}, \text{n-Bu}, \text{Ph}$; $\text{X} = \text{BF}_4, \text{ClO}_4, \text{PF}_6$) have been prepared by Kurosawa and his coworkers [1].

We have started a series of crystal structure analyses of the styrene-containing palladium(II) complexes mentioned above in order to establish the geometry of the styrene coordination to the palladium atom. We describe here the molecular structure of η^5 -cyclopentadienyltriethylphosphinestyrenepalladium(II) tetra-

fluoroborate, $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PEt}_3)(\text{styrene})]\text{BF}_4$. Concerning the structure of palladium-styrene complexes, there has been only an early study of $[\text{PdCl}_2(\text{styrene})]_2$ [2]. Therefore, the precise analysis of the present complex is actually the first exact geometry determination about the palladium—styrene bonding.

Experimental

The black, prismatic crystals of $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PEt}_3)(\text{styrene})]\text{BF}_4$ recrystallized from CH_2Cl_2 solution were supplied by Dr. Kurosawa. Oscillation and Weissenberg photographs showed the crystal to belong to the monoclinic system, and the systematic absences of reflections ($0k0$ with k odd and $h0l$ with l odd) determined the space group as $P2_1/c$ (No. 14). Accurate unit-cell dimensions were obtained from a least-squares fit of 2θ values of 25 strong reflections measured on a Rigaku automated, four-circle, single-crystal diffractometer.

Crystal data. $\text{C}_{19}\text{H}_{28}\text{PPd}\cdot\text{BF}_4$, mol.wt. 480.6, monoclinic, space group $P2_1/c$, a 10.229(3), b 11.262(3), c 18.760(5) Å, β 103.77(2)°, U 2099.1(9) Å³. D_c 1.521 g cm⁻³ for $Z = 4$, D_m 1.51 g cm⁻³ (by flotation in aqueous solution of ferric sulfate), $\mu(\text{Mo-K}\alpha)$ 9.82 cm⁻¹.

Intensity data collection

A well-shaped crystal with approximate dimensions 0.20 × 0.25 × 0.32 mm was used. Integrated intensities were measured on the Rigaku diffractometer using graphite-monochromatized Mo- $K\alpha$ radiation (λ 0.71069 Å). The setting angles of each reflection were computed by the Busing-Levy method [3] on a FACOM U-200 computer attached to the diffractometer. The $\theta - 2\theta$ scan technique with scan width of $\Delta 2\theta = (2.0 + 0.7 \tan \theta)^\circ$ and scan rate of 4° min⁻¹ were employed for the data collection. The background intensities were measured for 7.5 s at both ends of a scan. A total of 4588 unique reflections was collected up to a 2θ value of 54°, of which 3645 reflections ($|F_o| > 3\sigma(|F_o|)$) were considered as observed. Four standard reflections (600, 080, 44 $\bar{4}$ and 0 0 10) measured at regular intervals to check the crystal stability and orientation remained constant throughout the data collection. Lorentz and polarization corrections were carried out in the usual manner. Absorption ($0.10 < \mu R < 0.22$) and extinction corrections were ignored, which might limit the accuracy of the present structure determination.

Structure determination and refinement

The approximate coordinates of the palladium atom were readily located from a three-dimensional Patterson function. All of the remaining 26 non-hydrogen atoms were located by the subsequent Fourier syntheses.

The structure was refined by the block-diagonal least-squares procedure using the HBLS-V program [4], the function minimized being $\sum w(|F_o| - |F_c|)^2$. The refinement was carried out isotropically at the initial stage and then anisotropically for non-hydrogen atoms at the later stage. A difference Fourier map gave 28 peaks, which were assigned as those of hydrogen atoms. The further

refinement was done anisotropically for the non-hydrogen atoms and isotropically for the hydrogen atoms. At the final stage of the refinement, 10 strong reflections (020, 110, 220, $\bar{2}02$, $\bar{2}22$, $\bar{1}12$, $\bar{1}32$, 002, 022 and 112), which were considered as highly affected by extinction, were omitted. The weighting scheme used is $w = (\sigma_{cs}^2 + a|F_o| + b|F_o|^2)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics and the constants a and b employed at the final refinement are 0.0222 and 0.0011, respectively, though the unit weights were employed at the earlier stage of the refinements. The final R and R_w indices are 0.050 and 0.067 for 3635 observed reflections, respectively, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. The atomic scattering factors were taken from International Tables for X-ray Crystallography [5] for non-hydrogen atoms and those of Stewart et al. [6] for hydrogen atoms.

The final positional and thermal parameters are listed in Tables 1 and 2. A table of observed and calculated structure factors is available from the authors on request.

Results and discussion

Figure 1 represents an ORTEP drawing [7] of the molecule. The cationic complex is three-coordinate, the palladium atom being surrounded by the cyclopentadienyl (Cp) group, the triethylphosphine (PEt₃) ligand and the olefinic bond of styrene. A similar three-coordinate geometry around the metal atom has been observed in an ethylene-rhodium complex, [Rh(η^5 -C₅Me₅)(PPh₃)-(ethylene)] [8]. Bond lengths and bond angles are listed in Tables 3 and 4, respectively. The coordination geometry around the Pd atom is illustrated with selected bond distances and angles in Fig. 2. The Pd atom, the P atom of the PEt₃ ligand, the center of the Cp group (CCP) and the midpoint of the C(1)=C(2) double bond in the styrene ligand (CET) are approximately coplanar with each other. The equations of least-squares planes are listed in Table 5.

Figure 3 depicts a perspective view of the [Pd(η^5 -C₅H₅)(PEt₃)(styrene)] cation as viewed along the olefin-metal axis and the numbering system of atoms. In the geometry of the metal-styrene coordination, two rotational isomers are possible in the present complex. That is, the phenyl group of the styrene is located at the PEt₃ side in one rotamer, while at the Cp side in the other. Judging from Figs. 1 and 2, steric hindrance seems to be slightly less in the latter than the former. In fact, the ¹H NMR spectra of [Pd(η^5 -C₅H₅)(PEt₃)-(styrene)]ClO₄ show the latter rotamer to be dominant in solution [1]. Nevertheless, the former conformation is observed in the present crystal structure, although no significant attractive interaction is detected between the phenyl group of the styrene and the PEt₃ group. The olefin bond is almost perpendicular to the coordination plane of Pd. However, the C(1)=C(2) double bond is slightly inclined, the twist angle between the olefin bond and the P-Pd-CCP plane being 77.3°. Similar twists of the olefin bond in the styrene ligand have been observed in some complexes, for example, 77.6° in [PtCl₂(S(O)(Me)-(C₆H₄Me))(styrene)] [9] and 82.1° in [PtCl₂(NC₅H₄Me)(styrene)] [10]. However, in a five-coordinate platinum(II) complex, [PtCl₂(*t*-BuN=CHCH=NBu-*t*)

TABLE 1
 FINAL ATOMIC PARAMETERS FOR NON-HYDROGEN ATOMS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES
 Positional parameters in fraction of cell edges and thermal parameters in the form of $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0.75781(4)	0.24619(3)	0.490719(18)	0.00887(4)	0.00626(3)	0.002101(10)	0.00357(6)	0.00209(4)	-0.00022(3)
P	0.61235(13)	0.26164(10)	0.37786(7)	0.00870(12)	0.00464(9)	0.00185(4)	0.00219(17)	0.00232(10)	0.00039(9)
C(1)	0.8031(6)	0.0587(5)	0.4820(4)	0.0104(6)	0.0058(4)	0.0044(3)	0.0045(8)	0.0052(6)	0.0018(5)
C(2)	0.9150(5)	0.1188(5)	0.4738(3)	0.0088(6)	0.0063(4)	0.00297(17)	0.0066(8)	0.0009(5)	0.0002(4)
C(3)	0.9609(5)	0.1294(5)	0.4059(3)	0.0065(5)	0.0071(4)	0.00275(16)	0.0052(7)	0.0005(4)	0.0005(4)
C(4)	1.0499(6)	0.2170(6)	0.3996(4)	0.0090(6)	0.0105(5)	0.0041(3)	0.0026(10)	0.0033(6)	0.0011(6)
C(5)	1.1002(7)	0.2260(8)	0.3377(6)	0.0112(8)	0.0180(10)	0.0067(4)	0.0075(14)	0.0082(9)	0.0091(10)
C(6)	1.0610(7)	0.1462(9)	0.2812(4)	0.0136(9)	0.0266(13)	0.0038(3)	0.0206(18)	0.0060(8)	0.0045(9)
C(7)	0.9730(7)	0.0585(8)	0.2870(4)	0.0136(9)	0.0195(10)	0.0033(3)	0.0154(15)	0.0018(7)	-0.0032(8)
C(8)	0.9226(6)	0.0491(6)	0.3478(3)	0.0102(7)	0.0105(6)	0.00318(19)	0.0082(10)	0.0017(6)	-0.0021(6)
C(11)	0.7677(9)	0.4301(6)	0.5396(4)	0.0323(15)	0.0063(5)	0.0031(3)	0.0038(14)	0.0044(9)	-0.0025(6)
C(12)	0.8888(7)	0.3743(7)	0.5754(4)	0.0124(8)	0.0166(9)	0.0045(3)	-0.0068(13)	0.0026(8)	-0.0096(8)
C(13)	0.8480(9)	0.2801(7)	0.6122(4)	0.0237(13)	0.0142(8)	0.00214(18)	0.0105(16)	-0.0035(8)	-0.0023(6)
C(14)	0.7090(9)	0.2819(8)	0.6052(4)	0.0222(12)	0.0162(9)	0.0030(3)	-0.0009(16)	0.0089(9)	-0.0040(7)
C(15)	0.6624(7)	0.3688(7)	0.5585(4)	0.0164(9)	0.0139(8)	0.0039(3)	0.0107(13)	0.0020(8)	-0.0070(7)
C(21)	0.4936(6)	0.3832(6)	0.3765(3)	0.0088(6)	0.0068(4)	0.00270(16)	0.0055(8)	0.0034(5)	0.0015(4)
C(22)	0.4014(6)	0.4097(6)	0.3026(4)	0.0095(6)	0.0095(6)	0.0042(3)	0.0067(9)	0.0030(7)	0.0026(6)
C(31)	0.5094(6)	0.1299(5)	0.3502(3)	0.0143(8)	0.0066(5)	0.00293(18)	-0.0020(9)	0.0001(6)	0.0006(5)
C(32)	0.4334(7)	0.0901(6)	0.4057(5)	0.0140(9)	0.0094(6)	0.0059(4)	-0.0065(12)	0.0024(9)	0.0034(7)
C(41)	0.6882(6)	0.2895(6)	0.3012(3)	0.0109(7)	0.0103(5)	0.00256(17)	0.0074(10)	0.0048(6)	0.0021(5)
C(42)	0.7657(7)	0.4028(7)	0.3076(5)	0.0153(9)	0.0134(8)	0.0062(4)	0.0046(13)	0.0108(9)	0.0072(8)
B	0.3164(8)	0.2368(6)	0.1100(5)	0.0131(9)	0.0076(6)	0.0036(3)	-0.0000(11)	-0.0006(8)	-0.0006(6)
F(1)	0.3886(6)	0.1706(6)	0.1634(3)	0.0341(10)	0.0142(6)	0.0069(3)	0.0025(12)	-0.0050(8)	0.0078(6)
F(2)	0.3855(7)	0.3395(4)	0.1130(4)	0.0365(11)	0.0100(5)	0.0111(4)	-0.0083(12)	0.0114(10)	0.0012(7)
F(3)	0.3183(8)	0.1793(7)	0.0460(4)	0.0398(13)	0.0264(9)	0.0068(3)	0.0076(19)	-0.0019(10)	-0.0135(9)
F(4)	0.1964(7)	0.2632(6)	0.1133(6)	0.0156(8)	0.0330(13)	0.0137(6)	0.0079(13)	0.0086(10)	0.0009(10)

TABLE 2

FINAL ATOMIC PARAMETERS FOR HYDROGEN ATOMS ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Positional parameters in fraction of cell edges and thermal parameters in the form of $\exp[-B(\sin\theta/\lambda)^2]$.

Atom	x	y	z	B
H(1A)	0.743(6)	0.027(5)	0.440(3)	3.3(14)
H(1B)	0.817(7)	0.017(6)	0.538(4)	5.5(18)
H(2)	0.978(5)	0.143(4)	0.514(3)	1.2(10)
H(4)	1.071(8)	0.273(6)	0.436(4)	4.2(17)
H(5)	1.157(7)	0.291(7)	0.338(4)	4.7(17)
H(6)	1.088(7)	0.156(6)	0.239(4)	5.0(17)
H(7)	0.944(6)	0.005(5)	0.249(3)	3.3(14)
H(8)	0.869(6)	0.013(5)	0.354(3)	3.3(14)
H(11)	0.774(7)	0.490(7)	0.520(4)	6.6(20)
H(12)	0.954(7)	0.395(7)	0.570(4)	6.3(20)
H(13)	0.915(9)	0.223(7)	0.640(5)	6.2(22)
H(14)	0.648(7)	0.222(6)	0.624(4)	3.5(15)
H(15)	0.576(7)	0.389(6)	0.542(4)	5.5(18)
H(21A)	0.452(5)	0.358(5)	0.409(3)	2.1(12)
H(21B)	0.548(6)	0.452(6)	0.398(4)	4.1(15)
H(22A)	0.337(6)	0.346(5)	0.287(4)	3.5(14)
H(22B)	0.433(7)	0.425(6)	0.262(4)	4.7(17)
H(22C)	0.348(6)	0.456(6)	0.305(3)	3.6(14)
H(31A)	0.583(6)	0.073(6)	0.333(4)	4.4(16)
H(31B)	0.457(6)	0.149(5)	0.305(4)	3.2(14)
H(32A)	0.390(6)	0.024(6)	0.394(4)	4.4(16)
H(32B)	0.493(7)	0.069(6)	0.451(4)	5.4(18)
H(32C)	0.383(6)	0.161(5)	0.414(4)	3.3(14)
H(41A)	0.751(7)	0.225(6)	0.303(4)	3.7(16)
H(41B)	0.618(6)	0.294(6)	0.267(4)	2.8(13)
H(42A)	0.710(7)	0.461(6)	0.297(4)	4.6(16)
H(42B)	0.822(7)	0.400(6)	0.282(4)	5.6(18)
H(42C)	0.824(6)	0.409(5)	0.358(3)	3.1(14)

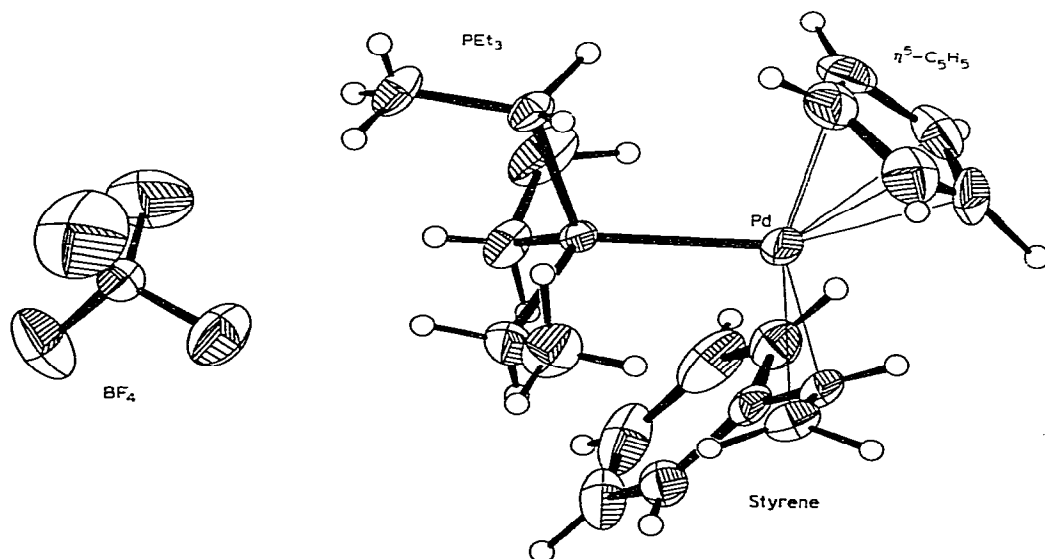


Fig. 1. An ORTEP drawing of $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PEt}_3)(\text{styrene})]\text{BF}_4$. Non-hydrogen atoms are represented by thermal ellipsoids at 30% probability levels, whereas temperature factors of H atoms are arbitrarily reduced for clarity.

TABLE 3

BOND LENGTHS (Å) ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

<i>(a) Bonds involving non-hydrogen atoms</i>			
Pd—P	2.286(1)	C(11)—C(12)	1.408(12)
Pd—C(1)	2.176(6)	C(12)—C(13)	1.384(12)
Pd—C(2)	2.234(5)	C(13)—C(14)	1.397(13)
Pd—C(11)	2.258(9)	C(14)—C(15)	1.324(11)
Pd—C(12)	2.320(7)	C(15)—C(11)	1.394(11)
Pd—C(13)	2.278(9)	P—C(21)	1.826(5)
Pd—C(14)	2.353(9)	C(21)—C(22)	1.508(8)
Pd—C(15)	2.251(7)	P—C(31)	1.822(6)
C(1)—C(2)	1.369(8)	C(31)—C(32)	1.509(10)
C(2)—C(3)	1.463(7)	P—C(41)	1.816(6)
C(3)—C(4)	1.366(8)	C(41)—C(42)	1.493(10)
C(4)—C(5)	1.382(12)	B—F(1)	1.325(10)
C(5)—C(6)	1.374(13)	B—F(2)	1.349(10)
C(6)—C(7)	1.358(12)	B—F(3)	1.369(11)
C(7)—C(8)	1.363(10)	B—F(4)	1.279(13)
C(8)—C(3)	1.399(8)		
<i>(b) Bonds involving hydrogen atoms</i>			
C(1)—H(1A)	0.95(6)	C(21)—H(21A)	0.88(6)
C(1)—H(1B)	1.13(7)	C(21)—H(21B)	0.99(6)
C(2)—H(2)	0.91(5)	C(22)—H(22A)	0.97(6)
C(4)—H(4)	0.92(8)	C(22)—H(22B)	0.92(7)
C(5)—H(5)	0.93(7)	C(22)—H(22C)	0.77(6)
C(6)—H(6)	0.91(7)	C(31)—H(31A)	1.09(7)
C(7)—H(7)	0.93(6)	C(31)—H(31B)	0.92(6)
C(8)—H(8)	0.91(6)	C(32)—H(32A)	0.87(7)
C(11)—H(11)	0.77(8)	C(32)—H(32B)	0.96(7)
C(12)—H(12)	0.74(8)	C(32)—H(32C)	0.99(6)
C(13)—H(13)	1.00(9)	C(41)—H(41A)	0.97(7)
C(14)—H(14)	1.04(7)	C(41)—H(41B)	0.85(6)
C(15)—H(15)	0.90(7)	C(42)—H(42A)	0.86(7)
		C(42)—H(42B)	0.84(7)
		C(42)—H(42C)	1.00(6)

(styrene)], the olefin bond of the styrene is coplanar with the equatorial PtNCCN plane [11]. If the approximate representation of the coordination geometry in the present complex is regarded as of the $\text{ML}_4(\text{olefin})$ type, where the Cp ligand occupies three L's *cis* to each other as pointed out by Kurosawa et al. [1], it seems to be favorable to take the geometry in which the olefin bond is strictly perpendicular to the P—Pd—CCP coordination plane. The twist of the olefin bond observed in the present and the other exemplified complexes may be caused by both the contacts between the olefin and the other ligands and effect of the molecular packing in the crystal. In the present complex, the phenyl group in the styrene comes into contact with one of the ethyl group in the PEt_3 ligand (C(3)···H(41A) 2.74(7) and C(8)···H(41A) 2.65(7) Å) and the olefin part with the Cp ligand (H(2)···C(12) 3.07(5) and H(2)···C(13) 2.95(5) Å). The degree of twist observed probably results from both contacts mentioned above.

Table 6 presents structural data for the metal—olefin bond in transitional

TABLE 4

SELECTED BOND ANGLES ($^{\circ}$) ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

P—Pd—C(1)	96.2(2)	C(15)—C(11)—C(12)	107.6(8)
P—Pd—C(2)	104.4(2)	C(11)—C(12)—C(13)	104.2(8)
C(1)—Pd—C(2)	36.2(2)	C(12)—C(13)—C(14)	111.3(8)
Pd—C(1)—C(2)	74.2(4)	C(13)—C(14)—C(15)	105.7(8)
Pd—C(1)—H(1A)	108(4)	C(14)—C(15)—C(11)	110.9(8)
Pd—C(1)—H(1B)	108(4)	Pd—P—C(21)	110.8(2)
C(2)—C(1)—H(1A)	119(4)	Pd—P—C(31)	114.0(2)
C(2)—C(1)—H(1B)	113(4)	Pd—P—C(41)	116.1(2)
H(1A)—C(1)—H(1B)	123(5)	C(21)—P—C(31)	105.6(3)
Pd—C(2)—C(1)	69.6(4)	C(21)—P—C(41)	105.5(3)
Pd—C(2)—C(3)	117.5(4)	C(31)—P—C(41)	104.0(3)
Pd—C(2)—H(2)	95(4)	P—C(21)—C(22)	115.5(4)
C(1)—C(2)—C(3)	126.1(5)	P—C(31)—C(32)	113.8(5)
C(1)—C(2)—H(2)	120(4)	P—C(41)—C(42)	113.8(5)
C(3)—C(2)—H(2)	113(4)	F(1)—B—F(2)	105.0(7)
C(2)—C(3)—C(4)	119.5(5)	F(1)—B—F(3)	106.0(7)
C(2)—C(3)—C(8)	122.4(5)	F(1)—B—F(4)	117.5(9)
C(4)—C(3)—C(8)	118.0(5)	F(2)—B—F(3)	109.0(7)
C(3)—C(4)—C(5)	121.0(7)	F(2)—B—F(4)	107.3(8)
C(4)—C(5)—C(6)	120.1(9)	F(3)—B—F(4)	111.6(8)
C(5)—C(6)—C(7)	119.4(9)		
C(6)—C(7)—C(8)	120.9(8)		
C(7)—C(8)—C(3)	120.6(6)		

metal-styrene complexes. As no precise data are available for the palladium-styrene complex, the present complex is compared with the platinum complexes listed in Table 6. The olefin bond lengths lie in the range between 1.36 and 1.53 Å in Table 6. The C(1)=C(2) bond length in the present complex (1.369(8) Å) is somewhat short but falls in this range. The Pd—C(1) distance

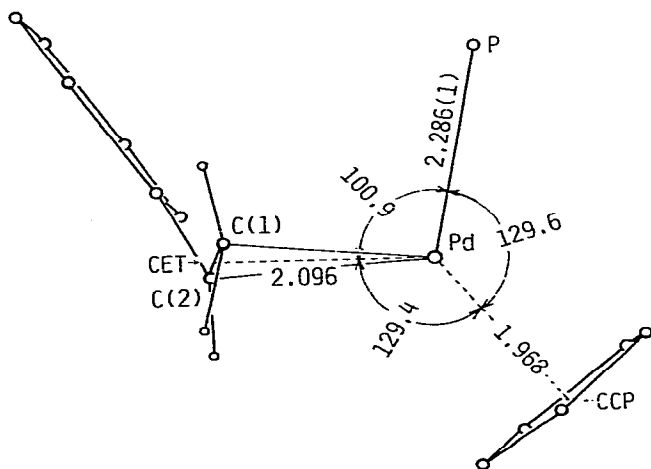


Fig. 2. The coordination geometry around the Pd atom projected onto the P—Pd—CCP plane along with selected distances and angles. Abbreviations: CCP, the center of the cyclopentadienyl ring. CET, the mid-point of the olefinic C(1)=C(2) bond in the styrene ligand.

TABLE 5
 LEAST-SQUARES PLANES ^a

Plane 1	The coordination plane through the Pd, P, CCP ^b and CET ^b					
Plane 2	The plane defined by the Pd, P and CCP ^b					
Plane 3	The cyclopentadienyl ring C(11)~C(15)					
Plane 4	The phenyl ring in styrene (C(3)~C(8))					
	A	B	C	D		
Plane 1	-0.7806	-0.5435	0.3087	3.0575		
Plane 2	-0.7538	-0.5785	0.3117	3.0081		
Plane 3	0.1073	-0.6045	-0.7893	10.1047		
Plane 4	-0.6811	0.5967	-0.4244	7.7299		
Deviations of atoms from the plane (Å)						
Plane 1	Pd	-0.029	P	0.009	CCP	0.012
	CET	0.009	C(1) ^c	0.677	C(2) ^c	-0.659
Plane 2	Pd	0.0	P	0.0	CCP	0.0
	CET ^c	0.129	C(1) ^c	0.793	C(2) ^c	-0.535
Plane 3	C(11)	-0.001	C(12)	-0.019	C(13)	0.030
	C(14)	-0.031	C(15)	0.021		
Plane 4	C(3)	0.001	C(4)	-0.001	C(5)	-0.000
	C(6)	0.002	C(7)	-0.002	C(8)	0.001

^a The equation of the plane is of the form: $AX + BY + CZ + D = 0$, where X , Y and Z are measured in Å units; $X = ax + cz\cos\beta$, $Y = by$ and $Z = cz\sin\beta$. ^b Abbreviations: see the caption to Fig. 2. ^c Not included in the calculation of the plane.

(2.176(6) Å) is significantly shorter than the Pd—C(2) distance (2.234(5) Å). Such asymmetrical coordination of two carbon atoms in asymmetrically substituted olefins to the metal atom was pointed out and discussed by Hoffmann and his coworkers [13]. The discrepancy of two metal—carbon distances in the present complex is similar to those observed in the platinum-styrene complexes, [PtCl₂(NC₅H₄Me)(styrene)] [10] and [PtCl₂(S(O)(Me)(C₆H₄Me))(styrene)] [9]. Hoffmann et al. [13] also pointed out that this bonding asymmetry is often accompanied by a shift of the entire olefin down to the substituted carbon side, so that the center of olefin lies below the coordination plane in square-planar olefin-ML₃ complexes. However, the midpoint of the olefin bond (CET) in the present complex lies 0.139 Å above the coordination plane defined by the Pd and P atoms and the CCP point. That is, the coordination plane bisects the olefin bond between the CET point and the substituted carbon (C(2)). This implies the relative geometry of the olefin to the metal atom is subjected to atomic contacts of the molecule as well as the electronic effect in the metal olefin bond.

Distances between the Pd atom and the five C atoms in the Cp ligand lie in a relatively wide range between 2.251 and 2.353 Å. The Pd—Cp distances in the cyclopentadienylpalladium complexes hitherto reported are listed in Table 7. The Pd—Cp distances in the present complex seem to be comparatively shorter than the others shown in Table 7. This shortening is partly due to the cationic nature of the metal atom. The Pd—C(11) and Pd—C(15) bonds located approxi-

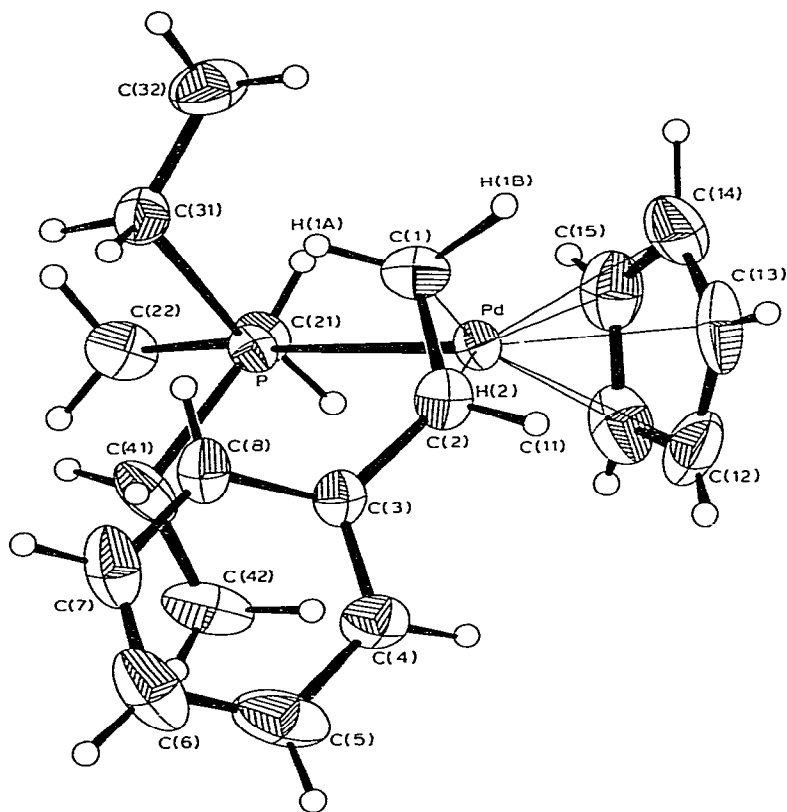


Fig. 3. A perspective view of the $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PET}_3)(\text{styrene})]$ cation viewed along the olefin-metal axis with the numbering system of atoms. Representations of atoms are same as those in Fig. 1.

mately *trans* to the olefin bond are significantly shorter than the others. Among the C—C bond lengths in the Cp ligand, the C(14)—C(15) of 1.324(11) Å is comparatively shorter than the others (1.384 ~ 1.408 Å). Such asymmetry and localization of the bonding in the cyclopentadienyl-transition metal complexes have been pointed out at the earlier [16,17] and actively discussed recently [18–25]. The bonding asymmetry hitherto reported is mainly classified into two types: an allyl-ene type involving one short, two intermediate and two long C—C bonds in the Cp ligand and a diene type having two short, one intermediate and two long bonds. Naturally, actual bonding modes are considered as a result of contributions from both types, though not necessarily in comparable degrees. Contribution of the allyl-ene type probably plays an important role in the present complex. A careful crystallography revealed very recently that the Cp group is coordinated asymmetrically to the metal atom and departs measurably from its own D_{5h} symmetry even in the complexes which possess cylindrical symmetry about the metal atom such as $\text{CpRe}(\text{CO})_3$ [24] and $\text{CpMn}(\text{CO})_3$ [25]. In view of this fact, together with the effect of deformation from the cylindrical symmetry of the $\text{Pd}(\text{PET}_3)(\text{styrene})$ moiety in the present complex, the asymmetry of the Cp group can be understood. As is seen in Table 5, the planarity of the Cp ring

TABLE 6

STRUCTURAL PARAMETERS OF THE METAL-OLEFIN BOND IN VARIOUS TRANSITION METAL COMPLEXES CONTAINING STYRENE LIGAND

Complex	Distance (Å) ^a		Angle (°) twist ^b	Reference
	M-C(1)	M-C(2)		
[Ru(PPh ₃) ₂ (styrene) ₂]	2.17(2)	2.23(2)	1.40	12
[PdCl ₂ (styrene) ₂] ₂ ^c	2.17(2)	2.15(2)	1.42	2
[Pd(η ³ -C ₅ H ₅ (PEt ₃)(styrene))]BF ₄	1.78 ^d	2.29 ^d	1.32	86
[PtCl ₂ (NC ₂ H ₄ Me)(p-NMe ₂ -styrene)]	2.175(6)	2.234(5)	1.369(8)	this work
[PtCl ₂ (NC ₂ H ₄ Me)(styrene)]	2.14(2)	2.26(1)	1.42(3)	10
[PtCl ₂ (NC ₂ H ₄ Me)(styrene)]	2.18(2)	2.24(1)	1.45(2)	10
[PtCl ₂ (NC ₂ H ₄ Cl)(p-NO ₂ -styrene)]	2.17(2)	2.22(2)	1.37(2)	10
[PtCl ₂ (S(O)(Me)(C ₆ H ₄ Me))(styrene)]	2.188(8)	2.219(9)	1.36(2)	9
[PtCl ₂ (t-BuN=CHCH=N-Bu-t)(styrene)]	2.16(4)	2.20(4)	1.53(5)	11

^a Styrene: H₂C(1)=C(2)H(C₆H₄). ^b Twist angle between the olefin bond and the coordination plane in ML₃(olefin) complex. ^c Not enough in precision due to the earlier study and omitted in the discussion of the text. ^d Not reported in the original paper.

TABLE 7

THE METAL-CARBON (Cp) DISTANCES IN η⁵-CYCLOPENTADIENYL-PALLADIUM COMPLEXES

Complex	Pd-C (Cp) distance (Å)		Mean	Reference
[Pd ₂ (μ-PhC≡CPh)(η ⁵ -C ₅ Ph ₅) ₂]	2.46	2.37	2.32	2.45
	2.30	2.37	2.35	2.27
[Pd(CHCH(OH)CH ₂ CH ₂ CH=CHCH ₂ CH ₂)(η ⁵ -C ₅ H ₅)]	2.34	2.25	2.33	2.37
	2.39	2.23	2.34	2.42
[Pd(η ⁵ -C ₅ H ₅)(PEt ₃)(styrene)]BF ₄	2.26	2.32	2.28	2.35
			2.25	2.25
			2.36	14
			2.35	15
			2.29	this work

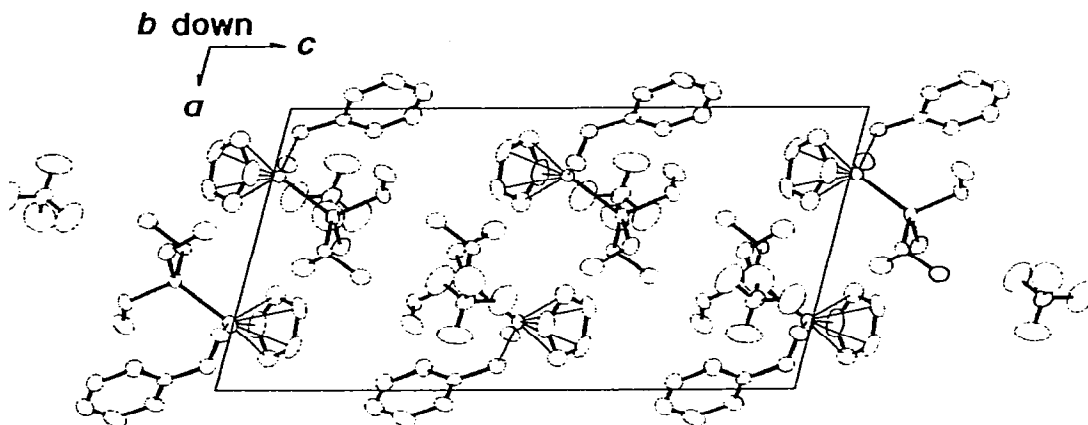


Fig. 4. The crystal structure viewed along the *b* axis. Atoms are represented by 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

is not so high (maximum atomic deviation 0.031 Å) compared with that of the phenyl ring in the styrene (0.002 Å). On the contrary, the Cp ring in CpMn(CO)₃ is so planar that the maximum deviation is only 0.005 Å [25]. Large deviations in the present complex are also due to the asymmetry of the Pd(PET₃)(styrene) moiety.

The crystal structure as viewed along the *b* axis is illustrated in Fig. 4 (an ORTEP drawing [7]). No abnormally short intermolecular atomic contacts are observed, the distances between non-hydrogen atoms less than 3.4 Å being C(2)(*x*, *y*, *z*)...C(2)(2-*x*, -*y*, 1-*z*) [3.215(7) Å], C(11) (*x*, *y*, *z*)...F(3)(1-*x*, 1/2+*y*, 1/2-*z*) [3.248(11) Å] and F(2)...C(1)(1-*x*, 1/2+*y*, 1/2-*z*) [3.370(9) Å]. The [Pd(η⁵-C₅H₅)(PET₃)(styrene)] cation seems to interact with four BF₄⁻ anions around it. The Pd...B distances are 5.499(8) (*x*, 1/2-*y*, 1/2+*z*), 5.622(8) (1+*x*, 1/2-*y*, 1/2+*z*), 5.830(8) (1-*x*, 1/2+*y*, 1/2-*z*) and 6.031(8) Å (1-*x*, -1/2+*y*, 1/2-*z*).

All computations were carried out on an ACOS 700 computer at Crystallographic Research Center, Institute for Protein Research, Osaka University.

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