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The Molecular Structure of μ-Cyclopentadienyl-μ-bromo-bis(triisopropylphosphine)dipalladium

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The crystal and molecular structure of the novel complex μ-(C₅H₅)-μ-Br-Pd₂{P[CH(CH₃)₂]₃}₂ has been determined by three-dimensional X-ray analysis. The monoclinic unit cell (space group $P2_1/c$) contains four molecules, and has the lattice parameters: $a = 13 \cdot 002$ (2), $b = 15 \cdot 551$ (2), $c = 15 \cdot 733$ (2) Å, $\beta = 116 \cdot 7$ (1)°. The Pd and P atoms lie almost on a straight line, with the two Pd atoms bonded together and bridged by the Br atom and by the cyclopentadienyl ring. This ring can be considered as formed by an alkene group plus an allyl group.

Introduction

In the course of investigations being carried out at this Institute to study transition-metal complexes (Felkin & Turner, 1977), a dimeric Pd complex was isolated, corresponding to the formula μ-(Cp)-μ-Br-Pd₂[P(iPr)₃]₂ (I).* Two other compounds with similar bridging groups had already been described by X-ray

* Cp: cyclopentadiene; iPr: isopropyl; Bz: benzene.

structural analysis: μ-(Cp)-μ-(C₄H₇)-Pd₂[P(Bz)₃]₂ (II) (Werner, Tune, Parker, Kruger & Brauer, 1975) and μ-(C₃H₅)-μ-I-Pd₂[P(Bz)₃]₂ (III) (Kobayashi, Iitaka & Yamasaki, 1972). In structures II and III, the Pd atoms are bonded to each other, and, furthermore, are bridged on opposite sides of the Pd—Pd bond: in complex II by a cyclopentadienyl ring and a methylallyl group, and in complex III by an allyl group and an I atom. In both structures the cyclopentadienyl or allyl groups are disordered, whereas, in complex I the absence of

disorder leads to better information on the metal–ring coordination.

A preliminary report on the preparation and structure of the title compound has already been published (Ducruix, Felkin, Pascard & Turner, 1975). Here we give a detailed description of the molecular geometry of this complex.

Experimental

After many attempts to crystallize single crystals, a dark-red prism was found (0·14 × 0·24 × 0·6 mm) which was surprisingly air-stable.

Three-dimensional X-ray intensity data were collected on a Philips PW 1100 four-circle automatic diffractometer, with a graphite monochromator and Mo $K\alpha$ radiation. Within $\theta \le 25°$, 2672 independent reflexions were measured with a scan width of 1°, at 0·02° s^{-1}. The background was measured at each end of the scan during half the time of the intensity measurement. In the final calculations, the 1933 intensities greater than $2\sigma(I)$ were used. The small size of the crystal made it unnecessary to correct for absorption.

Crystal data

μ-(C$_5$H$_5$)-μ-Br-Pd$_2${P[CH(CH$_3$)$_2$]$_3$}$_2$, C$_{23}$H$_{47}$P$_2$Pd$_2$Br. M_r = 677, monoclinic, space group $P2_1/c$, Z = 4, a = 13·002 (2), b = 15·551 (2), c = 15·733 (2) Å, β = 116·7 (1)°, V = 2842 Å^3, μ = 28 cm^{-1}.

Structure analysis

The structure was solved by Patterson analysis, which revealed the positions of the two Pd atoms and the Br atom. The P and C atoms appeared on subsequent Fourier difference series. When R reached a value of 8·4%, one of the isopropyl C atoms had a temperature factor of 24 Å^2. A difference series, calculated without this atom, showed two peaks with the same height, separated by 1·3 Å, which suggested that this C atom is disordered. Successive difference series showed no other trace of disorder for the remaining isopropyl groups.

We then resumed the refinement with all atoms vibrating anisotropically, except for the disordered C which was treated isotropically with an occupation factor of one half for each position. At this point we also introduced the anomalous-dispersion form factors, and the R value became 4·2%. From successive Fourier difference maps, we located density peaks which could be attributed to 39 of the 47 H atoms. When these were included in the refinement, the R value fell to 3·5%, but the angles and distances between the

H atoms were not considered as reliable, and we abandoned the H locations. The last anisotropic refinement cycle (with R = 4·2%) had an average δ/σ of 0·2.*

Table 1. Positional parameters (×10⁴)

Standard deviations in parentheses refer to the last digit.

	x	y	z
Pd(1)	6889 (1)	−2048 (1)	2645 (1)
Pd(2)	8243 (1)	−846 (1)	2568 (1)
Br	6736 (1)	−1516 (1)	1084 (1)
P(1)	5535 (3)	−3052 (2)	2488 (2)
P(2)	9273 (3)	203 (2)	2279 (2)
C(1)	4244 (9)	−2617 (8)	2546 (10)
C(2)	4956 (12)	−3641 (11)	1326 (10)
C(3)	6059 (10)	−3908 (7)	3450 (9)
C(4)	10585 (10)	−235 (8)	2222 (9)
C(5)	8456 (9)	657 (8)	1077 (8)
C(6)	9871 (9)	1054 (7)	3217 (9)
C(11)	4569 (11)	−2320 (10)	3585 (11)
C(12)	3753 (12)	−1847 (10)	1834 (13)
C(211)	3997 (29)	−4162 (23)	989 (24)
C(212)	3852 (30)	−3390 (24)	624 (25)
C(22)	5918 (12)	−4026 (10)	1146 (10)
C(31)	5160 (11)	−4603 (7)	3364 (10)
C(32)	7206 (9)	−4312 (8)	3562 (9)
C(41)	11389 (10)	−648 (8)	3226 (9)
C(42)	10241 (11)	−902 (8)	1430 (9)
C(51)	7268 (10)	993 (8)	916 (9)
C(52)	9086 (11)	1316 (8)	745 (9)
C(61)	8884 (10)	1544 (8)	3282 (9)
C(62)	10768 (10)	1691 (8)	3134 (9)
C'(1)	7759 (11)	−1915 (9)	4145 (8)
C'(2)	8849 (12)	−1811 (10)	4057 (9)
C'(3)	9064 (12)	−857 (10)	4082 (8)
C'(4)	8093 (15)	−453 (11)	4181 (10)
C'(5)	7393 (13)	−1029 (12)	4236 (9)

Table 2. Bond lengths (Å)

Standard deviations refer to the last digit.

Pd(1)–P(1)	2·282 (4)	C(3)–C(31)	1·553 (19)
Pd(1)–C'(1)	2·120 (11)	C(3)–C(32)	1·554 (19)
Pd(2)–P(2)	2·282 (4)	C(4)–C(41)	1·587 (18)
Pd(2)–C'(3)	2·128 (11)	C(4)–C(42)	1·525 (18)
P(1)–C(1)	1·850 (14)	C(5)–C(51)	1·540 (19)
P(1)–C(2)	1·875 (15)	C(5)–C(52)	1·542 (19)
P(1)–C(3)	1·897 (12)	C(6)–C(61)	1·535 (19)
P(2)–C(4)	1·875 (14)	C(6)–C(62)	1·579 (19)
P(2)–C(5)	1·843 (12)	C(211)–C(212)	1·306 (51)
P(2)–C(6)	1·873 (12)	C'(1)–C'(2)	1·494 (23)
C(1)–C(11)	1·563 (20)	C'(1)–C'(5)	1·485 (23)
C(1)–C(12)	1·566 (21)	C'(2)–C'(3)	1·508 (22)
C(2)–C(211)	1·378 (42)	C'(3)–C'(4)	1·478 (26)
C(2)–C(212)	1·417 (42)	C'(4)–C'(5)	1·307 (27)
C(2)–C(22)	1·523 (24)	Pd(1)–C'(2)	2·546 (14)
Pd(1)–Pd(2)	2·608 (1)	Pd(2)–C'(2)	2·589 (14)
Pd(1)–Br	2·512 (2)	Pd(1)–C'(5)	2·781 (17)
Pd(2)–Br	2·504 (2)	Pd(2)–C'(5)	2·700 (17)

Table 3. *Valency angles* (°)

Standard deviations refer to the last digit.

P(1)–Pd(1)–C'(1)	100·8 (4)	P(1)–C(2)–C(22)	111·7 (11)	Pd(1) -C'(1) -C'(5)	99·5 (9)
P(2)–Pd(2)–C'(3)	100·7 (4)	C(211)–C(2)–C(212)	55·7 (23)	C'(2)–C'(1)–C'(5)	105·5 (12)
Pd(1)–P(1)–C(1)	114·7 (4)	C(211)–C(2)–C(22)	112·0 (19)	C'(1)–C'(2)–C'(3)	106·0 (12)
Pd(1)–P(1)–C(2)	113·1 (5)	C(212)–C(2)–C(22)	126·4 (20)	Pd(2)–C'(3)–C'(2)	89·1 (9)
Pd(1)–P(1)–C(3)	114·3 (4)	P(1)–C(3)–C(31)	115·6 (9)	Pd(2)–C'(3)–C'(4)	95·2 (10)
C(1)–P(1)–C(2)	104·5 (7)	P(1)–C(3)–C(32)	110·9 (9)	C'(2)–C'(3)– C'(4)	105·3 (13)
C(1)–P(1)–C(3)	103·1 (6)	C(31)–C(3)–C(32)	112·0 (11)	C'(3)–C'(4)–C'(5)	111·7 (15)
C(2)–P(1)–C(3)	106·2 (6)	P(2)–C(4)–C(41)	107·8 (9)	C'(1)–C'(5)–C'(4)	111·4 (15)
Pd(2)–P(2)–C(4)	112·2 (4)	P(2)–C(4)–C(42)	110·3 (9)	Pd(1)– Br– Pd(2)	62·6 (1)
Pd(2)–P(2)–C(5)	111·0 (4)	C(41)–C(4)–C(42)	111·1 (11)	Br–Pd(1)–Pd(2)	58·5 (1)
Pd(2)–P(2)–C(6)	114·9 (4)	P(2)–C(5)–C(51)	111·9 (9)	Br–Pd(2)–Pd(1)	58·8 (1)
C(4)–P(2)–C(5)	102·0 (6)	P(2)–C(5)–C(52)	116·9 (9)	P(1)–Pd(1)–Br	113·7 (1)
C(4)–P(2)–C(6)	103·3 (6)	C(51)–C(5)–C(52)	111·4 (10)	P(2)–Pd(2)–Br	113·3 (1)
C(5)–P(2)–C(6)	112·4 (6)	P(2)–C(6)–C(61)	109·9 (9)	P(1)–Pd(1)–C'(1)	100·8 (4)
P(1)–C(1)–C(11)	109·5 (9)	P(2)–C(6)–C(62)	116·0 (9)	Pd(2)–Pd(1)–C'(1)	87·0 (4)
P(1)–C(1)–C(12)	109·4 (10)	C(61)–C(6)–C(62)	111·4 (10)	P(2)–Pd(2)–C'(3)	100·7 (4)
C(11)–C(1)–C(12)	110·8 (12)	C(2)–C(211)–C(212)	63·6 (25)	Pd(1)–Pd(2)–C'(3)	87·3 (4)
P(1)–C(2)–C(211)	124·0 (18)	C(2)–C(212)–C(211)	60·6 (24)		
P(1)–C(2)–C(212)	116·6 (18)	Pd(1)–C'(1)–C'(2)	87·8 (9)		

Fractional coordinates of the heavy atoms are given in Table 1. The atomic form factors were those from *International Tables for X-ray Crystallography* (1962) for Pd and Br and of Doyle & Turner (1968) for the P and C atoms.

Bond lengths and valency angles are listed in Tables 2 and 3.

Discussion

Molecular geometry

The structure of the molecule is illustrated by the *ORTEP* (Johnson, 1965) drawing shown in Fig. 1. The P–Pd–Pd–P atoms form almost a straight line (angle 172·3°). The two Pd atoms are bonded to each other (Pd–Pd 2·608 ± 0·001 Å) and to the same bridging Br atom (mean distance 2·508 ± 0·006 Å). As the complex is shown projected on the Pd–Br–Pd plane, it may be seen that the cyclopentadienyl ring is situated immediately above the Pd–Pd line, and inclined by 82·5° to the plane of the heavy atoms. Fig. 2 shows the projections perpendicular to this plane: C'(1) and C'(3) are situated above Pd(1) and Pd(2), at 2·12 and 2·13 Å respectively, and almost in the Pd–Br–Pd plane (see Table 4).
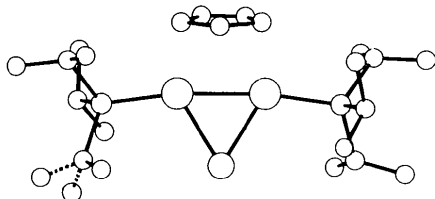
Palladium

The coordination of the Pd atoms is square planar with distortions, each Pd atom being bonded to another Pd, one P, one Br and one C atom of the cyclopentadienyl ring. Fig. 3 shows some interesting distances and angles involving the ligands coordinated around the Pd atoms. The Pd–Pd bond length is comparable with the values observed in similar structures: 2·686 ± 0·007 Å (Kobayashi *et al.*, 1972), 2·68 (?) Å (Werner *et al.*, 1975), 2·57 ± 0·013 Å (Allegra, Casagrande, Immirzi,

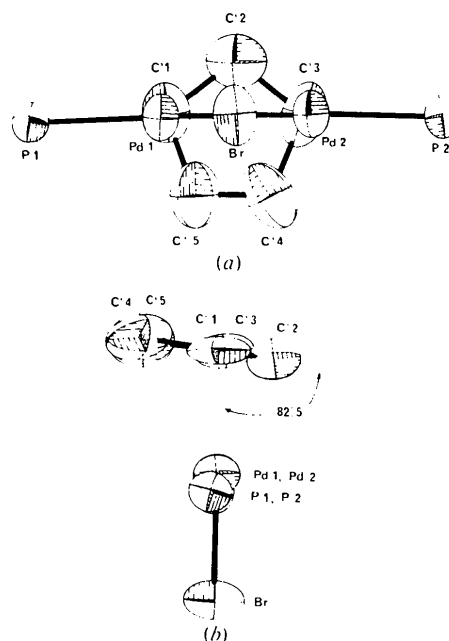Fig. 1. Projection of the molecular unit on the Pd(1)–Br Pd(2) plane.

Fig. 2. Position of the cyclopentadienyl ring over the heavy atoms. (*a*) Projection on the plane perpendicular to the Pd–Br–Pd plane and containing the Pd–Pd line. (*b*) Projection on the plane perpendicular to the plane of the heavy atoms and to the Pd- Pd bond.

Porri & Vitulli, 1970), and can be considered as a real σ bond. The thermal displacement of the Br atom is mainly perpendicular to the Pd—Br—Pd plane (see Fig. 2a).

Cyclopentadiene

Figs. 2 and 3 show the cyclopentadienyl ring. Its centre is shifted by 0·36 Å from the projected centre of the Pd—Pd bond. The atoms are practically coplanar (see Table 4); the inclination of the plane brings C'(2) to 2·21 Å from the middle of the Pd–Pd bond. C'(4)—C'(5) is 1·31 ± 0·03 Å, clearly depicting a double bond. The other distances in the ring are all similar (1·49 ± 0·02 Å), and this suggests a delocalization of the second double bond, which agrees well with the position of the triangle C'(1)—C'(2)—C'(3) above the Pd—Pd line.

It is clear, from Figs. 2 and 3, that the atoms vibrate anisotropically, and that the thermal motion occurs

principally in the plane of the ring. C'(2) has the largest thermal displacement.

This is very similar to what is observed in the structure of the complex $(Bz)_2$-Pd_2-$AlCl_4$ (Allegra *et al.*, 1970), where the Pd—Pd bond is sandwiched between the two benzene rings. The centres of these rings are shifted by 0·43 Å with respect to the projected Pd—Pd line (see Fig. 4a). Allegra suggests that C(6)—C(1)—C(2)—C(3) acts as a conjugated diene group in the *cis* conformation, π-coordinating the two Pd atoms, but, because of the low precision on the C—C bond (0·035 Å), it is impossible to say whether C(4)—C(5) has double-bond character or not.

Nevertheless, the scheme proposed by Allegra seems to describe quite well the metal–ring coordination observed between Pd and cyclopentadiene in the present complex: the five-membered ring can be regarded as an allyl plus an alkene group (Fig. 4c).

In μ-(Cp)-μ-(C_4H_7)-$Pd_2|P(Bz)_3|_2$ (Werner *et al.*, 1975), the cyclopentadiene ring is disordered and no precise conclusion could be drawn regarding its geometry.

In the structure of μ-allyl-μ-iodo-bis(triphenylphosphine)dipalladium (Kobayashi *et al.*, 1972) we find the same disposition of the Pd—Pd group: the allyl group occupies the place of the cyclopentadienyl group, with the two end C atoms above the Pd atoms and in the same plane as Pd—I—Pd; the allyl plane is inclined by 68° with respect to this plane, bringing the central atom to 2·0 Å from the Pd—Pd line. The allyl group is disordered, with the central atom flipping over between the two sites on each side of the Pd—I—Pd plane, whereas, in the present compound, the cyclopentadiene ring is fixed in one position.

Table 4. *Displacements (Å) of atoms from least-squares planes*

Standard deviations are in parentheses.

Plane I: $-0\cdot7180X + 0\cdot6952Y - 0\cdot0340Z + 7\cdot4292 = 0$
Plane II: $-0\cdot0943X + 0\cdot0414Y - 0\cdot9947Z + 6\cdot6010 = 0$

	Plane I	Plane II
Pd(1)	0*	
Pd(2)	0*	
Br	0*	
P(1)	0·106 (3)	
P(2)	0·039 (3)	
C'(1)	0·021 (15)	0·007 (11)*
C'(2)	−0·925 (17)	−0·003 (12)*
C'(3)	−0·082 (16)	−0·002 (11)*
C'(4)	1·304 (19)	0·012 (15)*
C'(5)	1·361 (18)	−0·014 (13)*

Dihedral angle I, II: 82·5°
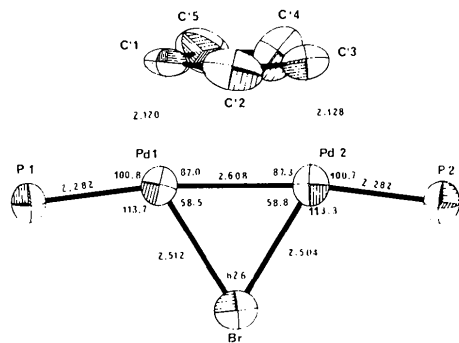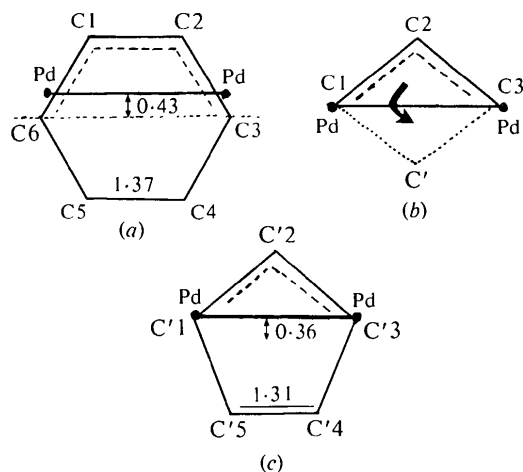
* Atom included in the calculation of the mean plane.

Fig. 3. Coordination around the Pd atoms.

Fig. 4. (a) $(C_6H_6)_2$-Pd_2-$(AlCl_4)_2$ (Allegra *et al.*, 1970). (b) μ-Allyl-μ-iodo-bis(triphenylphosphine)dipalladium (Kobayashi *et al.*, 1972). (c) This work.
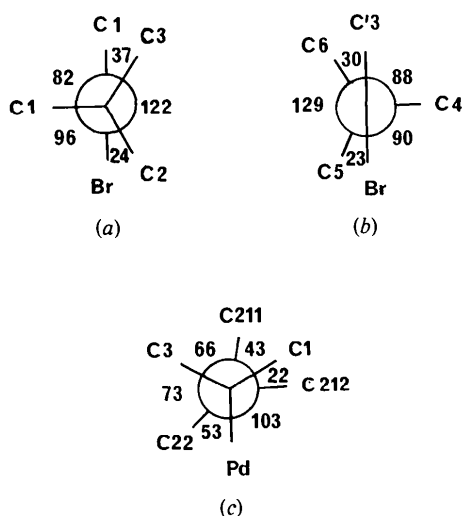
Fig. 5. Newman projections (a) around the P(1) → Pd(1) bond, (b) around the Pd(2) → P(2) bond, and (c) around the P(1) → C(2) bond.

Triisopropylphosphine

The mean Pd—P distance is 2·28 Å (±0·005 Å). The disposition of the isopropyl groups is represented in Fig. 5(a) and (b), where they appear perfectly staggered around the P(1)—Pd(1)—Pd(2)—P(2) line. The tetrahedra around the P atoms are distorted with all the Pd—P—C angles greater (average 113 ± 1°) than the C—P—C angles (105 ± 3°); Kobayashi finds comparable values: 116 ± 4° versus 102 ± 3°. The mean P—C bond length is 1·87 ± 0·015 Å and the average C—C distance is 1·55 ± 0·02 Å.

Only C(21) was observed to be disordered. The Newman projection (Fig. 5c) shows the disposition around the P(1)—C(2) bond. C(21) is statistically distri-buted between two positions: C(211) and C(212). It is suggested that the entire group oscillates around the P(1)—C(2) bond with C(21) replacing C(22), so that the occupation factor of C(22) is kept equal to unity. The strong anisotropy of C(2) and C(22) supports this hypothesis and explains the large values observed for the projected valency angles ∠C(22)—C(2)—C(211) 139° and ∠C(22)—C(2)—C(212) 156°. These values are not too different from the other analogous angles |e.g. ∠C(51)—C(5)—C(52) projected along P(2)- C(5) is 130°|.

The packing of the different molecular units in the crystal is determined by van der Waals interactions, and there are no intermolecular distances less than 3·30 Å.

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