CRYSTAL STRUCTURE OF DIBROMO(η^4-1,5-CYCLOOCTADIENE)-PALLADIUM(II)

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Received February 19, 1996
Accepted March 18, 1996

Dedicated to Professor Jaroslav Podlaha on the occasion of his 60th birthday.

The crystal structure of [(η^4-C_8H_{12})$PdBr_2$] has been determined by a single crystal X-ray diffraction with R = 3.82% for 2 147 independent diffractions. The compound crystallizes with the symmetry of orthorhombic space group $P2_12_12_1$ (No. 19) within the following parameters: a = 7.0785(5) Å, b = 11.1896(9) Å, c = 12.514(1) Å, V = 991.2(1) Å^3, Z = 4. The square planar arrangement of ligands around Pd(II) is distorted due to the steric requirements of 1,5-cyclooctadiene in a twisted boat conformation. Formula units are joined by the weak C2–H2···Br1(1 + x, y, z) hydrogen bonds.

Key words: Dibromo(η^4-1,5-cyclooctadiene)palladium(II); Crystal structure.

Dienes in dihalogeno(η^4-diene) complexes of the divalent platinum metals can be easily moved apart from two *cis*-positions and substituted by other ligands. These compounds are accessible by simple substitution reactions and are soluble in some organic solvents. Therefore, these complexes of Pt(II) and Pd(II) are often used as starting materials for preparations of other coordination species, typically phosphine complexes, not only in the solid state (e.g. ref.[1]) but also in situ by preparations of catalytically active systems (e.g. ref.[2]). According to the Cambridge Structural Database (CSD), the crystal structures of [(COD)PtX_2], where X_2 = Cl_2, Br_2, I_2, Ph_2, PhCl, acac etc. are known till now[3] (COD = η^4-1,5-cyclooctadiene). Along the palladium analogues, only the structure of [(COD)$PdCl_2$] was determined. In this work, the results of the solid state structure determination for [(COD)$PdBr_2$] are presented and discussed as a contribution to the completion of the structural data of the (η^4-diene)palladium(II) complexes.

EXPERIMENTAL

Synthesis of the Title Compound

The complex was prepared by the standard procedure[4] for a preparation of the dihalogeno(η^4-diene)palladium(II) and platinum(II) complexes. The reaction of a solution of $PdBr_2$ in concentrated hydrobromic acid with excess of 1,5-cyclooctadiene in aqueous ethanol gave a crude product. The substance was purified by the slow diffusion of petroleum ether (b.p. 40–60 °C) into dichloromethane solution of the raw product. The pure product was obtained in the form of well-developed ruby red microcrystals in the 66% yield. For $C_8H_{12}Br_2Pd$ (374.4) calculated: 25.66% C, 3.23% H, 42.68% Br; found: 25.66% C, 3.12% H, 42.72% Br. IR spectrum (Nujol): 1 344, 1 311, 1 245, 1 230, 1 173, 1 086, 990, 903, 864, 819, 786, 762, 678 cm^{-1} (for $[(COD)PdBr_2]$, ref.[4]: 1 333, 1 172, 1 083, 992, 905, 864, 823, 787, 764, 678 cm^{-1}, cf. $[(COD)RhCl]_2$, ref.[5]: 1 325, 1 311, 1 227, 1 210, 1 172, 1 153, 1 076, 993, 961, 866, 817, 795, 771 cm^{-1}).

Crystal Structure Determination

The integral intensities were measured on a four-circle diffractometer CAD4-MACHIII at 293(2) K using graphite monochromatized MoKα radiation (λ = 0.71073 Å) and θ–2θ scan. Considering the large absorption coefficient (μ(MoKα) = 9.87 mm^{-1}), the intensities were corrected for absorption by indexation of crystal faces using the standard analytical method (program AGNOSTIC, ref.[6]; minimal and maximal transmission coefficient: $T_{min} = 0.181$, $T_{max} = 0.246$).

The structure was solved by direct methods (SHELXS86, ref.[7]) yielding the positions of Pd and Br atoms. Other non-hydrogen atoms were identified after following Fourier synthesis. All hydrogen atoms were placed and fixed in theoretical positions with the isotropic thermal parameters equal to the mean thermal parameter of their bonding partners multiplied by 1.2. The refinement (SHELXL93, ref.[8]) by minimization of the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o^2) + (0.0457P)^2 + 0.0061P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$, converged to the values summarized in Table I. The extinction coefficient x was refined to 0.045(1) (empirical correction of the F_c values for primary and secondary extinction is incorporated in SHELXL93 in the form $F_c^{corr} = F_c\,[1 + 0.001xF_c^2\lambda^3 \sin^{-1}(2\theta)]^{-1/4}$). The coordinates and the mean thermal factors of non-hydrogen atoms are given in Table II, the selected interatomic distances and angles in Table III. Tables of the observed and calculated structure factors, anisotropic thermal factors of non-hydrogen atoms and isotropic thermal factors of hydrogen atoms in the standard form of the CIF files produced by SHELXL93, can be obtained from the authors upon request.

RESULTS AND DISCUSSION

The crystal structure of the title compound consists of isolated molecules of dibromo(η^4-1,5-cyclooctadiene)palladium(II). As expected, the ligands around Pd(II) form a distorted square (Fig. 1). In order to evaluate this, the centroids of both double bonds have been defined: CE1 (C1=C2; fractional coordinates 0.3862, 0.0861, 0.4833), CE2 (C5=C6; fractional coordinates 0.0652, –0.0672, 0.4607). Least-squares plane through ligands Br1, Br2, and centroids CE1, CE2 ($-3.317x + 5.882y + 8.885z - 3.501 = 0$) fails the planarity test ($\chi^2 = 107$); the average deviation of defining atoms from this plane is 0.018 Å. The distance of Pd(II) from ligands L.S. plane (0.017 Å) is the same order, therefore, the central atom remains within the plane of its ligands. The planarity is mainly affected by steric requirements of 1,5-cyclooctadiene. In comparison with exact square coordination in $PdBr_4^{2-}$ (ref.[10]), given by special position with site symmetry *P4/mmm*, in the title compound, the ligand polygon is distorted by a symmetrical shortening (without torsion) of one edge. The ratio of CE1–CE2 and Br1–Br2 distances is 0.83; the angle between lines CE1–CE2 and Br1–Br2 is 1.8°. The substitution of two bromine atoms by 1,5-cyclooctadiene leads to slight shortening of two remaining Pd–Br bonds (K_2PdBr_4: 2.444 Å; [(COD)$PdBr_2$]: Pd–Br1 2.4342(7), Pd–Br2 2.4253(7) Å).

On the other hand, geometry of 1,5-cyclooctadiene is strongly affected by coordination. In agreement with the theory (e.g. ref.[11]), the C=C bonds (1.365(8) and 1.375(8) Å) are significantly longer than in the non-coordinated molecule (1.333 and 1.334 Å in adduct of Zn(II) tetraphenylporphyrine complex with 1,5-cyclooctadiene, code SEMPIJ in CSD). The conformation of the non-coordinated 1,5-cyclooctadiene is described by the torsion angles C(n)–C(n + 1)–C(n + 2)–C(n + 3) 8.2, 66.3, –80.5, –0.5, 8.4, 67.4, –82.1 and 0.0° for n = 1–8, which correspond roughly to the boat conformation of the fully saturated cycle[12]. In view along the C1–C5 line, the opposite pairs of bonds C1–C2,

TABLE I
Crystallographic data, data collection and structure refinement[a]

Crystal system, space group	orthorhombic, $P2_12_12_1$ (No. 19)
a	7.0785(5) Å
b	11.1896(9) Å
c	12.514(1) Å
V; Z	991.2(1) $Å^3$; 4
D_{calc}	2.509 g cm^{-3}
D_{meas}	2.51 g cm^{-3} (flotation in aqueous $ZnBr_2$)
Diffractions for lattice parameters determination	25; $30 \le 2\theta \le 32°$
Crystal dimensions	0.18 × 0.21 × 0.29 mm^3
Diffraction collected; 2θ range	2 337; $4.8 \le 2\theta \le 54.0$ °
h, k, l range	$-9 \rightarrow 9$, $0 \rightarrow 14$, $0 \rightarrow 15$
Diffractions unique	2 147
Diffractions observed along $\mid F_o \mid > 4\sigma (F_o)$ criterion	1 937
Standard diffractions	3 monitored every 1 h; intensity fluctuation 4%
F(000)	704
No. of refined parameters	101
Max(Δ/σ) for the last L.S. cycle	0.00
$R(F)$, $wR(F^2)$, S for all diffractions	3.82%, 7.18%, 1.12
$R(F)$, $wR(F^2)$, S for observed diffractions	2.93%, 6.86%, 1.11
R_{int}, $R(\sigma)$	3.09%, 2.55%
Max. and min. heights in final Δρ map	0.68; –1.22 e $Å^{-3}$ (“ghosts” near Pd and Br)

[a] $R(F) = \sum \| F_o - F_c \| / \sum | F_o |$, $wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2]^{1/2}$, $S = [\sum (w(F_o^2 - F_c^2)^2) / (N_{diffrs} - N_{params})]^{1/2}$.

C4–C5, and C5–C6, C7–C8 etc. appears to be overlapped. On coordination, the conformation of C_8-cycle is changed as well. The multiple bonds of the coordinated 1,5-cyclooctadiene are perpendicular to the ligands L.S. plane (angles of the C=C bonds toward this plane are 89.8 and 90.4°). This reorientation of η^2-centers leads to a twist deforma-

TABLE II
Fractional coordinates (. 10^4) and isotropic thermal parameters (. 10^3, Å^2). U_{eq} is defined as one third of the trace of orthogonalized tensor $\boldsymbol{U}_{ij}$

Atom	x	y	z	U_{eq}
Pd	1469(1)	932(1)	3853(1)	30(1)
Br1	–1390(1)	1003(1)	2774(1)	45(1)
Br2	2537(1)	2775(1)	3032(1)	55(1)
C1	3429(9)	1233(5)	5189(5)	47(1)
C2	4294(8)	488(6)	4477(5)	44(1)
C3	4556(9)	–832(6)	4610(6)	57(2)
C4	2909(10)	–1586(6)	4184(6)	59(2)
C5	1045(8)	–991(5)	4193(5)	44(1)
C6	259(8)	–353(5)	5021(5)	47(1)
C7	1188(10)	–205(7)	6098(5)	58(2)
C8	2428(10)	888(7)	6185(5)	59(2)

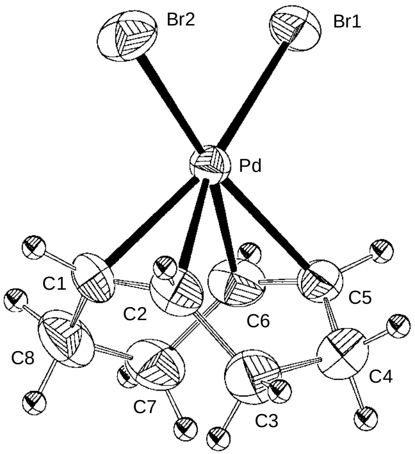

FIG. 1
The [(COD)PdBr$_2$] molecule. Thermal ellipsoids correspond to the 50% probability level (PLATON, ref.[9])

tion of the cycle; the transannular opposite bonds C(*n*)–C(*n* + 1) and C(4 + *n*)–C(5 + *n*), where *n* = 1, 2, 3 become overlapped (Fig. 2). The torsion angles are 88.5, –27.8, –46.7, –2.7, 91.0, –33.6, –41.7 and –5.7° in the same order as above.

TABLE III
Selected interatomic distances (Å) and angles (°)

Atoms	Bond lengths	Atoms	Angles
Pd–Br1	2.4342(7)	Br1–Pd–Br2	89.78(3)
Pd–Br2	2.4253(7)	Br1–Pd–C5	91.5(2)
Pd–C1	2.198(5)	Br1–Pd–C6	93.7(2)
Pd–C2	2.204(6)	Br2–Pd–C1	89.7(2)
Pd–C5	2.213(6)	Br2–Pd–C2	93.4(2)
Pd–C6	2.222(5)	C1–Pd–C5	95.1(2)
		C2–Pd–C5	80.6(2)
		C1–Pd–C6	80.9(2)
		C2–Pd–C6	88.3(2)
C1–C2	1.365(8)	C2–C1–C8	127.1(6)
C2–C3	1.498(9)	C1–C2–C3	125.9(6)
C3–C4	1.534(9)	C2–C3–C4	114.2(5)
C4–C5	1.478(9)	C3–C4–C5	115.3(5)
C5–C6	1.375(8)	C4–C5–C6	125.9(5)
C6–C7	1.509(8)	C5–C6–C7	123.6(6)
C7–C8	1.509(10)	C6–C7–C8	114.0(5)
C8–C1	1.485(9)	C7–C8–C1	115.3(5)

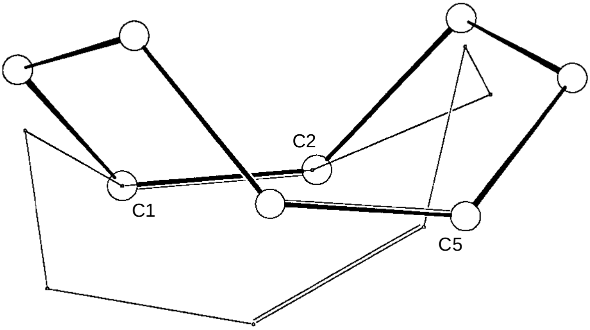

FIG. 2
Superposition of the 1,5-cyclooctadiene molecules in [(COD)$PdBr_2$] (bold lines) and in the adduct of the Zn(II) tetraphenylporphyrine complex with 1,5-cyclooctadiene (code SEMPIJ in CSD, thin lines). The superposition is defined by C1 atoms overlap, C1–C2 axis and C1, C2, C5 halfplane (PLUTO, ref.[13])

As regard to intermolecular forces, for Br atoms only distances Br1(1 + *x*, *y*, *z*)–H2 2.85 Å are shorter than van der Waals contact 3.05 Å and indicate the weak hydrogen bonds (Br1(1 + *x*, *y*, *z*)···H2–C2 157°, Br1(1 + *x*, *y*, *z*)–C2 3.77 Å). The Pd atoms are involved in Pd–H1(0.5 – *x*, 1.5 – *y*, –*z*) 3.11 Å and Pd–H8B(1.5 – *x*, 1 – *y*, 0.5 + *z*) 3.25 Å contacts; other distances exceed the sum of the van der Waals radii (3.50 Å). For the crystal packing see Fig. 3.

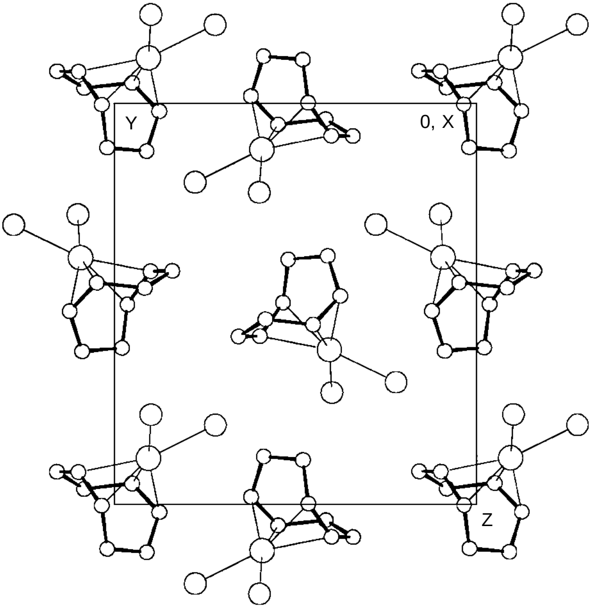

FIG. 3
Crystal packing scheme for [(COD)PdBr$_2$]; view along the crystallographic *a* axis (PLUTO, ref.[13])

This work was supported by the Grant Agency of the Czech Republic, Grants No. 203/96/0111 and 203/93/2463.

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