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[(2,3,5,6- η)-Bicyclo[2.2.1]hepta-2,5-diene]dibromidopalladium(II)

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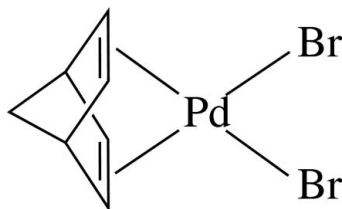
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.026; wR factor = 0.071; data-to-parameter ratio = 18.2.

In the title complex, $[\text{PdBr}_2(\text{C}_7\text{H}_8)]$, the Pd^{II} ion lies in a distorted square-planar environment defined by the two Br atoms and the mid-points of the two π -coordinated double bonds of bicyclo[2.2.1]hepta-2,5-diene. The complex is disposed about a crystallographic mirror plane parallel to the ac plane passing through the Pd, Br atoms and the centre of the diene ligand.

Related literature

For the preparation of $[\text{PdX}_2(\text{nbd})]$ ($X = \text{Cl}$ or Br ; nbd = norbornadiene), see: Alexander *et al.* (1960). For the crystal structure of $[\text{PdCl}_2(\text{nbd})]$, see: Baenziger *et al.* (1965). For the gas electron diffraction structure of norbornadiene, see: Yokozeki & Kuchitsu (1971).



Experimental

Crystal data

$[\text{PdBr}_2(\text{C}_7\text{H}_8)]$	$V = 854.6(2) \text{ \AA}^3$
$M_r = 358.35$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 12.758(2) \text{ \AA}$	$\mu = 11.44 \text{ mm}^{-1}$
$b = 7.4313(11) \text{ \AA}$	$T = 296 \text{ K}$
$c = 9.0138(14) \text{ \AA}$	$0.22 \times 0.20 \times 0.15 \text{ mm}$

Data collection

Bruker SMART 1000 CCD diffractometer	5210 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	944 independent reflections
$T_{\text{min}} = 0.126$, $T_{\text{max}} = 0.180$	673 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	52 parameters
$wR(F^2) = 0.071$	H-atom parameters constrained
$S = 0.99$	$\Delta\rho_{\text{max}} = 1.10 \text{ e \AA}^{-3}$
944 reflections	$\Delta\rho_{\text{min}} = -1.79 \text{ e \AA}^{-3}$

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZZ172).

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supporting information

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[(2,3,5,6- η)-Bicyclo[2.2.1]hepta-2,5-diene]dibromidopalladium(II)

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S1. Comment

The title complex, [PdBr₂(C₇H₈)], is isomorphous with the analogous Pd(II) complex [PdCl₂(C₇H₈)] (Baenziger *et al.*, 1965). In the complex, the central Pd^{II} ion is essentially in a square-planar environment defined by the two Br atoms and the two midpoints (M1, M2) of the π -coordinated double bonds of the bicyclo[2.2.1]hepta-2,5-diene (norbornadiene; nbd) ligand [M1 and M2 denote the midpoints of the olefinic bonds C1—C1a and C2—C2a, respectively; symmetry code: (*a*) *x*, 1/2 - *y*, *z*] (Fig. 1). The complex is disposed about a crystallographic mirror plane parallel to the *ac* plane passing through the Pd atom, the Br atoms and the centre of the ligand with the special positions (*x*, 1/4, *z*) (Fig. 2). The pairs of Pd—Br and Pd—C bond lengths are almost equal (Pd—Br: 2.4258 (11) and 2.4294 (10) Å; Pd—C: 2.165 (5) and 2.170 (5) Å). The nbd ligand coordinates symmetrically to the Pd atom, and displays a slight increase in the double-bond distances (1.389 (10) and 1.388 (10) Å) compared with the non-coordinating double bonds of nbd in the gas phase (1.343 (3) Å; Yokozeki & Kuchitsu, 1971).

S2. Experimental

To a solution of (bicyclo[2.2.1]hepta-2,5-diene)dichloridopalladium(II) (0.200 g, 0.742 mmol) in EtOH (20 ml) was added NaBr (0.816 g, 7.931 mmol), and refluxed for 1 h. The formed precipitate was separated by filtration and washed with EtOH and water and dried under vacuum, to give an orange powder (0.053 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH₃CN solution.

S3. Refinement

H atoms were positioned geometrically and allowed to ride on their respective parent atoms [C—H = 0.98 (CH) or 0.97 Å (CH₂) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

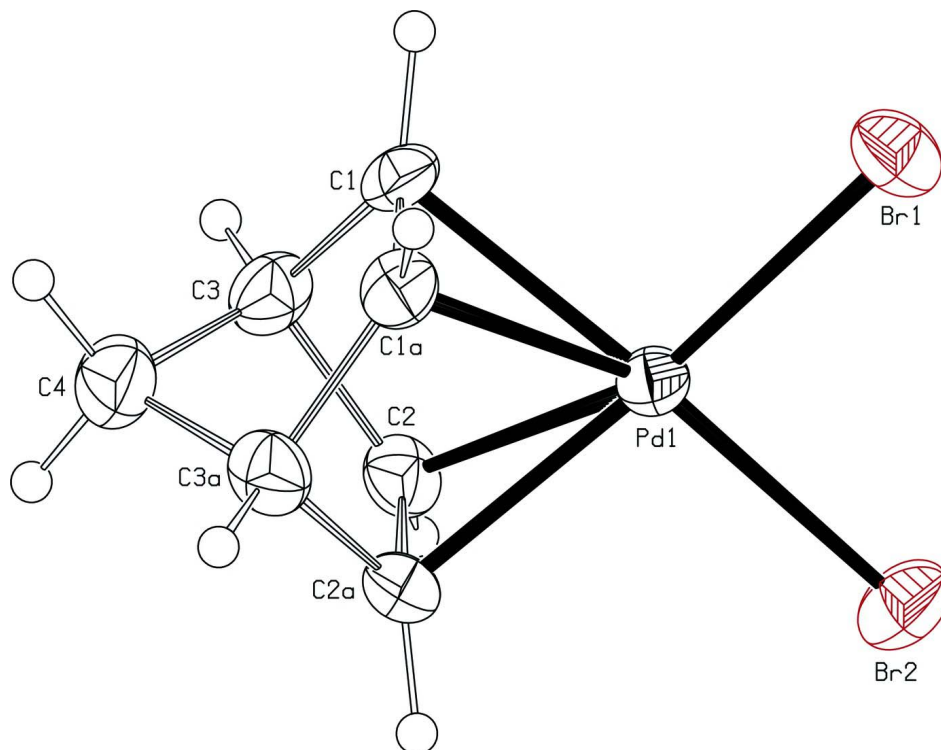


Figure 1

The structure of the title complex, with displacement ellipsoids drawn at the 40% probability level for non-H atoms [Symmetry code: (a) $x, 1/2 - y, z$].

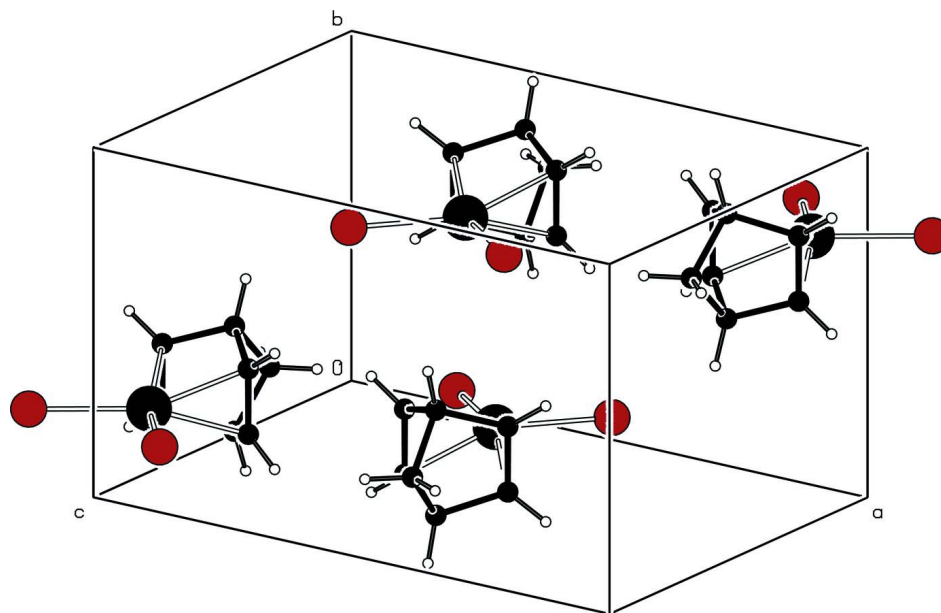


Figure 2

View of the unit-cell contents of the title complex.

[(2,3,5,6- η)-Bicyclo[2.2.1]hepta-2,5-diene]dibromidopalladium(II)*Crystal data*[PdBr₂(C₇H₈)] $M_r = 358.35$ Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

 $a = 12.758$ (2) Å $b = 7.4313$ (11) Å $c = 9.0138$ (14) Å $V = 854.6$ (2) Å³ $Z = 4$ $F(000) = 664$ $D_x = 2.785$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2031 reflections

 $\theta = 2.7$ – 27.9° $\mu = 11.44$ mm⁻¹ $T = 296$ K

Block, orange

 $0.22 \times 0.20 \times 0.15$ mm*Data collection*

Bruker SMART 1000 CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2000)

 $T_{\min} = 0.126$, $T_{\max} = 0.180$

5210 measured reflections

944 independent reflections

673 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.042$ $\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 2.8^\circ$ $h = -14 \rightarrow 15$ $k = -8 \rightarrow 9$ $l = -11 \rightarrow 6$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.026$ $wR(F^2) = 0.071$ $S = 0.99$

944 reflections

52 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0331P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 1.10$ e Å⁻³ $\Delta\rho_{\min} = -1.79$ e Å⁻³*Special details*

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pd1	0.06852 (4)	0.2500	0.92135 (7)	0.0312 (2)
Br1	0.19165 (7)	0.2500	1.12643 (11)	0.0462 (3)
Br2	-0.08564 (6)	0.2500	1.07957 (11)	0.0491 (3)
C1	0.1765 (4)	0.1566 (7)	0.7528 (6)	0.0363 (14)
H1	0.2388	0.0844	0.7752	0.044*

C2	-0.0067 (4)	0.1566 (7)	0.7196 (6)	0.0380 (14)
H2	-0.0709	0.0844	0.7192	0.046*
C3	0.0934 (4)	0.0997 (8)	0.6402 (7)	0.0419 (15)
H3	0.0967	-0.0241	0.6031	0.050*
C4	0.1048 (6)	0.2500	0.5270 (11)	0.052 (2)
H4A	0.1727	0.2500	0.4786	0.063*
H4B	0.0492	0.2500	0.4536	0.063*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.0263 (3)	0.0349 (4)	0.0325 (4)	0.000	0.0009 (3)	0.000
Br1	0.0491 (5)	0.0448 (5)	0.0448 (6)	0.000	-0.0147 (4)	0.000
Br2	0.0430 (5)	0.0488 (6)	0.0556 (7)	0.000	0.0181 (4)	0.000
C1	0.025 (2)	0.046 (3)	0.038 (4)	0.007 (2)	0.006 (2)	-0.005 (3)
C2	0.032 (3)	0.048 (3)	0.034 (3)	-0.006 (2)	-0.007 (3)	-0.002 (3)
C3	0.043 (3)	0.040 (3)	0.042 (4)	0.003 (3)	0.002 (3)	-0.013 (3)
C4	0.043 (5)	0.073 (7)	0.040 (6)	0.000	0.005 (4)	0.000

Geometric parameters (Å, °)

Pd1—C1 ⁱ	2.165 (5)	C2—C2 ⁱ	1.388 (10)
Pd1—C1	2.165 (5)	C2—C3	1.523 (7)
Pd1—C2 ⁱ	2.170 (5)	C2—H2	0.9800
Pd1—C2	2.170 (5)	C3—C4	1.520 (9)
Pd1—Br1	2.4258 (11)	C3—H3	0.9800
Pd1—Br2	2.4294 (10)	C4—C3 ⁱ	1.520 (9)
C1—C1 ⁱ	1.389 (10)	C4—H4A	0.9700
C1—C3	1.527 (7)	C4—H4B	0.9700
C1—H1	0.9800		
C1 ⁱ —Pd1—C1	37.4 (3)	Pd1—C1—H1	123.2
C1 ⁱ —Pd1—C2 ⁱ	65.8 (2)	C2 ⁱ —C2—C3	106.1 (3)
C1—Pd1—C2 ⁱ	78.2 (2)	C2 ⁱ —C2—Pd1	71.35 (14)
C1 ⁱ —Pd1—C2	78.2 (2)	C3—C2—Pd1	96.4 (3)
C1—Pd1—C2	65.8 (2)	C2 ⁱ —C2—H2	123.2
C2 ⁱ —Pd1—C2	37.3 (3)	C3—C2—H2	123.2
C1 ⁱ —Pd1—Br1	97.05 (14)	Pd1—C2—H2	123.2
C1—Pd1—Br1	97.05 (14)	C4—C3—C2	101.0 (5)
C2 ⁱ —Pd1—Br1	157.65 (14)	C4—C3—C1	100.2 (5)
C2—Pd1—Br1	157.65 (14)	C2—C3—C1	101.1 (4)
C1 ⁱ —Pd1—Br2	157.97 (13)	C4—C3—H3	117.2
C1—Pd1—Br2	157.97 (13)	C2—C3—H3	117.2
C2 ⁱ —Pd1—Br2	97.71 (14)	C1—C3—H3	117.2
C2—Pd1—Br2	97.71 (14)	C3 ⁱ —C4—C3	94.6 (7)
Br1—Pd1—Br2	94.41 (4)	C3 ⁱ —C4—H4A	112.8
C1 ⁱ —C1—C3	106.1 (3)	C3—C4—H4A	112.8
C1 ⁱ —C1—Pd1	71.29 (13)	C3 ⁱ —C4—H4B	112.8

C3—C1—Pd1	96.5 (3)	C3—C4—H4B	112.8
C1 ⁱ —C1—H1	123.2	H4A—C4—H4B	110.3
C3—C1—H1	123.2		
C2 ⁱ —Pd1—C1—C1 ⁱ	65.45 (15)	C2 ⁱ —Pd1—C2—C3	104.9 (3)
C2—Pd1—C1—C1 ⁱ	102.59 (16)	Br1—Pd1—C2—C3	-40.3 (6)
Br2—Pd1—C1—C1 ⁱ	146.8 (4)	Br2—Pd1—C2—C3	-162.5 (3)
C1 ⁱ —Pd1—C1—C3	-104.8 (3)	C2 ⁱ —C2—C3—C4	-33.3 (5)
C2 ⁱ —Pd1—C1—C3	-39.3 (3)	Pd1—C2—C3—C4	-105.7 (4)
C2—Pd1—C1—C3	-2.2 (3)	C2 ⁱ —C2—C3—C1	69.5 (4)
Br1—Pd1—C1—C3	162.8 (3)	Pd1—C2—C3—C1	-2.9 (4)
Br2—Pd1—C1—C3	42.0 (6)	C1 ⁱ —C1—C3—C4	34.0 (4)
C1 ⁱ —Pd1—C2—C2 ⁱ	-65.40 (15)	Pd1—C1—C3—C4	106.4 (4)
C1—Pd1—C2—C2 ⁱ	-102.69 (16)	C1 ⁱ —C1—C3—C2	-69.5 (4)
Br1—Pd1—C2—C2 ⁱ	-145.2 (4)	Pd1—C1—C3—C2	2.9 (4)
C1 ⁱ —Pd1—C2—C3	39.5 (3)	C2—C3—C4—C3 ⁱ	51.1 (6)
C1—Pd1—C2—C3	2.2 (3)	C1—C3—C4—C3 ⁱ	-52.5 (6)

Symmetry code: (i) $x, -y+1/2, z$.