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Key indicators

Single-crystal X-ray study
 $T = 168\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.014\text{ \AA}$
 R factor = 0.046
 wR factor = 0.114
Data-to-parameter ratio = 17.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*cis*-[1,3-Bis(diphenylphosphino)propane]-
dibromoplatinum(II)In the title compound, $[\text{PtBr}_2(\text{C}_{27}\text{H}_{26}\text{P}_2)]$, the molecule adopts a distorted square-planar metal coordination, with the six-membered metallocyclic ring in a twist-boat conformation.

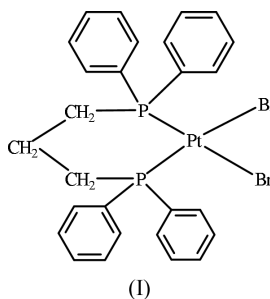
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Comment

The title compound, *cis*- $[\text{PtBr}_2(\text{dppp})_2]$, (I), [dppp is 1,3-bis-(diphenylphosphino)propane] was prepared, unexpectedly, from the reaction between the corresponding trifluoromethylsulfonate complex *cis*- $[\text{Pt}(\text{CF}_3\text{SO}_3)_2(\text{dppp})]$ and $\text{Re}(\text{CO})_3(\text{DAAD})_2\text{Br}$ (DAAD is 2,6-diazaanthracene-9,10-dione; Morgan *et al.*, 2002). The molecular structure of *cis*- $[\text{PtBr}_2(\text{dppp})]$ has the Pt atom in a slightly distorted square-planar environment (Fig. 1). The two bromo ligands are in a *cis* configuration, imposed by the chelating dppp ligand. This is similar to the structures found for the chloro analogue *cis*- $[\text{PtCl}_2(\text{dppp})]$, (II) (Robertson & Wickramasinghe, 1987), and the isomorphous palladium complex *cis*- $[\text{PdCl}_2(\text{dppp})]$, (III) (Steffen & Palenik, 1976).



Distortion in the square-planar Pt coordination sphere is signalled by angles about Pt ranging from $88.12(4)^\circ$ to $91.95(6)^\circ$ (Table 1). The r.m.s. deviation from the Br_2PtP_2 plane is 0.089 \AA , with P2 showing the largest deviation of $0.1133(8)\text{ \AA}$. The angle between the PtP_2 and PtBr_2 planes is $8.01(5)^\circ$. Similar distortions were found in (II) (Robertson & Wickramasinghe, 1987) and have been attributed to steric strain within the chelating ligand (Steffen & Palenik, 1976). This is further indicated by the significant deviations from tetrahedral angles observed in the alkyl chain of the dppp moiety. Torsion angles around the six-membered $\text{Pt}-\text{P}-\text{C}-\text{C}-\text{P}$ chelate ring are consistent with a twist-boat conformation.

Relatively few structures of square-planar Pt^{II} complexes with a PtBr_2P_2 ligand set have been reported. The data suggest that $\text{Pt}-\text{Br}$ bond lengths *trans* to the P atoms of bidentate phosphine ligands are generally longer than those in *cis*- $[\text{PtBr}_2(\text{monodentate phosphine})_2]$ structures (Sembiring *et al.*, 1999; Bhattacharyya *et al.*, 1996) or in *trans*- $[\text{PtBr}_2\text{P}_2]$ complexes (Messmer & Amma, 1966; Cameron *et al.*, 1990).

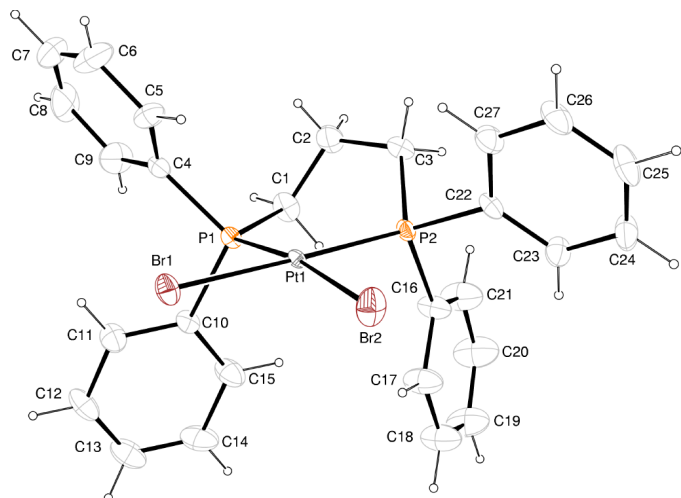


Figure 1
Perspective drawing of the title molecule, showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles with arbitrary radii.

The Pt—Br and Pt—P bond lengths observed for (I) are within the expected ranges (Orpen *et al.*, 1989). Furthermore, the Pt—P distances are identical within experimental error, while the Pt—Br distances differ [2.4951 (9) and 2.4855 (10) Å], mirroring the bond-length variations observed in (II) (Robertson & Wickramasinghe, 1987) and (III) (Steffen & Palenik, 1976). The Pt—Br distances observed for (I) are also similar to those found for the previously reported *cis*-PtBr₂(bidentate phosphine) structures (Wilson *et al.*, 1994; Sevillano *et al.*, 2000).

Molecules of (I) are reasonably well separated in the unit cell, with the shortest intermolecular contact not involving H atoms being for C6...C24ⁱ, of 3.4765 (9) Å [symmetry code: (i) $x, y - 1, z$]. The shortest contact involving the Br atoms is H8...Br2ⁱⁱ [H8...Br2ⁱⁱ 2.875 (1), C8...Br2 3.770 (1) Å and C8—H8...Br2 157.5 (2)°; symmetry code: (ii) $x + 1, y - 1, z$].

Experimental

Re(CO)₃(DAAD)₂Br (115 mg, 0.15 mmol) and *cis*-[Pt(CF₃SO₃)₂(dppp)] (135 mg, 0.15 mmol) were dissolved in dichloromethane (30 ml). The solution was stirred for 20 h at ambient temperature. The orange precipitate was filtered off and washed with dichloromethane, hexane, diethyl ether and ethyl acetate. Crystallization was achieved in *d*₆-DMSO over a period of months at ambient temperature.

Crystal data

[PtBr₂(C₂₇H₂₆P₂)]
 $M_r = 767.33$
 Triclinic, $P\bar{1}$
 $a = 8.709$ (2) Å
 $b = 10.760$ (3) Å
 $c = 14.429$ (4) Å
 $\alpha = 88.272$ (3)°
 $\beta = 80.296$ (4)°
 $\gamma = 73.540$ (3)°
 $V = 1278.0$ (6) Å³

$Z = 2$
 $D_x = 1.994$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5652 reflections
 $\theta = 4.9$ – 52.7 °
 $\mu = 8.76$ mm⁻¹
 $T = 168$ (2) K
 Block, pale brown
 $0.51 \times 0.33 \times 0.30$ mm

Data collection

Siemens SMART diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\min} = 0.046$, $T_{\max} = 0.072$
 15 666 measured reflections
 5118 independent reflections

4792 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 26.4$ °
 $h = -10 \rightarrow 10$
 $k = -10 \rightarrow 13$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.114$
 $S = 1.23$
 5118 reflections
 289 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 9.6036P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.007$
 $\Delta\rho_{\max} = 2.38$ e Å⁻³
 $\Delta\rho_{\min} = -4.26$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Br1—Pt1	2.4951 (9)	P1—C1	1.850 (8)
Br2—Pt1	2.4855 (10)	C1—C2	1.530 (12)
Pt1—P2	2.2384 (19)	C2—C3	1.544 (12)
Pt1—P1	2.2394 (19)	C3—P2	1.850 (8)
P2—Pt1—P1	91.67 (7)	Br2—Pt1—Br1	88.12 (4)
P2—Pt1—Br2	91.95 (6)	C1—P1—Pt1	115.4 (3)
P1—Pt1—Br2	171.34 (5)	C2—C1—P1	111.1 (6)
P2—Pt1—Br1	178.72 (5)	C1—C2—C3	116.8 (7)
P1—Pt1—Br1	88.45 (6)	C2—C3—P2	117.0 (6)

The final difference Fourier map revealed large residual density peaks around the Pt atom. Inspection of the absorption correction data showed a significant decrease in R_{int} (from 0.097 to 0.033) following the correction. It is possible, however, that selection of a smaller crystal and/or application of numerical absorption corrections may have resulted in better residual density values. All H atoms were included in calculated positions using a riding model, with Csp^2 —H and Csp^3 —H bond distances of 0.95 and 0.99 Å, respectively, and U_{iso} values equal to $1.2U_{\text{eq}}$ of the carrier C atoms.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997) and TITAN2000 (Hunter & Simpson, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997) and TITAN2000; molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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