

[Bis(diphenylphosphino)methane]- [1,3-bis(diphenylphosphino)propane]- platinum(II) dibromide

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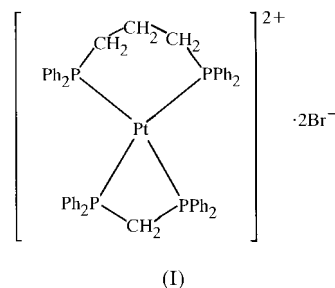
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The asymmetric unit of the title compound, [Pt(C₂₅H₂₂P₂)-(C₂₇H₂₆P₂)]Br₂ or [Pt(dppm)(dppp)]Br₂, where dppm is bis(diphenylphosphino)methane and dppp is 1,3-bis(diphenylphosphino)propane, consists of a discrete [Pt(dppm)(dppp)]²⁺ cation and two Br⁻ anions at van der Waals distances. This is the first reported platinum(II) complex containing both dppm and dppp ligands. Noticeable features are that the coordination of platinum by the differing dppm and dppp ligands produces a distorted coordination geometry with differing ligand bite angles (and to a lesser extent bond distances), and that the strain induced by the formation of the four-membered dppm chelate ring has a marked effect upon the bond angles at the P atoms of this ligand.

Comment

Owing to their application as catalysts, transition metal complexes with diphosphine ligands have been the subject of several investigations, as these ligands give rise to a variety of interesting species, the structures of which are a function of the ligand and of the method of preparation (Ahter *et al.*, 2000). There is also considerable current interest in exploiting the coordinative capabilities of phosphorus-donor ligands in order to facilitate the synthesis of platinum(II) complexes (Ferguson *et al.*, 2001; Lobana *et al.*, 2000). However, the best-defined systems involve only a limited number of diphosphine ligands, *i.e.* dppm [bis(diphenylphosphino)methane], dppe [bis(diphenylphosphino)ethane] and dppp [bis(diphenylphosphino)propane] (Lobana *et al.*, 1998; Azam *et al.*, 1999). The interest in such compounds is greatly enhanced by the variety of possible coordination modes of the diphosphine ligands (monodentate, bidentate by chelation or acting as a bridge). A limited number of platinum(II) complexes containing mixed diphosphine ligands (Irisli *et al.*, 1997) are

known and we now report the first example of a crystal structure analysis of a platinum(II) complex containing both dppm and dppp ligands.



The asymmetric unit of the title compound, (I), consists of a discrete [Pt(dppm)(dppp)]²⁺ cation and two Br⁻ anions (Fig. 1 and Table 1). The shortest Pt···Br distances are Pt···Br1 and Pt···Br2 of 4.991 (2) and 3.990 (3) Å, respectively, the shorter of which would make the Pt atom five-coordinate. Other short contacts involving Br are given in Table 2.

The most striking feature of the cationic platinum(II) complex of (I) is the simultaneous presence of the six- and four-membered chelate rings formed by the dppp and dppm ligands, respectively. Neither chelate ring is planar. The six-membered dppp chelate ring has a chair conformation, with Pt–P1–C1–C2 and Pt–P2–C3–C2 torsion angles of 59.0 (16) and –59.5 (13)°, respectively, and with the Pt and C2 atoms located 0.98 (1) Å above and 0.72 (2) Å below the plane defined by atoms P1, P2, C1 and C3. The Pt, P3, C4 and P4 atoms of the four-membered dppm chelate ring are situated at the apices of a flattened tetrahedron, with displacements from the least-squares plane so defined of –0.180 (5), 0.236 (6), –0.295 (6) and 0.240 (6) Å, respectively.

In (I), the Pt atom is coordinated by the four P atoms of the two diphosphine ligands in a distorted square-planar arrangement, with *trans* P1–Pt–P3 and P2–Pt–P4 angles of 169.48 (14) and 167.79 (14)°, respectively, and diphosphine ligand bite angles, P1–Pt–P2 for dppp and P3–Pt–P4 for dppm, of 89.88 (14) and 69.84 (14)°, respectively. The distortion of the coordination plane defined by atoms P1, P2, P3 and P4 is also shown by their displacements [–0.018 (2), 0.018 (2), –0.022 (2) and 0.022 (2) Å, respectively] from the mean plane. The Pt atom lies within 0.107 (2) Å of this plane.

The Pt–P bond distances [2.322 (4)–2.337 (4) Å, with an average of 2.330 Å] are in good agreement with the mean Pt–P distance (2.340 Å) observed in the [(dppe)Pt(PPh₃)-(CHNMe₂)]²⁺ complex (Ferguson *et al.*, 2001), but longer than the average value (2.263 Å) found in *cis*-[1,2-bis(diphenylphosphino)ethane]bis(pyridine-2-thiolato)platinum(II) (Lobana *et al.*, 2000). However, in (I), the shortness of the mean Pt–P distance for dppp (2.323 Å) compared with that for dppm (2.337 Å) may be noted; the difference in ligand bite angles has already been noted above.

In comparing the ligands themselves as they occur in (I), the bond distances other than the Pt–P bond lengths commented on above are in no way unusual. Thus, for example, the P–C distances in the present complex lie in the range 1.794 (15)–1.859 (16) Å, with a mean of 1.821 Å, and are in good agree-

ment with the values reported for P–C distances in dppm and dppp ligands in other complexes (Lobana *et al.*, 1998; Azam *et al.*, 1999). Likewise, the dimensions of the phenyl rings are as expected and do not show any significant features of special interest. Significant differences between the dppp and dppm ligands are observed, however, in the bond angles at the P and methylene C atoms. For dppp, the situation is comparatively normal, with intra-ring angles at the P and C atoms in the

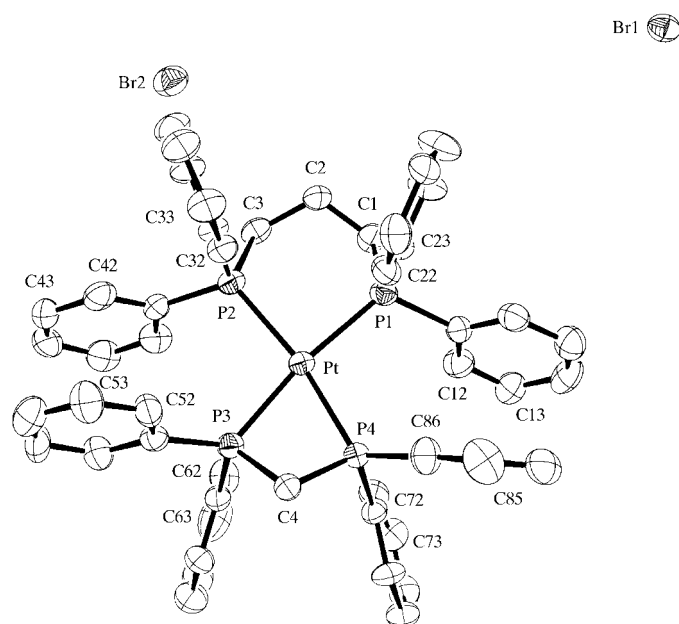


Figure 1

A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Only selected phenyl C atoms, corresponding to the usage C*i*–C*i*6, where *i* = 1–8 and identifies a particular phenyl ring, are labelled.

range 114.2 (11)–115.4 (12)° (excluding the ligand bite angle), and Pt–P–C and C–P–C angles in the ranges 111.2 (5)–115.2 (5) and 102.2 (7)–107.2 (8)°, respectively. In contrast, for dppm, while the C–P–C angles lie in a comparable range of 104.2 (7)–108.9 (7)°, the intra-ring and other Pt–P–C angles are very different. Here, the intra-ring angles, again excluding the ligand bite angle, are much smaller [range 91.2 (5)–93.6 (7)°], and while one Pt–P–C_{phenyl} angle is as large as 124.4 (5) or 125.8 (5)°, the other is only 115.9 (6) or 117.8 (5)°. Clearly, the four-membered chelate ring of dppm represents a highly strained situation which may extend as far as to promote differences between the dihedral angles between pairs of phenyl groups bonded to the same P atom, 77.3 (7) and 74.0 (7)° for P1 and P2 of dppp, and 72.5 (7) and 70.4 (7)° for P3 and P4 of dppm.

Experimental

The title complex was prepared according to the method of Irisli *et al.* (1997). Recrystallization from methanol yielded colourless crystals suitable for X-ray analysis.

Crystal data

[Pt(C₂₅H₂₂P₂)(C₂₇H₂₆P₂)]Br₂
M_r = 1151.69
 Triclinic, *P* $\bar{1}$
a = 12.534 (2) Å
b = 13.044 (2) Å
c = 17.633 (2) Å
 α = 104.059 (9)°
 β = 96.781 (9)°
 γ = 114.31 (1)°
V = 2469.8 (6) Å³

Z = 2
D_x = 1.549 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 9.9–18.0°
 μ = 4.62 mm⁻¹
T = 293 (2) K
 Rectangular prism, colourless
 0.12 × 0.08 × 0.04 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (MolEN; Fair, 1990)
T_{min} = 0.80, *T_{max}* = 0.99
 10 023 measured reflections
 10 023 independent reflections

7119 reflections with *I* > 2σ(*I*)
 θ_{\max} = 26.3°
h = 0 → 15
k = –16 → 14
l = –21 → 21
 3 standard reflections
 frequency: 120 min
 random variation: ±0.8%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.045
wR(*F*²) = 0.154
S = 1.28
 10023 reflections
 532 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.080P)^2 + 0.929P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.007$
 $\Delta\rho_{\max} = 2.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.61 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Pt–P1	2.322 (4)	P2–C41	1.813 (16)
Pt–P2	2.323 (4)	P3–C4	1.847 (15)
Pt–P3	2.337 (4)	P3–C51	1.794 (15)
Pt–P4	2.336 (4)	P3–C61	1.816 (16)
P1–C1	1.827 (15)	P4–C4	1.822 (16)
P1–C11	1.859 (16)	P4–C71	1.812 (14)
P1–C21	1.815 (16)	P4–C81	1.843 (15)
P2–C3	1.814 (15)	C1–C2	1.48 (2)
P2–C31	1.818 (15)	C2–C3	1.54 (2)
P1–Pt–P2	89.88 (14)	C31–P2–Pt	114.6 (5)
P1–Pt–P4	100.33 (14)	C51–P3–C61	106.2 (7)
P1–Pt–P3	169.48 (14)	C51–P3–C4	107.9 (7)
P2–Pt–P4	167.79 (14)	C61–P3–C4	107.0 (8)
P2–Pt–P3	99.48 (14)	C51–P3–Pt	125.8 (5)
P3–Pt–P4	69.84 (14)	C61–P3–Pt	115.9 (6)
C21–P1–C1	107.2 (8)	C4–P3–Pt	91.2 (5)
C21–P1–C11	105.7 (7)	C71–P4–C4	107.6 (8)
C1–P1–C11	102.2 (7)	C71–P4–C81	104.2 (7)
C21–P1–Pt	111.2 (5)	C4–P4–C81	108.9 (7)
C1–P1–Pt	114.4 (6)	C71–P4–Pt	117.8 (5)
C11–P1–Pt	115.2 (5)	C4–P4–Pt	91.9 (5)
C41–P2–C3	102.3 (8)	C81–P4–Pt	124.4 (5)
C41–P2–C31	104.5 (8)	C2–C1–P1	115.4 (12)
C3–P2–C31	104.3 (7)	C1–C2–C3	114.7 (14)
C41–P2–Pt	115.2 (5)	C2–C3–P2	114.2 (11)
C3–P2–Pt	114.5 (5)	P4–C4–P3	93.6 (7)
Pt–P1–C1–C2	59.0 (16)	Pt–P3–C4–P4	–30.1 (6)
Pt–P2–C3–C2	–59.5 (13)		

H atoms were placed in calculated positions, with C–H distances of 0.93 and 0.97 Å for aromatic and methylene H atoms, respectively, and were refined as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(C). PLATON (Spek, 1990) indicated the presence of solvent-accessible voids.

Table 2

Short contacts involving bromine (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C1—H1B \cdots Br2 ⁱ	0.97	2.91	3.76 (2)	147
C3—H3A \cdots Br2 ⁱ	0.97	2.85	3.71 (2)	148
C46—H46 \cdots Br2 ⁱ	0.93	2.94	3.86 (2)	170
C62—H62 \cdots Br2 ⁱ	0.93	2.94	3.77 (2)	149
C4—H4B \cdots Br1 ⁱⁱ	0.97	2.84	3.78 (2)	163
C52—H52 \cdots Br1 ⁱⁱⁱ	0.93	2.81	3.70 (2)	159
C86—H86 \cdots Br1 ⁱⁱⁱ	0.93	2.88	3.73 (2)	153

 Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $1+x, 1+y, 1+z$; (iii) $1-x, 1-y, 1-z$.

However, no additional electron density was found in the difference map. The largest difference peak was 0.71 Å from Pt and attributable to the ripple caused by series termination.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993); cell refinement: *CAD-4 EXPRESS*; data reduction: *CAD-4 EXPRESS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1466). Services for accessing these data are described at the back of the journal.

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