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trans-Di-μ-bromo-bis[bromo(triethylphosphine-κP)platinum(II)]

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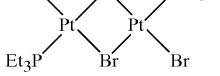
The title compound, $[Pt_2Br_4(C_6H_{15}P)_2]$, is a centrosymmetric dinuclear platinum(II) complex consisting of two square-planar platinum centres connected by two bridging Br atoms.

Comment

Bridged chloride complexes of the form $[PtCl_2(PR_3)]_2$ have been used extensively as starting materials in the synthesis of mononuclear platinum–phosphine complexes, which are formed through cleavage of the bridging Pt—Cl bond (Chatt & Venanzi, 1955; Meidine & Nixon, 1988; Dillon & Goodwin, 1992, 1994). Similar synthetic methodology can also be applied to bromide analogues (Cornet, 2002). However, while the crystal structures of the chloro-bridged complexes $[PtCl_2(PMe_3)]_2$, $[PtCl_2(PEt_3)]_2$ and $[PtCl_2(PPr_3)]_2$ are known (Boag & Ravetz, 1996; Blake *et al.*, 1989; Black *et al.*, 1969), structures of complexes exhibiting the central heavy-atom skeleton $[PtCl_2P]_2$ are surprisingly rare, with only a handful known (Simms *et al.*, 1987; Cobley *et al.*, 2000).

The title complex, (I), was prepared by the $CHCl_2$-mediated reaction of equimolar quantities of $PtBr_2$ and $[PtBr_2(PEt_3)_2]$. Given the rarity of crystal structures containing the $[PtCl_2P]_2$ fragment, it is unsurprising that (I) is the first structure to be reported containing the $[PtBr_2P]_2$ motif.



(I)

The chloride complexes $[PtCl_2(PR_3)]_2$ (where R = CH_3, C_2H_5 and C_3H_7) and the title compound are closely related, and all four complexes possess an inversion centre in the middle of the dimer, with the PR_3 ligands in a *trans* geometry (Fig. 1). In addition, all four structures are asymmetric around the bridging halide ligands, but this asymmetry is reduced in (I) with respect to the chloride complexes (Table 1). This degree of asymmetry in (I) is presumably due to the relative positions of the Cl, Br and P atoms in the *trans* influence series and the increased ionic radius of the bromide ligand. These factors also appear to reduce the effect bridging has on the bond lengths, since the bonds to the bridging Br atoms are only 0.023 and 0.122 Å longer than those to the terminal Br atoms, compared with averages of 0.033 and 0.146 Å in $[PtCl_2(PR_3)]_2$ (where R = CH_3, C_2H_5 and C_3H_7; Boag & Ravetz, 1996; Blake *et al.*, 1989; Black *et al.*, 1969, respectively).

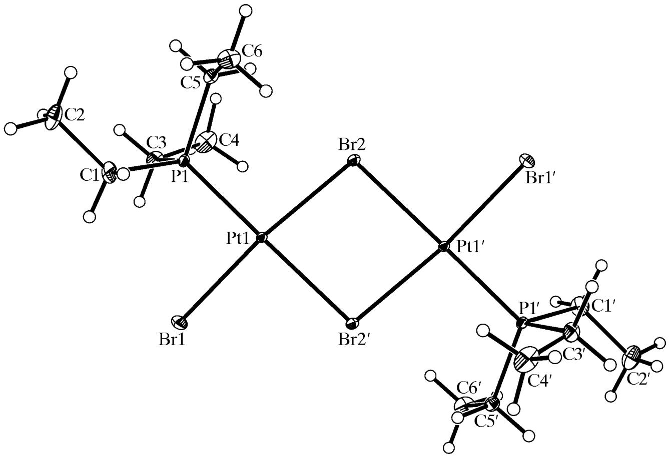


Figure 1
A view of (I), with selected atoms labelled. Symmetry equivalents related by $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$ are also shown and are indicated by primes. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level.

Experimental

$PtBr_2$ (1.48 g, 4.2 mmol) in PhCN (10 ml) was heated to 373 K to give a bright-orange solution and a yellow precipitate on cooling {*cis*-$[PtBr_2(PhCN)_2]$, yield 81%}. PEt_3 (1.75 g, 2.18 ml, 14.8 mmol) was then added to a solution of $[PtBr_2(PhCN)_2]$ (1.77 g, 3.15 mmol) in CH_2Cl_2 (15 ml) and the mixture stirred for 3 h. Evaporation of the solvent produced a white solid {*cis*-$[PtBr_2(PEt_3)_2]$, yield 83%}, some of which (1.45 g, 2.45 mmol) was added to a solution of $PtBr_2$ (1.03 g, 2.9 mmol) in $(CHCl_2)_2$ and heated to 423 K for 4 h. The yellow crystals of (I) obtained on cooling were recrystallized from CH_2Cl_2 (yield 79%). Analysis calculated for $C_{12}H_{30}Br_4P_2Pt_2$: C 15.23, H 3.20%; found: C 15.27, H 3.23%. ^{31}P NMR ($CDCl_3$): δ 10.9 (singlet with Pt satellites, $^1J_{P-Pt}$ = 3701 Hz, $^3J_{P-Pt}$ = 24.4 Hz, $^4J_{P-P}$ = 1.6 Hz). The AA'XX' part of the spectrum was insufficiently resolved for $^2J_{Pt-Pt}$ to be evaluated (Kiffen *et al.*, 1975).

Crystal data

$[Pt_2Br_4(C_6H_{15}P)_2]$
M_r = 946.12
Monoclinic, $C2/c$
a = 26.522 (6) Å
b = 6.8720 (13) Å
c = 13.811 (4) Å
β = 120.930 (7)°
V = 2159.3 (9) Å^3
Z = 4
D_x = 2.910 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7378 reflections
θ = 1.9–30.6°
μ = 20.48 mm^{-1}
T = 120 (2) K
Block, clear intense orange
0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD 1K area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.058, T_{max} = 0.129
10 540 measured reflections
2355 independent reflections
2158 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 27.0°
h = −32 → 33
k = −8 → 8
l = −17 → 17

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.046$
$S = 1.11$
2355 reflections
94 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 10.3265P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.85$ e Å^{-3}
$\Delta\rho_{\min} = -1.75$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °) for (I) and the related chloro complexes $[PtCl_2(PMe_3)]_2$, $[PtCl_2(PEt_3)]_2$ and $[PtCl_2(PPr_3)]_2$ (Hal = Cl or Br).

	$[PtCl_2(PMe_3)]_2$	$[PtCl_2(PEt_3)]_2$	$[PtCl_2(PPr_3)]_2$	(I)
Pt—P	2.205 (3)	2.212 (3)	2.230 (9)	2.2266 (11)
Pt—Hal$_{\text{terminal}}$	2.281 (3)	2.282 (3)	2.279 (9)	2.4229 (7)
Pt—Hal$_{\text{bridging}}$	2.309 (3)	2.318 (3)	2.315 (8)	2.4455 (7)
	2.423 (3)	2.431 (3)	2.425 (8)	2.5451 (6)
Pt—Hal—Pt	96.19 (10)	96.48 (10)	96.4 (3)	96.17 (2)
Hal—Pt—Hal	83.81 (10)	83.52 (9)	83.6 (2)	83.83 (2)

All H atoms were placed geometrically and refined using a riding model (C—H = 0.98 and 0.99 Å), with their U_{iso}(H) values fixed at 1.2 or 1.5 times U_{eq} of the parent C atom. Although there are difference density holes larger than 1 e Å^{-3}, they are within 1 Å of the Pt atom.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXS97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1034). Services for accessing these data are described at the back of the journal.

References

Black, M., Mais, R. H. B. & Owston, P. G. (1969). *Acta Cryst.* B**25**, 1760–1766.
Blake, A. J., Gould, R. O., Marr, A. M., Rankin, D. W. H. & Schröder, M. (1989). *Acta Cryst.* C**45**, 1218–1219.
Boag, N. M. & Ravetz, M. S. (1996). *Acta Cryst.* C**52**, 1942–1943.
Bruker (1998). *SMART-NT*, *SAINT-NT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chatt, J. & Venanzi, L. M. (1955). *J. Chem. Soc.* pp. 2787–2793.
Cobley, C. J., Ellis, D. D., Orpen, A. G. & Pringle, P. G. (2000). *J. Chem. Soc. Dalton Trans.* pp. 1101–1107.
Cornet, S. M. M. (2002). PhD thesis, University of Durham, England.
Dillon, K. B. & Goodwin, H. P. (1992). *J. Organomet. Chem.* **428**, 169–171.
Dillon, K. B. & Goodwin, H. P. (1994). *J. Organomet. Chem.* **469**, 125–128.
Kiffen, A. A., Masters, C. & Visser, J. P. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1311–1315.
Meidine, M. F. & Nixon, J. F. (1988). Private communication to K. B. Dillon.
Sheldrick, G. M. (1997*a*). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Simms, B. L., Shang, M., Lu, J., Youngs, W. J. & Ibers, J. A. (1987). *Organometallics*, **6**, 1118–1126.