Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Archer, C. M., Dilworth, J. R., Jobanputra, P., Thompson, R. M., McPartlin, M., Povey, D. C., Smith, G. W. & Kelly, J. D. (1990). *Polyhedron*, **9**, 1497–1502.
Bishop, M. W., Butler, G., Chatt, J., Dilworth, J. R. & Leigh, G. J. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1843–1850.
Bishop, M. W., Chatt, J., Dilworth, J. R., Hursthouse, M. B. & Motevalli, M. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1600–1602.
Block, E., Gernon, M., Kang, H., Ofori-Okai, G. & Zubieta, J. (1991). *Inorg. Chem.* **30**, 1736–1747.
Chatt, J., Crichton, B. A. L., Dilworth, J. R., Dahlstrom, P., Gutkoska, R. & Zubieta, J. (1982). *Inorg. Chem.* **21**, 2383–2391.
Chatt, J., Pearman, A. J. & Richards, R. L. (1975). *J. Organomet. Chem.* **101**, C45–C47.
Chatt, J., Pearman, A. J. & Richards, R. L. (1977). *J. Chem. Soc. Dalton. Trans.* pp. 2139–2142.
Dilworth, J. R., Harrison, S. A., Walton, D. R. M. & Schweda, E. (1985). *Inorg. Chem.* **24**, 2594–2595.
Dilworth, J. R., Jobanputra, P., Parrott, S. J., Thompson, R. M., Povey, D. C. & Zubieta, J. A. (1992). *Polyhedron*, **11**, 147–155.
Kopf, J. & Rübcke, H.-C. (1993). *CADSHEL. Program for Reduction of Enraf–Nonius CAD-4 Data.* Version 3.1. University of Hamburg, Germany.
Nicholson, T., de Vries, N., Davison, A. & Jones, A. G. (1989). *Inorg. Chem.* **28**, 3813–3819.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Walker, N. (1993). *DIFABS.* Version 9.0. BASF AG, Germany.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

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5,5-Bis(dimethylphenylphosphine)-4,6-dithia-5-pallada-*arachno*-nonaborane

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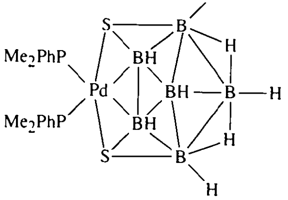
Abstract

The title compound $[5,5\text{-}(PMe_2Ph)_2$-*arachno*-$5,4,6\text{-}PdS_2B_6H_8]$ contains a nine-vertex PdS_2B_6 cage with the Pd atom η^4-bonded to two S and two B atoms. The Pd—S distances are notably asymmetric at 2.3588 (14) and 2.6759 (15) Å, whereas the interatomic distances of symmetry-related pairs of Pd—B, S—B and B—B atoms indicate symmetric bonding. The two *exo* cage dimethylphenylphosphine ligands are attached to the Pd atom with Pd—P 2.2986 (15) and 2.2876 (13) Å. Bridging H atoms in the $S_2B_6H_8$ moiety are asymmetrically bonded.

Comment

There is much current interest in transition element derivatives of thia-boranes containing more than one S atom (Mazighi, Carroll & Sneddon, 1992; Murphy *et al.*, 1994; Murphy, 1994). The title compound, (1), is the first monomeric PdS_2B_6 complex to be structurally characterized.



(1)

The X-ray analysis shows that the Pd atom in (1) is bonded to two PMe_2Ph ligands as well as to a S_2B_2 section of the $S_2B_6H_8$ cage (Fig. 1). The nine-vertex cage structure can be described in terms of Wade's rules as a variation of [*arachno*-B_9H_{15}] with the $Pd(PMe_2Ph)_2$ unit equivalent to BH and each S to BH_2 (Wade, 1976). The *exo*-cage Pd—P distances of 2.2986 (15) and 2.2876 (13) Å may be compared with previously reported Pd—PMe_2Ph distances in palladaheteroborane cages, such as 2.311 (3) and 2.327 (3) Å in $[3,3\text{-}(PMe_2Ph)_2$-*closo*-$3,2,1\text{-}PdAs_2B_9H_9]$,

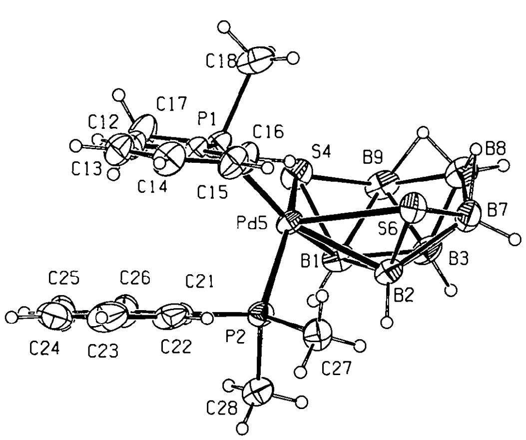


Fig. 1. A view of (1) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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(2) (Jasper, Roach, Stipp, Huffman & Todd, 1993), and 2.3301 (7) and 2.3354 (8) Å in [2,2-$(PMe_2Ph)_2$-*closo*-2,1-$PdTeB_{10}H_{10}$], (3) (Ferguson *et al.*, 1993).

The Pd—S interactions in (1) are remarkably asymmetric [Pd5—S6 2.6759 (15), Pd5—S4 2.3588 (14) Å]. This is not typical of previously published structures of metalladithiaboranes, most of which exhibit closely similar metal–sulfur distances. Examples are 2.235 (1) and 2.231 (1) Å in [7-(η^5-C_5H_5)-*arachno*-7,6,8-$CoS_2B_6H_8$], (4) (Zimmerman & Sneddon, 1981), 2.3614 (14) and 2.3607 (14) Å in [5-(η^5-C_5Me_5)-*arachno*-5,4,6-$RhS_2B_6H_8$], (5) (Murphy *et al.*, 1994), 2.369 (2) and 2.367 (2) Å in [7-(η^6-C_6Me_6)-*arachno*-7,6,8-$RuS_2B_6H_8$], (6), and 2.409 (4) and 2.402 (4) Å in [1-(η^6-C_6Me_6)-Cl-*hypho*-1,2,5-$RuS_2B_6H_9$], (7) (Mazighi, Carroll & Sneddon, 1992). However, some asymmetry is observed in the metal–sulfur distances in [7,7-(dppe)-*arachno*-7,6,8–$NiS_2B_6H_8$], (8) [2.311 (2) and 2.240 (1) Å; Mazighi, Carroll & Sneddon, 1992], but this is less pronounced than in (1).

The Pd—B distances in (1) of 2.261 (6) and 2.280 (5) Å are typical of palladaboranes (Orpen *et al.*, 1994). These distances are surprisingly similar given the asymmetric nature of the Pd—S interactions. The $PdS_2B_6H_8$ cup has potentially mirror symmetry and comparison of such symmetry-related S—B and B—B dimensions adjacent to the Pd—S bonds shows them to be similar despite the asymmetrical Pd—S bonding (Table 2). Maxima corresponding with the H atoms bridging B7—B8 and B8—B9 were clearly visible in difference map sections and both H78 and H89 appear closer to B8 than B7 or B9 (Table 2). A similar situation exists in [5-(η^5-C_5Me_5)-*arachno*-5,4,6-$RhS_2B_6H_8$], (5) (Murphy *et al.*, 1994).

In (1), the dihedral angle between the Pd5–P1–P2 and Pd5–B3–B8 atom planes is 27.8 (4)°, which compares with the value of 12.7° between the planes containing the equivalent sets of atoms in (8). The dihedral angle between the Pd5–S4–S6 and Pd5—P1—P2 planes is 70.9 (1)°.

Experimental

The reaction between equimolar quantities of [tmndH][*hypho*-1,2-$S_2B_6H_9$] (Murphy, 1994) [tmnd = *N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine] and [Pd$(PMe_2Ph)_2Cl_2$] in CH_2Cl_2 solution afforded crystals of the title compound in 25% yield.

Crystal data

[Pd$(B_6H_8S_2)(C_8H_{11}P)_2$]
$M_r = 519.72$
Triclinic
$P\bar{1}$
$a = 9.530$ (3) Å
$b = 10.268$ (2) Å
$c = 13.235$ (3) Å
$\alpha = 70.34$ (2)°
$\beta = 86.15$ (2)°
$\gamma = 84.81$ (2)°
$V = 1213.8$ (6) Å^3
$Z = 2$
$D_x = 1.422$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10.05$–19.95°
$\mu = 1.069$ mm^{-1}
$T = 294$ (1) K
Plate
0.41 × 0.20 × 0.08 mm
Orange–red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: four ψ scans at 4° steps (North, Phillips & Mathews, 1968)
$T_{\min} = 0.834$, $T_{\max} = 0.991$
4241 measured reflections
4241 independent reflections
2972 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max} = 25°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: none
variation 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0380$
$wR(F^2) = 0.0913$
$S = 1.000$
4241 reflections
244 parameters
H atoms: B—H(bridge) from $\Delta\rho$ map, others riding [C—H 0.93–0.98, B—H(terminal) 1.10 Å]
$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.683$ e Å^{-3}
$\Delta\rho_{\min} = -0.503$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
B1	0.1209 (6)	−0.0135 (5)	0.3095 (5)	0.057 (2)
B2	0.1663 (5)	0.1276 (5)	0.1880 (5)	0.0490 (14)
B3	0.2332 (6)	−0.0500 (6)	0.2071 (5)	0.056 (2)
S4	−0.05589 (14)	−0.09189 (12)	0.32249 (12)	0.0614 (4)
Pd5	−0.05735 (4)	0.15210 (3)	0.25537 (3)	0.04185 (13)
S6	0.06234 (13)	0.19766 (12)	0.05892 (10)	0.0528 (3)
B7	0.1962 (6)	0.0510 (7)	0.0689 (5)	0.062 (2)
B8	0.1675 (7)	−0.1304 (6)	0.1258 (6)	0.067 (2)
B9	0.0991 (6)	−0.1698 (5)	0.2611 (5)	0.059 (2)
P1	−0.29891 (12)	0.18793 (13)	0.25398 (11)	0.0485 (3)
P2	0.00313 (13)	0.34835 (12)	0.28202 (10)	0.0447 (3)
C11	−0.3755 (4)	0.3641 (5)	0.1991 (4)	0.0443 (11)
C12	−0.4835 (5)	0.4215 (5)	0.2484 (4)	0.0576 (13)
C13	−0.5360 (5)	0.5578 (6)	0.2011 (5)	0.067 (2)
C14	−0.4798 (5)	0.6370 (6)	0.1053 (5)	0.0664 (15)
C15	−0.3733 (5)	0.5819 (5)	0.0535 (4)	0.0632 (14)
C16	−0.3206 (5)	0.4462 (5)	0.1007 (4)	0.0561 (13)
C17	−0.3903 (6)	0.1133 (6)	0.3826 (5)	0.084 (2)
C18	−0.3678 (6)	0.1025 (6)	0.1694 (5)	0.076 (2)
C21	−0.1321 (5)	0.4429 (5)	0.3389 (4)	0.0514 (12)
C22	−0.1815 (6)	0.5773 (6)	0.2853 (5)	0.071 (2)
C23	−0.2845 (7)	0.6436 (7)	0.3337 (8)	0.095 (2)
C24	−0.3334 (7)	0.5774 (10)	0.4351 (8)	0.102 (3)
C25	−0.2867 (7)	0.4442 (10)	0.4896 (6)	0.102 (3)
C26	−0.1871 (6)	0.3753 (7)	0.4418 (5)	0.075 (2)
C27	0.0707 (6)	0.4783 (5)	0.1624 (4)	0.0619 (14)
C28	0.1437 (5)	0.3150 (6)	0.3759 (4)	0.0668 (15)

Table 2. *Selected geometric parameters (Å, °)*

B1—B2	1.823 (8)	Pd5—P1	2.2986 (15)
B1—B3	1.788 (9)	Pd5—P2	2.2876 (13)
B1—S4	1.905 (6)	S6—B7	1.858 (6)
B1—Pd5	2.261 (6)	B7—B8	1.798 (9)
B1—B9	1.949 (8)	B8—B9	1.789 (9)
B2—B3	1.815 (7)	P1—C11	1.811 (5)
B2—Pd5	2.280 (5)	P1—C17	1.813 (5)
B2—S6	1.921 (6)	P1—C18	1.822 (5)
B2—B7	1.980 (9)	P2—C21	1.818 (5)
B3—B7	1.814 (9)	P2—C27	1.816 (5)
B3—B8	1.736 (9)	P2—C28	1.819 (5)
B3—B9	1.797 (8)	B7—H78	1.47
S4—Pd5	2.3588 (14)	B8—H89	1.13
S4—B9	1.883 (6)	B8—H78	1.15
Pd5—S6	2.6759 (15)	B9—H89	1.47
B1—S4—B9	61.9 (3)	S4—Pd5—P2	146.81 (5)
Pd5—S4—B9	109.7 (2)	S4—Pd5—P1	94.86 (5)
B1—S4—Pd5	63.0 (2)	B1—Pd5—S6	84.9 (2)
B1—Pd5—B2	47.3 (2)	B2—Pd5—S6	44.73 (15)
B1—Pd5—P2	108.3 (2)	S6—Pd5—P2	98.13 (5)
B2—Pd5—P2	88.20 (14)	S6—Pd5—P1	112.87 (5)
B1—Pd5—P1	143.03 (14)	S4—Pd5—S6	102.14 (5)
B2—Pd5—P1	157.25 (15)	B2—S6—B7	63.2 (3)
P1—Pd5—P2	101.15 (5)	Pd5—S6—B7	106.7 (2)
B1—Pd5—S4	48.65 (14)	B2—S6—Pd5	56.7 (2)
B2—Pd5—S4	88.00 (13)		

Fig. 1 was prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1995*a*). Examination of the structure with *PLATON* showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*-4 and *CELDIM* (Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*94. Program(s) used to refine structure: *NRCVAX*94 and *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*94, *PLATON* (Spek, 1995*a*) and *PLUTON* (Spek, 1995*b*). Software used to prepare material for publication: *NRCVAX*94 and *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1335). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1992). *CAD-4-PC*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G., Gallagher, J. F., McGrath, M., Sheehan, J. P., Spalding, T. R. & Kennedy, J. D. (1993). *J. Chem. Soc. Dalton Trans.* pp. 27–34.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Jasper, S. A., Roach, S., Stipp, J. N., Huffman, J. C. & Todd, L. J. (1993). *Inorg. Chem.* **31**, 3072–3080.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Mazighi, K., Carroll, P. J. & Sneddon, L. G. (1992). *Inorg. Chem.* **31**, 3197–3204.

Murphy, M. P. (1994). PhD thesis, University College, Cork, Ireland.

Murphy, M., Spalding, T. R., Kennedy, J. D., Thornton-Pett, M., Abdul-Malik, K. M., Hursthouse, M. B. & Holub, J. (1994). *J. Chem. Soc. Chem. Commun.* pp. 2403–2404.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1994). *Structure Correlation*, Vol. 2, edited by H.-B. Bürgi & J. D. Dunitz, p. 785. Weinheim: VCH.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1995*a*). *PLATON. Molecular Geometry Program.* July 1995 version. University of Utrecht, The Netherlands.

Spek. A. L. (1995*b*). *PLUTON. Molecular Graphics Program.* July 1995 version. University of Utrecht, The Netherlands.

Wade, K. (1976). *Adv. Inorg. Chem. Radiochem.* **18**, 1–66.

Zimmerman, G. J. & Sneddon, L. G. (1981). *J. Am. Chem. Soc.* **103**, 1102–1111.

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Bromo[tris(2-cyanoethyl)phosphine]gold(I), [(CEP)AuBr]

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Abstract

In $[AuBr(C_9H_{12}N_3P)]$, two C≡N groups of the tris(2-cyanoethyl)phosphine (CEP) ligand are positioned in the vicinity of square-planar coordination sites so as to shield the central Au^I atom in at least two directions. Although the disposition of two of the C≡N groups is indicative of Au···C≡N interactions, these groups do not participate in the metal coordination. The observed shielding of the metal atom is similar to that reported for one of the polymorphs of the monomeric complex [(CEP)AuCl].

Comment

We have been studying the chemistry and crystal structures of linear monomeric gold(I) complexes with ligands having phosphorus, sulfur and selenium donors as a part of our research program dealing with model compounds for gold drugs (Hussain & Schlemper, 1987; Hussain, 1986; Hussain & Isab, 1984, 1985*a*,*b*; Isab & Hussain, 1986). The triorganophosphine tris(2-