

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.

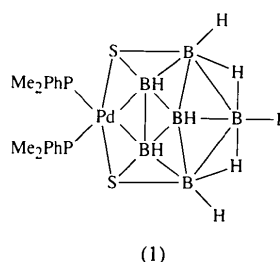
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Pd—S distances are notably asymmetric at 2.3588 (14) and 2.6759 (15) Å, whereas the interatomic distances of symmetry-related pairs of Pd—B, S—B and B—B atoms indicate symmetric bonding. The two *exo* cage dimethylphenylphosphine ligands are attached to the Pd atom with Pd—P 2.2986 (15) and 2.2876 (13) Å. Bridging H atoms in the S₂B₆H₈ 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 PdS₂B₆ complex to be structurally characterized.



The X-ray analysis shows that the Pd atom in (1) is bonded to two PMe₂Ph ligands as well as to a S₂B₂ section of the S₂B₆H₈ cage (Fig. 1). The nine-vertex cage structure can be described in terms of Wade's rules as a variation of [*arachno*-B₉H₁₅] with the Pd(PMe₂Ph)₂ unit equivalent to BH and each S to BH₂ (Wade, 1976). The *exo*-cage Pd—P distances of 2.2986 (15) and 2.2876 (13) Å may be compared with previously reported Pd—PMe₂Ph distances in palladaheteroborane cages, such as 2.311 (3) and 2.327 (3) Å in [3,3-(PMe₂Ph)₂-*closo*-3,2,1-PdAs₂B₉H₉],

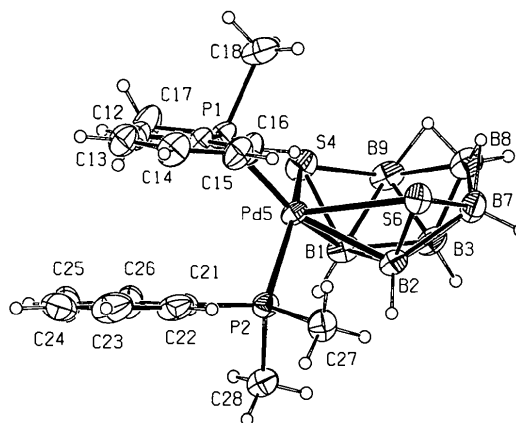


Fig. 1. A view of (1) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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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-(PMe₂Ph)₂-*arachno*-5,4,6-PdS₂B₆H₈] contains a nine-vertex PdS₂B₆ cage with the Pd atom η⁴-bonded to two S and two B atoms. The

(2) (Jasper, Roach, Stipp, Huffman & Todd, 1993), and 2.3301 (7) and 2.3354 (8) Å in [2,2-(PMe₂Ph)₂-closo-2,1-PdTeB₁₀H₁₀], (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-(η⁵-C₅H₅)-*arachno*-7,6,8-CoS₂B₆H₈], (4) (Zimmerman & Sneddon, 1981), 2.3614 (14) and 2.3607 (14) Å in [5-(η⁵-C₅Me₅)-*arachno*-5,4,6-RhS₂B₆H₈], (5) (Murphy *et al.*, 1994), 2.369 (2) and 2.367 (2) Å in [7-(η⁶-C₆Me₆)-*arachno*-7,6,8-RuS₂B₆H₈], (6), and 2.409 (4) and 2.402 (4) Å in [1-(η⁶-C₆Me₆)-*Cl-hypho*-1,2,5-RuS₂B₆H₉], (7) (Mazighi, Carroll & Sneddon, 1992). However, some asymmetry is observed in the metal–sulfur distances in [7,7-(dppe)-*arachno*-7,6,8-NiS₂B₆H₈], (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 PdS₂B₆H₈ 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-(η⁵-C₅Me₅)-*arachno*-5,4,6-RhS₂B₆H₈], (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-S₂B₆H₉] (Murphy, 1994) [tmnd = *N,N,N',N'*-tetramethylnaphthalene-1,8-diamine] and [Pd(PMe₂Ph)₂Cl₂] in CH₂Cl₂ solution afforded crystals of the title compound in 25% yield.

Crystal data

[Pd(B₆H₈S₂)(C₈H₁₁P)₂]

M_r = 519.72

Triclinic

P $\bar{1}$

a = 9.530 (3) Å

b = 10.268 (2) Å

c = 13.235 (3) Å

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 10.05–19.95°

μ = 1.069 mm^{−1}

T = 294 (1) K

α = 70.34 (2)°

β = 86.15 (2)°

γ = 84.81 (2)°

V = 1213.8 (6) Å³

Z = 2

D_x = 1.422 Mg m^{−3}

Data collection

Enraf–Nonius CAD-4

diffractometer

θ/2θ 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* > 2σ(*I*)]

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0380

wR(*F*²) = 0.0913

S = 1.000

4241 reflections

244 parameters

H atoms: B—H(bridge) from

Δρ map, others riding

[C—H 0.93–0.98, B—

H(terminal) 1.10 Å]

Plate

0.41 × 0.20 × 0.08 mm

Orange-red

θ_{max} = 25°

h = −11 → 11

k = 0 → 12

l = −14 → 15

3 standard reflections

frequency: 120 min

intensity decay: none

variation 1.0%

w = 1/[σ²(*F*_o²) + (0.0436*P*)²]
where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = 0.003

Δρ_{max} = 0.683 e Å^{−3}

Δρ_{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 (Å²)

	$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{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 *ORTEPII* (Johnson, 1976) as implemented in *PLATON* (Spek, 1995a). 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: *DATRD2* in *NRCVAX94* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX94*. Program(s) used to refine structure: *NRCVAX94* and *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX94*, *PLATON* (Spek, 1995a) and *PLUTON* (Spek, 1995b). Software used to prepare material for publication: *NRCVAX94* and *SHELXL93*.

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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.

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

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Abstract

In [AuBr(C₉H₁₂N₃P)], 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, 1985a,b; Isab & Hussain, 1986). The triorganophosphine tris(2-