Synthesis and Crystal Structure of $[Pd(PPh_3)S_2B_6H_8]_2$: a Dimeric Metallaheteroborane with Heteroatoms acting Both as Cluster Atoms and Two-electron Donor Sites

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The novel palladadithiaborane dimer [*arachno*-$Pd(PPh_3)S_2B_6H_8]_2$ contains sulfur atoms that are simultaneously cluster atoms and *exo*-polyhedral two-electron donors to palladium atoms in the adjacent cage.

Sulfur, selenium, and tellurium atoms, which are incorporated into *closo*, *nido*, or *arachno* heteroborane cages, apparently lack a general ability to act as *exo*-cage donor sites. MO calculations of neutral thiaborane clusters indicate that the sulfur sites are positively charged,[1a–d] and that the amount of positive charge progressively reduces in a series of related *closo*, *nido*, *arachno* and *hypho* clusters.[1c,d] Thus, the sulfur atoms become more like those in ligands such as R_2S, RS^- and dithiolates. An AMPAC MO calulation of the [*hypho*-$7,8,S_2B_6H_9]^-$ anion indicates that the two HOMOs are 80% located on the sulfur atoms and directed away from the cluster towards incoming electrophiles/Lewis acids. In accord with this, the potential for [*hypho*-$7,8\text{-}S_2B_6H_9]^-$ to act as a bidentate ligand has been recently demonstrated in [9-(η^6-C_6Me_6)-9-Cl-*hypho*-$9,7,8\text{-}RuS_2B_6H_9$] **2** where the ruthenium atom is bonded to the dithiaborane cage by the sulfur atoms only.[2] Two interpretations were initially suggested for the electronic structure of this complex.[2] Either it can be viewed as a nine-vertex *hypho*-RuS_2B_6 cluster or as an η^2-*S*,*S′* dithiolene-type coordination complex of ruthenium(II). The latter explanation appeared to be preferred though both were reasonably valid.[2]

We now report the first metallathiaborane containing sulfur atoms that bond simultaneously as cluster atoms and as two-electron donors to metal atoms in other cluster cages.

Orange crystals of a compound tentatively identified as the *hypho*-type species [$9,9\text{-}(PPh_3)_2\text{-}9\text{-}Cl\text{-}9,7,8\text{-}PdS_2B_6H_9$] **3** were obtained from the reaction between [$PdCl_2(PPh_3)_2$] and [tmndH][*hypho*-$7,8\text{-}S_2B_6H_9$]† **4** in CH_2Cl_2 [tmnd = *N*,*N*,*N′*,*N′*-tetramethylnaphthalene-1,8-diamine]. On attempted recrystallisation from CH_2Cl_2–toluene solution, small red–orange crystals of the toluene solvate of $[Pd(PPh_3)S_2B_6H_8]_2$ **5** precipitated.‡ The crystal structure of **5**, Fig. 1, was solved using data collected with a FAST area-detector diffractometer.§ Compound **5** is seen to be a symmetric dimer based on two interlinked, identical {PdS_2B_6} cages. Within each {PdS_2B_6} cage each sulfur atom is bonded to two boron atoms as in the precursor anion [*hypho*-$S_2B_6H_9]^-$. However, one sulfur, S(5), in each cage is also bound to the palladium atom Pd(6) and the other sulfur atom, S(9), acts as a two-electron intercluster donor to the palladium atom Pd(6′) in the adjacent cage. Each palladium has an *exo*-polyhedral PPh_3 ligand attached. According to cluster electron counting rules, each [$(S')(PPh_3)PdS_2B_6H_8$] cage is an *arachno* species and takes the shape of the *n*-B_9H_{15} species rather than the more common geometry of the [*iso*-$B_9H_{14}]^-$ moiety. Interestingly, the intracage Pd(6)–S(5) distance of 2.3750(10) Å is significantly shorter than the intercage Pd(6)–S(9′) distance, 2.4278(10) Å. ‘Normal’ palladium to sulfur distances in a number of coordination complexes are generally in the range 2.30 to 2.35 Å, but a few are reported to exceed 2.375 Å.[3] The intercage Pd(6)–S(5′) distance is non-bonding at 3.214(1) Å. The geometry at palladium may be described as distorted square planar with two-centre interactions between Pd(6) and each of S(5), S(9′) and P(1), and a three-centre bond between Pd(6) and B(1)/B(2), Fig. 1. The palladium has a stronger interaction with B(2) compared with B(1). In **5** the mean of the S–B distances to S(9) is 1.892 Å, notably shorter than the mean to S(5), 1.923 Å. The B–S–B angles differ significantly, being 62.1(2)° at S(9) and 59.2(2)° at S(5). These data can be compared to the related distances and angles in eight-vertex *hypho*-$7,8\text{-}Me_2\text{-}7,8\text{-}S_2B_6H_8$ **6** and nine-vertex *hypho*-$9\text{-}CH_2\text{-}7,8\text{-}S_2B_6H_8$ **7** which contain sulfur atoms that are more symmetrically bonded [range of B–S distances in **6** 1.918(5) to 1.924(5) Å and in **7** 1.900(7) to 1.923(7) Å: B–S–B angles in **6** 59.0(2)° and in **7** 58.5(3) and 58.6(3)°].[4] The S–B distances in **5**, **6** and **7** are close to the value of 1.89 Å typical of a two electron two-centre bond. However, it must be noted that such bonds have a large range *i.e.* 1.800[5a] to 1.94.[5b]

Recently, a series of monomeric *arachno* $MS_2B_6H_9$ clusters with η^4-S_2B_2-to-metal linkages have been characterised which are clearly different from the $MS_2B_6H_9$ structure in **5**.[6] These have cluster geometries based on that of [*iso*-$B_9H_{14}]^-$ and include [$5\text{-}(L)\text{-}5,4,6\text{-}MS_2B_6H_8$] [LM = ($\eta^6$-$C_6Me_6$)Ru **8**,[2]

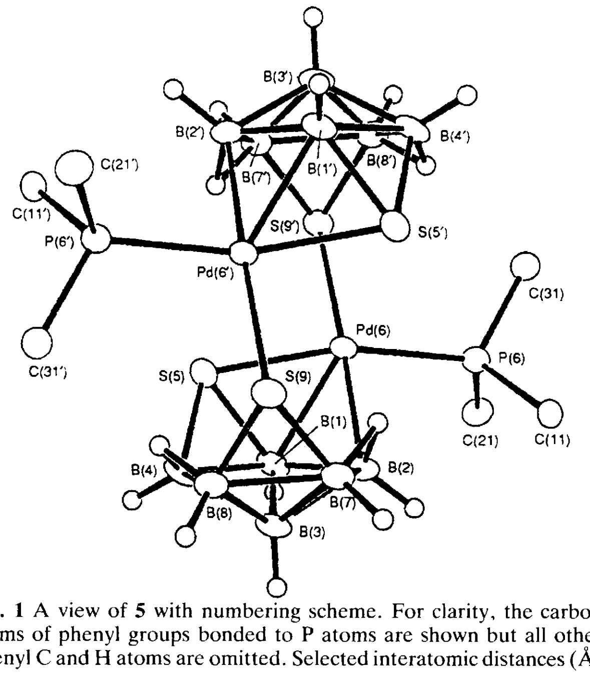

Fig. 1 A view of **5** with numbering scheme. For clarity, the carbon atoms of phenyl groups bonded to P atoms are shown but all other phenyl C and H atoms are omitted. Selected interatomic distances (Å) and angles (°): Pd(6)–S(9′) 2.4278(10), Pd(6)–S(5) 2.3750(10), Pd(6)–P(6) 2.3126(10), Pd(6)–B(1) 2.261(5), Pd(6)–B(2) 2.214(5), S(9)–B(8) 1.874(5), S(7)–B(7) 1.909(5), S(5)–B(4) 1.948(4), S(5)–B(1) 1.897(5), B(4)–B(8) 1.837(7), B(2)–B(7) 1.816(7), B(7)–B(8) 1.952(6), B(1)–B(4) 1.901(6), B(1)–B(2) 1.785(7), B–B distances to B(3) range from B(3)–B(4) 1.752(7) to B(3)–B(8) 1.825(6); angles at Pd, S(9′)–Pd(6)–S(5) 90.88(3), S(9′)–Pd(6)–P(6) 96.25(3), B(2)–Pd(6)–S(5) 86.93(12), B(2)–Pd(6)–P(6) 85.80(12), S(9′)–Pd(6)–B(2) 177.80(12), P(6)–Pd(6)–S(5) 160.72(4), B(1)–Pd(6)–S(5) 48.24(12), B(1)–Pd(6)–B(2) 47.0(2), and at S, B(1)–S(5)–B(4) 59.2(2), Pd(6)–S(5)–B(1) 62.74(14), B(7)–S(9)–B(8) 62.1(2), B(8)–S(9)–Pd(6′) 111.8(2), B(7)–S(9)–Pd(6′) 115.66(14).

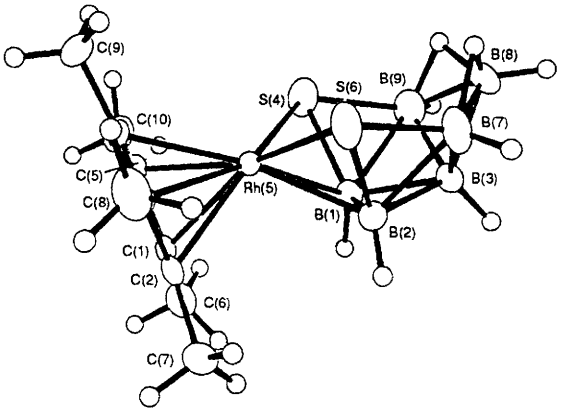

Fig. 2 A view of molecule 1, compound **10** with numbering scheme. Selected interatomic distances (Å) and angles (°): Rh(5)–S(4) 2.3614(14), Rh(5)–S(6) 2.3607(14), Rh(5)–B(1) 2.219(5), Rh(5)–B(2) 2.213(5), Rh(5)–C_{ring} range 2.171(4) to 2.205(4), S(4)–B(1) 1.940(6), S(4)–B(9) 1.882(6), S(6)–B(2) 1.938(5), S(6)–B(7) 1.888(6), B(1)–B(2) 1.802(9), B(1)–B(9) 1.911(8), B(2)–B(7) 1.931(8); angles at Rh, S(4)–Rh(5)–S(6) 101.10(6), S(4)–Rh(5)–B(1) 50.0(2), S(6)–Rh(5)–B(2) 50.0(2), B(1)–Rh(5)–B(2) 48.8(2), and at S atoms, Rh(5)–S(4)–B(1) 61.2(2), Rh(5)–S(6)–B(2) 61.0(2), B(1)–S(4)–B(9) 60.0(3), B(2)–S(6)–B(7) 60.6(2).

$(PPhMe_2)_2Pd$ **9**,[6b] and (η^5-C_5Me_5)Rh **10**[6¶]. Crystals of [5-(η^5-C_5Me_5)-*arachno*-5,4,6-$RhS_2B_6H_8$] **10** contain two independent molecules in the asymmetric part of the unit cell which have very similar $MS_2B_6H_9$ bonding parameters. In **10**, Fig. 2 (molecule 1),|| the rhodium atom is symmetrically bonded to the η^4-S_2B_2-moiety with mean Rh-S distances of 2.3611(14) and 2.3666(13) Å in molecules 1 and 2 respectively.|| These may be compared with mean Rh-S distances in complexes of dithiolates, 2.308, and thioethers, 2.430 Å.[3]

In the light of the structure of **5**, the data from other *arachno* and *hypho* compounds mentioned above, and the results of MO calculations on thiaboranes, a reasonable model of the electronic structure of the $\{MS_2B_6H_8\}$ cages in **5** would contain both localised two-centre sulfur–metal and sulfur–boron bonds and multicentre bonds in the MB_6H_8 region of the compound.

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Footnotes

† [tmndH][*hypho*-7,8-$S_2B_6H_9$] **4**. A solution 4,6-$S_2B_7H_9$[7] (0.100 g, 0.672 mmol) in ethanol (5 cm^3) was added to a solution of tmnd (0.144 g, 0.672 mmol) in ethanol (10 cm^3). After stirring at room temp. for 90 min gas evolution had ceased. The reaction mixture was filtered affording a white solid which was washed with chilled ethanol (10 cm^3). Recrystallisation from CH_2Cl_2–toluene gave colourless needle crystals of [tmndH][*hypho*-7,8-$S_2B_6H_9$] (0.192 g, 80.9%). IR: ν_{max}(KBr) 2550s, 2512s, 2463vs (BH) cm^{-1}. $^{11}B\{^1H\}$ NMR (CD_2Cl_2, 297 K): δ (multiplicity, intensity) +4.4 (s, 2B), −24.5 (s, 2B), −27.3 (s, 1B), −54.5 (s, 1B).

‡ $[(PPh_3)PdS_2B_6H_8]_2.C_7H_8$, **5**·$C_7H_8$. To a suspension of $[Pd(PPh_3)_2Cl_2]$ (0.100 g, 0.142 mmol) in dichloromethane (20 cm^3) was added [tmndH][7,8-$S_2B_6H_9$] (0.052 g, 0.142 mmol). The reaction mixture was stirred at room temp. for 20 h. It was concentrated under reduced pressure and subjected to preparative TLC (CH_2Cl_2 : heptane) (3:2). An orange band (R_f = 0.45) was extracted into CH_2Cl_2. Recrystallisation from CH_2Cl_2–hexane gave orange crystals of a compound tentatively assigned as [9,9-$(PPh_3)_2$-9-Cl-*hypho*-9,7,8-$PdS_2B_6H_9$] **3** (0.010 g, 8.7%). IR: ν_{max} (KBr) 2538s(sh), 2531s(sh), 2515s (BH) cm^{-1}. NMR data (CD_2Cl_2, 297 K): {ordered as proposed assignment, δ(^{11}B), [δ (^1H)/ppm]}: BH(2) and BH(5) +3.5 [+3.00] and *ca.* +1.0 [+3.48], BH(3) and BH(4) *ca.* −20.7 [+1.94] and −22.0 [+1.93], BH(6) *ca.* −22.0 [+2.60], BH(1) −53.7 [−0.46]; μH(3,4) −0.67, μH(5,6) −1.20 and μH(2,6) −1.37; δ(^{31}P) +21.8 at 219 K. Attempted recrystallisation of **3** from a CH_2Cl_2–toluene solution over a period of three weeks afforded small red–orange crystals of $[(PPh_3)PdS_2B_6H_8]_2 \cdot C_7H_8$, **5**·$C_7H_8$ (90.0%). IR: ν_{max} (KBr) 2525s(sh), 2520s(sh), 2503s, 2495s(sh) (BH) cm^{-1}.

§ *Crystal data* for **5**·C_7H_8: $C_{36}H_{46}B_{12}P_2Pd_2S_4.C_7H_8$, red–orange crystal, M_r = 1103.6, monoclinic, space group $P2_1/n$, a = 10.246(2), b = 17.1844(8), c = 14.2576(5) Å, β = 93.223(13)°, U = 2506.3(4) $Å^3$, Z = 2, D_c = 1.462 Mg m^{-3}, $F(000)$ = 1116, μ(Mo-Kα) = 0.98 mm^{-1}, T = 150 K. A total of 8001 reflections collected to 2θ = 50° on a FAST area-detector diffractometer using previously described procedures.[8] The structure was solved by heavy-atom methods (SHELXS-86)[9a] and refined anisotropically by full-matrix least-squares based on all unique F^2 (SHELXL-93).[9b] Restraints were applied to the phenyl rings such that they remained flat with overall C_{2v} symmetry. Ligand hydrogen atoms were included with a riding model, cluster hydrogen atoms were freely refined. The asymmetric part of the unit cell of **5** contained a toluene solvate molecule which was disordered across a centre of symmetry at $\frac{1}{2}$, 0, $\frac{1}{2}$. The final $\omega R(F^2)$ for all 8001 reflections was 0.0963 with a conventional $R(F)$ of 0.0338 [for 3168 reflections with $I > 2.0\ \sigma(I)$] for 345 parameters.

¶ [5-(η^5-C_5Me_5)-5,4,6-$RhS_2B_6H_8$] **10**, (compare ref. 6*a*). A solution of [tmndH][7,8-$S_2B_6H_9$] (0.050 g, 0.141 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (0.044 g, 0.071 mmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred at room temp. for 3 h. It was concentrated under reduced pressure and subjected to preparative TLC (CH_2Cl_2 : heptane) (3:2). The major yellow band was extracted into CH_2Cl_2. Recrystallisation from CH_2Cl_2–EtOH gave orange crystals of [5-(η^5-C_5Me_5)-5,4,6-*arachno*-$RhS_2B_6H_8$] **10** (0.038 g, 63.8%). IR: ν_{max}(KBr) 2541m(sh), 2512s, 2500m(sh) (BH) cm^{-1}. NMR data (CD_2Cl_2, 294–297 K) {ordered as relative intensity, δ(^{11}B), [^1J(^{11}B–^1H)/Hz], δ(^1H)}: 2BH +3.6 [155] +3.64, 2BH −10.3 [169] +1.85, 1BH −35.6 [149 d: 58 t] +1.52 and −1.25, 1BH −41.2 [144] +0.40; δ(^1H)(C_5Me_5) +1.89.

|| *Crystal data* for **10**: $C_{10}H_{23}B_6RhS_2$, orange crystal, M_r = 375.17, monoclinic, space group $P2_1/c$, a = 14.967(2), b = 13.963(2), c = 16.1880(13) Å, β = 103.187(7)°, U = 3293.8(7) $Å^3$, Z = 8, D_c = 1.513 Mgm^{-3}, $F(000)$ = 1520, μ(Mo-Kα) = 1.269 mm^{-1}, T = 180 K. A total of 5804 reflections collected to 2θ = 50° on a Stoe STAD14 diffractometer using ω/θ scans and an on-line profile fitting method.[10] The structure was solved and refined as for compound **5** above. The asymmetric part of the unit cell of **10** contained two molecules which differed principally by a rotation (*ca.* 36°) of the C_5Me_5 ligand relative to the rhodathiaborane cage. The final $\omega R(F^2)$ for all 5804 reflections was 0.0791 with a conventional $R(F)$ of 0.0339 [for 4330 reflections with $I > 2.0\sigma(I)$] for 417 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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