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9-(Triphenylphosphine-*P*)-*arachno*-6-thiadecaborane(11) Trichloromethane (1/1)

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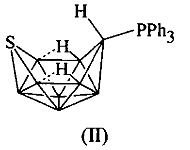
Abstract

The title compound, $C_{18}H_{26}B_9PS.CHCl_3$ is shown to have an *arachno* ten-vertex $\{6\text{-}SB_9H_{11}\}$ cluster structure with a PPh_3 ligand in the *exo*-9-position. The two bridging H atoms occupy asymmetric positions [average B—H_{bridge} values 1.21 (4) and 1.35 (4) Å] displaced away from the S atom.

Comment

Dicarbaborane chemistry dominates the molecular polyhedral chemistry of boron (Štíbr, 1992; Saxena & Hosmane, 1993). There is, however, tremendous potential for much added variety in other heteroborane chemistry, which is, by comparison, sparsely represented. The next best represented polyhedral heteroboranes are those of sulfur, and there is increasing interest in the investigation of this area (*e.g.* Jelínek *et al.*, 1991). One current focus is on the ten-vertex *arachno*-6-thiadecaboranes, for both their intrinsic interest and as starting substrates for further syntheses (Ferguson *et al.*, 1990; Holub *et al.*, 1994; Adams *et al.*, 1995). In this context, a structural report on [9-(Cy_2PPh)-*arachno*-6-SB_9H_{11}], (I) (where Cy is cyclohexyl) (Rosair *et al.*, 1996), which alluded to an apparent uncertainty in the structure of its 9-(PPh_3) congener, (II) (Štíbr *et al.*, 1996; Nestor *et al.*, 1991), prompted us to report our structural work on compound (II).



(II)

The title compound (II), as isolated from the reaction of PPh_3 with *nido*-6-SB_9H_{11} (Štíbr *et al.*, 1996), is seen to adopt an *exo*-(PPh_3) configuration, like the Cy_2PPh analogue, (I), and other 9-ligand derivatives that have been structurally characterized (Štíbr *et al.*, 1996; Hilty & Rudolph, 1979). The reported NMR parameters for [9-(PPh_3)-*arachno*-6-SB_9H_{11}], as isolated from the thermolysis of [*exo*-9-{Cl-*trans*-$(PPh_3)_2$-*cis*-H_2Ir}-*arachno*-6-SB_9H_{11}] (Nestor *et al.*, 1991), for which the possibility of an *endo*-9-(PPh_3) placement was tentatively proposed (though not equivocally established), are somewhat different from those reported for the *exo*-9-(PPh_3) species structurally established here (Štíbr *et al.*, 1996). The *endo*-9-(PPh_3) structure was initially proposed on the basis of a lower ^1H NMR shielding of the B9 proton (Nestor *et al.*, 1991), but more recent systematic work (Štíbr *et al.*, 1996) has shown that such a lower shielding is in fact quite general for the *exo*-structured compounds. On the other hand, the little information available (Štíbr *et al.*, 1996) suggests that *exo* and *endo* isomers in these [9-*L*-*arachno*-6-*E*B_9H_{11}] systems (where *E* = NH as well as S) often do have very similar NMR properties.

The crystallographic data obtained in this study assist comparison with compounds with other ligands *L* in the *exo*-9-*L*-*arachno*-6-SB_9H_{11} system (Table 2), of which *L* = NEt_3 (Hilty & Rudolph, 1979), (III), and MeCN (Štíbr *et al.*, 1996), (IV), have also been reported. There appear to be differential effects of the ligands on intracluster distances adjacent to the ligand site. Thus, distances from the substituted site B9 to its adjacent B atoms are shorter for *L* = MeCN, (IV), than for the stronger ligand NEt_3, (III), whereas those for the two reasonably strong phosphine ligands are intermediate between the two, though closer to the value for *L* = NEt_3, (III). Other interboron distances and S—B distances are very similar among all four compounds for equivalent sites.

An interesting general structural feature that now appears to be consistently emerging for all ten-vertex *arachno*-6-heterodecaboranes is a marked asymmetry of the bonding from the bridging H atoms to the B atoms that they bridge. These are the open-face positions α and β to the heteroatom. Thus, the results

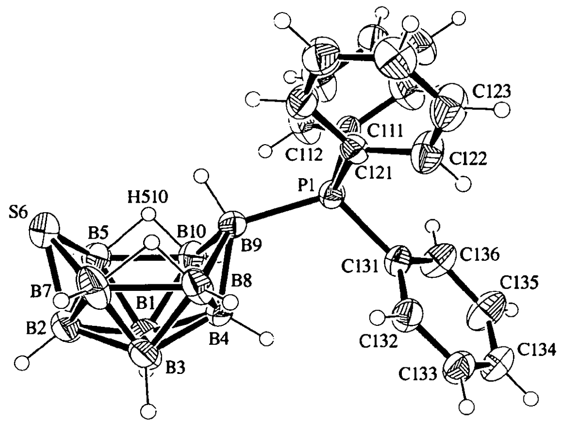


Fig. 1. Perspective view of a single molecule of (II) drawn with 40% probability displacement ellipsoids and with H atoms shown as small circles of arbritrary radii.

for the title compound (II) suggest longer B—H_{bridge} distances on the side adjacent (α) to the heteroatom [mean 1.35 (4) Å] compared to those remote (β) from the heteroatom [mean 1.21 (4) Å]. Similar differential effects are also observed in ten-vertex *arachno*-9,6-metallaheterodecaboranes (Kukina *et al.*, 1985; Jones *et al.*, 1994; Hilty, Thompson *et al.*, 1979; Faridoon *et al.*, 1989; Kim *et al.*, 1998).

Experimental

The title compound [9-(PPh_3)-6-SB_9H_{11}], (II), was prepared according to the method of Štíbr *et al.* (1996) and recrystallized as colourless prisms from chloroform–hexane. Characterization data have been reported elsewhere (Štíbr *et al.*, 1996).

Crystal data

$C_{18}H_{26}B_9PS.CHCl_3$
M_r = 522.08
Monoclinic
$P2_1/c$
a = 11.1590 (12) Å
b = 25.112 (2) Å
c = 9.6630 (9) Å
β = 90.641 (9)°
V = 2707.7 (5) Å^3
Z = 4
D_x = 1.281 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54186 Å
Cell parameters from 28 reflections
θ = 35.3–39.7°
μ = 4.383 mm^{-1}
T = 200 (2) K
Prism
0.41 × 0.37 × 0.31 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω/θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.199, T_{max} = 0.251
4341 measured reflections
4256 independent reflections

3131 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 64.75°
$h = -13 \rightarrow 13$
$k = -29 \rightarrow 0$
$l = -10 \rightarrow 11$
2 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.146
S = 1.006
4256 reflections
378 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 3.8423P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = −0.021
$\Delta\rho_{max}$ = 0.285 e Å^{-3}
$\Delta\rho_{min}$ = −0.378 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

B1—B2	1.742 (7)	B4—B10	1.740 (6)
B1—B5	1.769 (6)	B4—B8	1.744 (6)
B1—B4	1.771 (6)	B5—B10	1.843 (6)
B1—B10	1.783 (6)	B5—H510	1.33 (4)
B1—B3	1.792 (7)	S6—B2	1.913 (5)
B2—B3	1.741 (6)	S6—B5	1.913 (5)
B2—B7	1.882 (7)	S6—B7	1.932 (5)
B2—B5	1.886 (6)	B7—B8	1.856 (6)
B3—B7	1.764 (8)	B7—H78	1.36 (4)
B3—B4	1.773 (6)	B8—H78	1.21 (4)
B3—B8	1.781 (6)	B10—H510	1.21 (4)

Table 2. *Comparison of distances and angles involving the ligand-substituted B9 atoms in compounds $LB_9H_{11}S$*

Distances	PPh_3, (II)	Cy_2PPh^a, (I)	NEt_3, (III)	$MeNC^b$, (IV)
B9—B4	1.719 (5)	1.732 (9)	1.723 (5)	1.742 (5)
B9—B8	1.861 (5)	1.896 (9)	1.904 (5)	1.872 (4)
B9—B10	1.888 (5)	1.897 (10)	1.904 (5)	1.872 (4)
B9—H9	1.12 (3)	1.10 (5)	1.09 (4)	1.05 (3)
Angles at B9				
B4—B9—B8	58.1 (2)	57.2 (4)	56.9 (2)	57.8 (2)
B4—B9—B10	57.5 (2)	57.2 (4)	57.0 (2)	57.8 (2)
B8—B9—B10	104.4 (3)	102.5 (4)	103.4 (2)	104.4 (2)

Notes: (*a*) a common B—$H_{terminal}$ distance was refined. (*b*) There is a crystallographic mirror plane passing through atoms S6, B2, B4 and B9.

Phenyl rings were restrained to be flat and of overall C_{2v} symmetry. All terminal and bridging borane H atoms were located from Fourier difference syntheses and all associated parameters were refined freely. Phenyl H atoms were included with a riding model in calculated positions [C—H = 0.95 Å and U(H) = $1.2U_{eq}$(C)]. A disordered chloroform solvent molecule was modelled as two parts having site occupancies in the ratio 4:1 (occupancy parameters refined for both parts), and each part was treated with equivalent rigid bond and similarity restraints.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*3 (Farrugia, 1997). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1503). Services for accessing these data are described at the back of the journal.

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3-Acetoxy-6-hydroxy-2,4-dimethoxyacetophenone†

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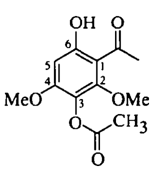
Abstract

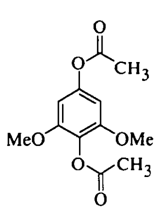
The title compound, $C_{12}H_{14}O_6$, has been isolated from a Fries reaction on 3,6-dihydroxy-2,4-dimethoxyacetophenone. Its molecular structure contains an intramolecular hydrogen-bonded unit involving the $-COCH_3$ and $-OH$ substituents. The best plane through the acetoxy group makes a dihedral angle of 88.74 (5)° with the plane of the aromatic ring.

Comment

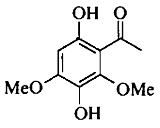
Acetophenones are useful synthons for the preparation of a wide variety of polyphenolic compounds such as chalcones and flavones (Parmar *et al.*, 1996). The synthesis of 3,6-dihydroxy-2,4-dimethoxyacetophenone, (III), was attempted *via* the Fries reaction on compound (II). However, this reaction failed to produce the desired product and instead the partially protected compound (I) (Fig. 1) was obtained as one of the side products; this latter compound has potential in the synthesis of bioactive flavonoids. The X-ray structure of (I) has been determined in order to obtain an unambiguous characterization.



(I)



(II)



(III)

The bond lengths and angles are unexceptional. The variation in C—O bond lengths within the methoxy groups is as expected, *i.e.* O—C_{sp^3} > O—C_{sp^2} (*e.g.* Mukherjee *et al.*, 1996). The methoxy substituent at C4 is almost coplanar with the aromatic ring, but that at C2 is twisted to give a C9—O2—C2—C3 torsion angle of 61.2 (2)°. The acetoxy group is also twisted, making a dihedral angle of 88.7 (1)° with the plane of the aromatic ring. The O1—C7—C1—C6—O6—H6 unit is essentially planar (r.m.s. deviation 0.018 Å) as a result of

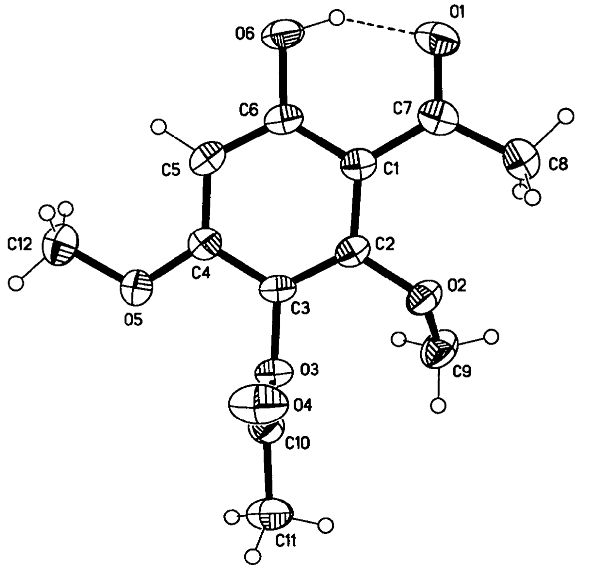


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

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† Alternative name: 3-acetyl-4-hydroxy-2,6-dimethoxyphenyl ethanoate.