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8-($Ph_2PCH_2CH_2PPh_2$)-8,7-*nido*-$RhSB_9H_{10}.2CH_2Cl_2$

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Abstract

The synthesis and the solid-state structure determination by a low-temperature single-crystal X-ray diffraction study of 8-[1,2-bis(diphenylphosphinoethane)]-9,10-μ-hydrido-8-rhoda-7-thia-*nido*-undecaborane(10), [$Rh(B_9H_{10}S)(C_{26}H_{24}P_2)$].$2CH_2Cl_2$, as the bis(dichloromethane) solvate are reported. In terms of conventional electron-counting rules, this species has an anomalous polyhedral geometry; two one-electron agostic type Rh—H—C interactions are proposed as the source of an additional skeletal electron pair which satisfies cluster-bonding requirements.

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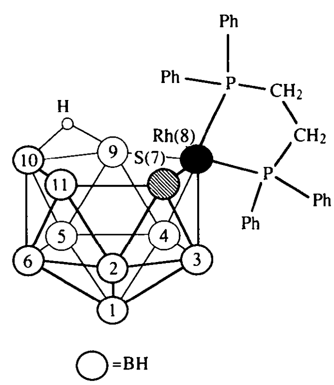
Comment

We are, at present, investigating examples of unusual structural behaviour in metallaheteroboranes. As part of this programme we have become interested in the anomalous geometries observed in 11-vertex rhodathiaboranes (Ferguson *et al.*, 1990; Murphy, Spalding, Ferguson & Gallagher, 1992) which display a *nido* cage architecture while apparently possessing a cluster electron count more appropriate to a *closo* geometry (Wade, 1976; Mingos, 1984). Herein we present the synthesis and structural characterization of a further example of such species, namely 8-(Ph_2P—CH_2CH_2—PPh_2)-9,10-μ-H-8,7-*nido*-$RhSB_9H_9$, (I), and discuss a possible solution to this problem.



(I)

The title rhodathiaborane crystallizes with no crystallographically imposed symmetry and no close intermolecular contacts. Two molecules of dichloromethane co-crystallize with this species. This high proportion of solvate causes the crystal lattice to be very unstable with respect to solvent loss: crystal growth by solvent diffusion has to be arrested to avoid diffusion of dichloromethane out of the lattice; crystal transfer was therefore performed at 195 K (dry-ice bath) and data were collected at 210 K.

A perspective view of a single molecule, with the atomic numbering scheme adopted, is shown in Fig. 1.

As with previous examples of species of this type, the 11-vertex $RhSB_9$ polyhedron shows gross *nido*-icosahedral geometry. The Rh(8)—S(7) distance in the present compound is 2.366 (2) Å, shorter than in the 8,8-(PPh_3)$_2$- (Ferguson *et al.*, 1990) (*A*) and 8,8-(PPh_3)$_2$-9-(OEt)- (Murphy, Spalding, Ferguson & Gallagher, 1992) (*B*) analogues, where the correspond-

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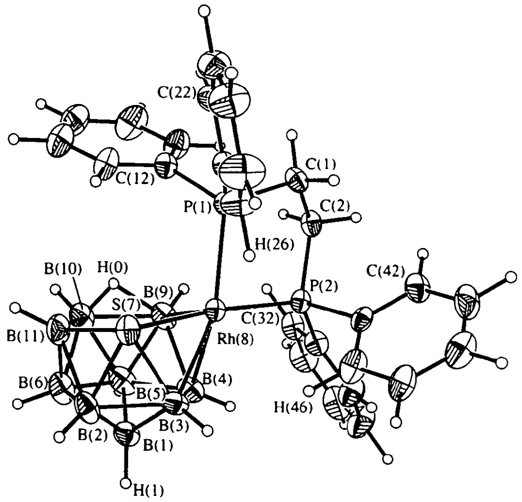

Fig. 1. Perspective view of 8-(dppe)-8,7-*nido*-$RhSB_9H_{10}$ (50% displacement ellipsoids, except for H atoms which have artificial radii of 0.1 Å for clarity).

ing separations are 2.3769 (6) and 2.375 (2) Å, respectively. In all three compounds the equivalent Rh—B and S—B distances are essentially similar. Likewise, the Rh(8)—P(2) distance (*trans* to sulfur) is 2.237 (2) Å, somewhat less than Rh(8)—P(1) (*cis* to sulfur) which is 2.321 (2) Å [*cf.* 2.2906 (5) and 2.4197 (5) Å in (*A*); 2.278 (2) and 2.417 (1) Å in (*B*)]. Cage B—B separations lie in the range 1.730 (12)–1.879 (11) Å, typical of metalla(hetero)boranes of this kind.

The environment of the Rh atom resembles a distorted octahedron with a vacant coordination site *trans* to B(9). We note, however, the presence of two close Rh···H approaches in the vicinity of this vacant position [Rh(8)···H(26) is 3.174 and Rh(8)···H(46) is 2.809 Å]; the coordinates of the midpoint (*X*) of the H(26)—H(46) vector lie in the direction of this unoccupied site. [The three angles P(1)—Rh(8)—P(2), P(1)—Rh(8)—*X* and P(2)—Rh(8)—*X* are 84.22 (6), 88 and 87°, respectively: the metal vertex effectively constitutes a conical fragment.] This observation prompts us to suggest the existence of two long-range agostic type (Brookhart & Green, 1983; Brookhart, Green & Wong, 1988) Rh↼H—C interactions which supply the metal centre with an additional two electrons and thereby render a cluster electron count consistent with the observed geometry. Indeed, a similar scenario is found to occur around the Rh atom in the previously reported analogues (*A* and *B*) of the present compound. Future contributions will further address the above phenomena.

Experimental

The title compound is synthesized in good yield by the interaction of $[Rh(dppe)_2Cl]_2$, formed *in situ* (*cf.* Albano, Aresta & Manassero, 1980), and the thiaborane precursor under oxygen-free conditions. A solution of $Ph_2PCH_2CH_2PPh_2$ (dppe, 0.21 g, 0.52 mmol) in toluene (7 ml) was added slowly to a suspension of $[Rh(CH_2{=}CH_2)_2Cl]_2$ (0.10 g, 0.26 mmol) (Fairlie & Bosnich, 1988) in toluene (10 ml); the mixture was stirred for 22 h then frozen to 77 K. Solid $Cs[SB_9H_{12}]$ (Rudolph & Pretzer, 1983) (0.14 g, 0.52 mmol) was added to the frozen orange–yellow suspension, the mixture allowed to warm to room temperature and stirred for 5 h, during which time the solution was observed to darken. Filtration (Celite, 1 atm) and evaporation *in vacuo* yielded the crude product as an orange powder. This was purified by preparative thin-layer chromatography (silica gel; CH_2Cl_2/*n*-hexane, 3:2; product R_f 0.4) to yield the title compound in 56% yield (0.154 g, 0.29 mmol). Analysis: found, C 48.19, H 5.08%; calculated for $C_{26}H_{34}B_9P_2RhS$, C 48.74, H 5.35%. The compound was crystallized by slow diffusion of *n*-hexane into dichloromethane solution at 243 K.

Crystal data

$[Rh(B_9H_{10}S)(C_{26}H_{24}P_2)]$.-2$CH_2Cl_2$	Mo $K\alpha$ radiation
M_r = 810.63	λ = 0.71069 Å
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	θ = 8–10°
a = 11.161 (2) Å	μ = 0.91 mm^{-1}
b = 11.338 (6) Å	T = 210 (1) K
c = 17.206 (13) Å	Rhombic block
α = 98.726 (56)°	0.45 × 0.4 × 0.4 mm
β = 107.306 (40)°	Orange
γ = 111.682 (39)°	
V = 1845.8 Å^3	
Z = 2	
D_x = 1.458 Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.2280
ω–2θ scans	θ_{max} = 25°
Absorption correction: none	h = 0 → 13
6131 measured reflections	k = −13 → 12
5771 independent reflections	l = −20 → 15
5364 observed reflections [$F \geq 2.0\sigma(F)$]	2 standard reflections frequency: 480 min intensity decay: <3.5%

Refinement

Refinement on F	$\Delta\rho_{max}$ = 0.83 e Å^{-3} (near Rh, S)
R = 0.0528	$\Delta\rho_{min}$ = −1.14 e Å^{-3}
wR = 0.0846	Extinction correction: none
S = 1.618	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) (Rh); *SHELX*76 (Sheldrick, 1976)
5364 reflections	
359 parameters	
$w = 1/[\sigma^2(F) + 0.000391F^2]$	
$(\Delta/\sigma)_{max}$ = 0.001	

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

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

	x	y	z	U_{eq}
Rh(8)	0.10159 (4)	0.23566 (4)	0.18360 (2)	0.0225 (3)
S(7)	0.11964 (15)	0.23326 (4)	0.04986 (9)	0.0329 (9)
B(1)	0.4036 (7)	0.2508 (6)	0.1661 (4)	0.034 (4)

B(2)	0.3064 (7)	0.2417 (6)	0.0623 (5)	0.040 (5)
B(3)	0.2224 (7)	0.1522 (6)	0.1292 (4)	0.036 (4)
B(4)	0.3169 (7)	0.2520 (7)	0.2379 (4)	0.035 (4)
B(5)	0.4478 (7)	0.4029 (7)	0.2413 (4)	0.038 (5)
B(6)	0.4354 (7)	0.3974 (6)	0.1346 (5)	0.040 (5)
B(9)	0.2969 (7)	0.4072 (6)	0.2532 (4)	0.031 (4)
B(10)	0.3738 (7)	0.4957 (6)	0.1842 (5)	0.039 (5)
B(11)	0.2809 (8)	0.3938 (7)	0.0706 (5)	0.048 (5)
P(1)	−0.06066 (14)	0.32101 (13)	0.17119 (9)	0.0268 (9)
P(2)	0.06739 (14)	0.20171 (13)	0.30155 (9)	0.0253 (9)
C(1)	−0.1253 (6)	0.3010 (6)	0.2570 (3)	0.034 (4)
C(2)	−0.0118 (6)	0.3051 (5)	0.3363 (3)	0.030 (4)
C(11)	0.0233 (4)	0.4997 (3)	0.18605 (18)	0.032 (4)
C(12)	0.0528 (4)	0.5403 (3)	0.11858 (18)	0.042 (4)
C(13)	0.1266 (4)	0.6749 (3)	0.12856 (18)	0.051 (5)
C(14)	0.1709 (4)	0.7690 (4)	0.20602 (18)	0.055 (5)
C(15)	0.1414 (4)	0.7285 (3)	0.27350 (18)	0.059 (5)
C(16)	0.0676 (4)	0.5938 (3)	0.26352 (18)	0.044 (4)
C(21)	−0.2162 (3)	0.2552 (3)	0.0744 (2)	0.028 (3)
C(22)	−0.2937 (3)	0.3264 (3)	0.0542 (2)	0.036 (4)
C(23)	−0.4158 (3)	0.2711 (3)	−0.0191 (2)	0.045 (5)
C(24)	−0.4603 (3)	0.1445 (3)	−0.0722 (2)	0.048 (5)
C(25)	−0.3828 (3)	0.0733 (3)	−0.0520 (2)	0.059 (5)
C(26)	−0.2607 (3)	0.1286 (3)	0.0213 (2)	0.042 (4)
C(31)	0.2028 (4)	0.2187 (3)	0.3993 (2)	0.031 (4)
C(32)	0.2954 (4)	0.3439 (3)	0.4569 (2)	0.036 (4)
C(33)	0.4010 (4)	0.3566 (3)	0.5305 (2)	0.048 (5)
C(34)	0.4139 (4)	0.2439 (3)	0.5465 (2)	0.054 (5)
C(35)	0.3213 (4)	0.1187 (3)	0.4889 (2)	0.060 (6)
C(36)	0.2158 (4)	0.1061 (3)	0.4153 (2)	0.045 (5)
C(41)	−0.0651 (4)	0.0311 (3)	0.2671 (2)	0.029 (4)
C(42)	−0.1699 (4)	−0.0077 (4)	0.2992 (2)	0.037 (4)
C(43)	−0.2717 (4)	−0.1392 (3)	0.2695 (2)	0.047 (5)
C(44)	−0.2686 (4)	−0.2319 (3)	0.2077 (2)	0.049 (5)
C(45)	−0.1637 (4)	−0.1931 (3)	0.1756 (2)	0.043 (4)
C(46)	−0.0620 (4)	−0.0616 (3)	0.2053 (2)	0.042 (4)
C(1*S*)	0.8552 (7)	0.6712 (7)	0.3824 (4)	0.053 (5)
Cl(1*S*)	0.88088 (18)	0.54710 (16)	0.42582 (10)	0.0528 (12)
Cl(2*S*)	0.9828 (2)	0.83078 (18)	0.44954 (14)	0.0727 (15)
C(2*S*)	0.5842 (8)	0.2122 (9)	0.3942 (6)	0.079 (7)
Cl(3*S*)	0.5329 (4)	0.0492 (3)	0.3362 (2)	0.145 (3)
Cl(4*S*)	0.7290 (3)	0.2621 (3)	0.4889 (3)	0.144 (3)

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

Cage B—B—B angles not given in this table are in the range 57.2 (4)–64.6 (4)°.

Rh(8)—S(7)	2.3659 (17)	B(3)—B(4)	1.787 (10)
Rh(8)—B(3)	2.239 (7)	B(4)—B(5)	1.771 (11)
Rh(8)—B(4)	2.228 (7)	B(4)—B(9)	1.843 (10)
Rh(8)—B(9)	2.139 (7)	B(5)—B(6)	1.790 (11)
Rh(8)—P(1)	2.3214 (16)	B(5)—B(9)	1.773 (11)
Rh(8)—P(2)	2.2365 (16)	B(5)—B(10)	1.797 (11)
S(7)—B(2)	1.996 (8)	B(6)—B(10)	1.752 (11)
S(7)—B(3)	2.062 (8)	B(6)—B(11)	1.730 (12)
S(7)—B(11)	1.918 (9)	B(9)—B(10)	1.866 (10)
B(1)—B(2)	1.757 (11)	B(10)—B(11)	1.859 (11)
B(1)—B(3)	1.759 (10)	P(1)—C(1)	1.834 (6)
B(1)—B(4)	1.783 (10)	P(1)—C(11)	1.829 (4)
B(1)—B(5)	1.791 (11)	P(1)—C(21)	1.814 (4)
B(1)—B(6)	1.770 (11)	P(2)—C(2)	1.838 (6)
B(2)—B(3)	1.879 (11)	P(2)—C(31)	1.823 (4)
B(2)—B(6)	1.768 (11)	P(2)—C(41)	1.815 (4)
B(2)—B(11)	1.840 (12)	C(1)—C(2)	1.542 (9)
S(7)—Rh(8)—B(3)	53.13 (19)	Rh(8)—P(1)—C(21)	120.07 (14)
S(7)—Rh(8)—B(4)	90.1 (2)	C(1)—P(1)—C(11)	106.3 (2)
S(7)—Rh(8)—B(9)	94.4 (2)	C(1)—P(1)—C(21)	105.1 (2)
S(7)—Rh(8)—P(1)	99.22 (6)	S(7)—B(2)—B(3)	64.2 (3)
S(7)—Rh(8)—P(2)	170.62 (6)	S(7)—B(2)—B(11)	59.8 (4)
B(3)—Rh(8)—B(4)	47.2 (3)	Rh(8)—B(3)—S(7)	66.6 (2)
B(3)—Rh(8)—B(9)	85.9 (3)	Rh(8)—B(3)—B(4)	66.1 (3)
B(3)—Rh(8)—P(1)	151.89 (19)	S(7)—B(3)—B(2)	60.6 (3)
B(3)—Rh(8)—P(2)	122.28 (19)	Rh(8)—B(4)—B(3)	66.7 (3)
B(4)—Rh(8)—B(9)	49.9 (3)	Rh(8)—B(4)—B(9)	62.5 (3)
B(4)—Rh(8)—P(1)	152.4 (2)	C(11)—P(1)—C(21)	105.20 (18)
B(4)—Rh(8)—P(2)	90.8 (2)	Rh(8)—P(2)—C(2)	110.1 (2)
B(9)—Rh(8)—P(1)	103.2 (2)	Rh(8)—P(2)—C(31)	124.68 (14)
B(9)—Rh(8)—P(2)	93.3 (2)	Rh(8)—P(2)—C(41)	104.37 (14)
P(1)—Rh(8)—P(2)	84.22 (6)	C(2)—P(2)—C(31)	104.5 (2)
Rh(8)—S(7)—B(2)	107.1 (2)	C(2)—P(2)—C(41)	106.0 (2)
Rh(8)—S(7)—B(3)	60.3 (2)	C(31)—P(2)—C(41)	105.84 (19)
Rh(8)—S(7)—B(11)	105.6 (3)	P(1)—C(1)—C(2)	110.3 (4)
B(2)—S(7)—B(3)	55.1 (3)	P(2)—C(2)—C(1)	108.5 (4)
B(2)—S(7)—B(11)	56.1 (3)	P(1)—C(11)—C(12)	117.4 (3)
B(3)—S(7)—B(11)	96.7 (3)	P(1)—C(11)—C(16)	122.4 (3)
Rh(8)—B(9)—B(4)	67.6 (3)	P(1)—C(21)—C(22)	121.3 (3)
Rh(8)—B(9)—B(10)	113.8 (4)	P(1)—C(21)—C(26)	118.7 (3)
B(9)—B(10)—B(11)	111.0 (5)	P(2)—C(31)—C(32)	120.3 (3)
S(7)—B(11)—B(2)	64.1 (4)	P(2)—C(31)—C(36)	119.7 (3)
S(7)—B(11)—B(10)	113.9 (5)	P(2)—C(41)—C(42)	121.8 (3)
Rh(8)—P(1)—C(1)	109.3 (2)	P(2)—C(41)—C(46)	118.2 (3)
Rh(8)—P(1)—C(11)	110.02 (14)		

Data reduction was carried out using *CADABS* (Gould & Smith, 1986). *SHELX*76 (Sheldrick, 1976) was used to solve the structure *via* Patterson and difference Fourier syntheses, as well as for refinement. Molecular graphics were produced using *SHELXTL/PC* (Sheldrick, 1990). Molecular geometry calculations were performed with *CALC* (Gould & Taylor, 1986). Phenyl rings were constrained to be regular hexagons (C—C 1.395 Å). Cage terminal H atoms, phenyl and methylene H atoms were set in idealized positions (C—H 1.08, B—H 1.10 Å). The cage bridging H atom was located by difference Fourier synthesis and its position fixed thereafter. For all H atoms a common isotropic displacement parameter was refined [$U = 0.063\,(4)$ Å^2 at convergence].

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1131). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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