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The Synthesis and Structure of an Icosahedral Thiadirhodadodecaborane Complex, 7-Chloro-2,3-bis(η-pentamethylcyclopentadienyl)-1-thia-2,3-dirhoda-*closo*-dodecaborane(9), $C_{20}H_{38}B_9ClRh_2S$

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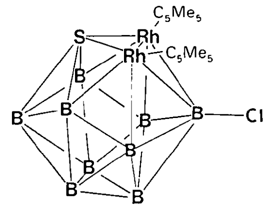
Abstract. $M_r = 649\cdot1$, monoclinic, $P2_1/c$, $a = 8\cdot724$ (1), $b = 15\cdot964$ (1), $c = 20\cdot454$ (2) Å, $\beta = 106\cdot77$ (1)°, $V = 2727$ (1) Å^3, $Z = 4$, $D_x = 1\cdot58$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7096$ Å, $\mu = 13\cdot7$ cm^{-1}, $F(000) = 1304$, $T = 293$ K, $R = 0\cdot028$ for 3955 reflexions. The molecule (III) can be described as a distorted icosahedron composed of two rhodium, one sulphur and nine boron vertices; each Rh atom is also coordinated by a C_5Me_5 ligand. The incorporation of a terminal chlorine atom into the structure [B—Cl 1·793 (4) Å] was unexpected. The rhodium atoms occupy adjacent vertices with Rh—Rh 2·778 (1) Å. Other principal bond lengths are: Rh—S 2·351 and 2·362 (1), Rh—B 2·181–2·311 (6), Rh—C(cyclopentadienyl) 2·183–2·295 (5), S—B 2·014–2·104 (7), B—B 1·737–1·859 (7) Å.

Introduction. Despite its ready accessibility from $[B_{10}H_{14}]^{2-}$ (Hertler, Klanberg & Muetterties, 1967) the reactions of the *arachno*-thiaborane anion $[6\text{-}SB_9H_{12}]^-$ (I) with transition-metal substrates have received surprisingly little study. In the presence of excess triphenylphosphine, (I) is reported to react with M^+ (M = Cu, Ag, Au) to give a closely related series of compounds of the type $[M(SB_9H_{12})(PPh_3)_n]$ (n = 1–3) (Klanberg, Muetterties & Guggenberger, 1968). A member of this series (M = Au, n = 3) was shown by crystallographic methods to have an ionic structure in which (I) functioned as a counter-ion rather than as a ligand (Guggenberger, 1974). More interestingly, the anion (I) reacts with $[PtHCl(PEt_3)_2]$ to yield the complex $[PtH(SB_9H_{10})(PEt_3)_2]$ (Kane, Guggenberger & Muetterties, 1970), which contains an $[\eta^4\text{-}SB_9H_{10}]^-$ ligand bonded to platinum through sulphur and B(5), B(8) and B(9) of the precursor $[SB_9H_{12}]^-$, thus forming a *nido*-[PtSB$_9$] cage. Deprotonation of (I) by strong bases generates $[SB_9H_{11}]^{2-}$, from which complexes of the type $[M(\eta^4\text{-}SB_9H_{11})_2]^{2-}$ (M = Ni, Pd) have been prepared (Siedle, McDowell & Todd, 1974). We describe here the isolation and X-ray crystallographic characterization of a rhodium(II) complex derived from the reaction of (I) with $[RhCl_2(\eta\text{-}C_5Me_5)]_2$ (II); the complex (III) contains $[SB_9H_8Cl]^{4-}$, a chlorine-substituted $[SB_9H_9]^{4-}$ ligand.



(III)

Experimental. The reaction of the Cs$^+$ salt of (I) with $[RhCl_2(\eta\text{-}C_5Me_5)]_2$ (II) in refluxing tetrahydrofuran (2:1 molar ratio) was found by TLC analysis to yield at least six products. The major component of this mixture was an orange-red crystalline solid which was separated from the crude reaction product by dry-column chromatography. Slow evaporation of a solution of the orange-red material in CH_2Cl_2–hexane yielded dark-red crystals. Preliminary photographic studies allowed provisional values for the cell dimensions to be

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calculated, and the systematic absences ($h0l$ absent if $l = 2n + 1$, $0k0$ absent if $k = 2n + 1$) indicated space group $P2_1/c$ uniquely. Intensity data collected with Hilger & Watts four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $0{\cdot}15 \times 0{\cdot}15 \times 0{\cdot}20$ mm crystal; 12 reflexions with $10 < \theta < 20°$ for determining lattice constants and orientation matrix; for data collection $2 < \theta < 25°$, ω–2θ scans, ω width 0·60°; intensities of three standard reflexions measured every 150 min showed no significant variation; Lp corrections; 4803 unique reflexions, 3955 (82%) with $I > 3\sigma(I)$, no absorption correction. Structure solved by heavy-atom method using *SHELX*76 (Sheldrick, 1976); refinement of non-hydrogen atoms with anisotropic thermal parameters by full-matrix least-squares calculations on F. H atoms from difference maps included in observed positions; their positional parameters were not refined but two overall isotropic thermal parameters were, one for methyl hydrogens, the other for boron hydrogens. Final $R = 0{\cdot}028$, $R_w = 0{\cdot}034$ for observed data, $w = 1/\sigma^2(F)$. Final difference map had a peak of 0·7 e Å^{-3}, 1·4 Å from the S atom (where the S lone pair would be), other peaks ranged from 0·4 to −0·7 e Å^{-3}; 300 parameters in final refinement cycles, max. $\Delta/\sigma = 0{\cdot}32$ for U_{11} of C(131), max. coordinate $\Delta/\sigma = 0{\cdot}041$ for x of B(2); atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965), allowance for anomalous dispersion (Cromer & Liberman, 1970). Final fractional coordinates with mean isotropic temperature factors are in Table 1. Table 2 contains molecular dimensions.[*] Other programs used include *ORTEP*II (Johnson, 1976). The molecular structure of (III) is shown in Fig. 1.

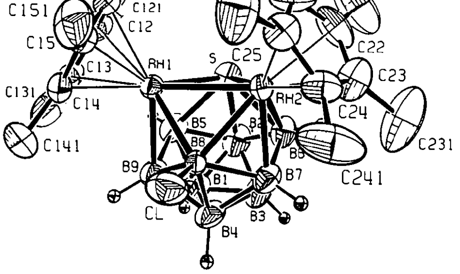

Fig. 1. A view of the molecule (III) with the crystallographic numbering scheme.

Table 1. *Final fractional coordinates* (×10^5 *for* Rh, ×10^4 *for others*) *and* B_{eq} *values* (Å^2) *for* (III) *with e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i U_{ii}.$$

	x	y	z	$B_{\rm eq}$
Rh(1)	25718 (3)	23457 (2)	7310 (1)	2·7 (1)
Rh(2)	32943 (3)	34004 (2)	18595 (1)	2·6 (1)
Cl	−414 (1)	3789 (1)	702 (1)	4·9 (1)
S	4134 (1)	2003 (1)	1847 (1)	4·0 (1)
B(1)	723 (8)	1253 (4)	1714 (3)	5·4 (2)
B(2)	2717 (8)	1319 (4)	2265 (3)	5·3 (2)
B(3)	1167 (8)	1922 (3)	2434 (3)	5·1 (2)
B(4)	−159 (7)	2255 (4)	1658 (3)	4·8 (2)
B(5)	2253 (7)	1238 (3)	1325 (3)	4·7 (2)
B(6)	3020 (7)	2403 (3)	2578 (3)	4·3 (2)
B(7)	1194 (6)	2977 (3)	2155 (3)	4·1 (2)
B(8)	779 (5)	2981 (3)	1214 (2)	2·6 (2)
B(9)	454 (6)	1860 (3)	965 (3)	4·2 (2)
C(11)	4106 (5)	2637 (3)	17 (2)	3·8 (2)
C(12)	3884 (6)	1759 (3)	63 (2)	4·5 (2)
C(13)	2207 (7)	1593 (3)	−199 (2)	5·0 (2)
C(14)	1404 (6)	2387 (3)	−377 (2)	4·2 (2)
C(15)	2593 (5)	3018 (3)	−249 (2)	3·8 (2)
C(111)	5703 (6)	3046 (4)	124 (3)	6·2 (2)
C(121)	5161 (8)	1145 (4)	284 (3)	7·4 (2)
C(131)	1430 (10)	747 (4)	−346 (3)	8·7 (2)
C(141)	−342 (6)	2543 (5)	−733 (3)	6·3 (2)
C(151)	2270 (8)	3919 (4)	−458 (3)	5·7 (2)
C(21)	5332 (5)	4291 (3)	1858 (3)	4·8 (2)
C(22)	5404 (6)	4052 (3)	2533 (3)	4·9 (2)
C(23)	3982 (7)	4342 (3)	2665 (2)	5·1 (2)
C(24)	3031 (5)	4734 (3)	2067 (2)	3·9 (2)
C(25)	3888 (5)	4713 (2)	1582 (2)	3·8 (2)
C(211)	6718 (8)	4248 (5)	1524 (5)	10·2 (2)
C(221)	6819 (9)	3631 (6)	3047 (5)	9·6 (2)
C(231)	3592 (13)	4355 (5)	3340 (3)	10·6 (2)
C(241)	1494 (7)	5224 (4)	1964 (4)	7·9 (2)
C(251)	3429 (10)	5185 (4)	916 (3)	7·9 (2)

Table 2. *Selected interatomic distances* (Å)

Rh(1)–Rh(2)	2·778 (1)	B(3)–B(4)	1·754 (7)
Rh(1)–S	2·362 (1)	B(3)–B(6)	1·737 (9)
Rh(1)–B(5)	2·209 (6)	B(3)–B(7)	1·782 (8)
Rh(1)–B(8)	2·311 (5)	B(4)–B(7)	1·749 (7)
Rh(1)–B(9)	2·181 (6)	B(4)–B(8)	1·807 (8)
Rh(1)–C(11)	2·295 (5)	B(4)–B(9)	1·769 (9)
Rh(1)–C(12)	2·227 (5)	B(5)–B(9)	1·824 (8)
Rh(1)–C(13)	2·195 (5)	B(6)–B(7)	1·826 (7)
Rh(1)–C(14)	2·201 (4)	B(7)–B(8)	1·852 (6)
Rh(1)–C(15)	2·277 (4)	B(8)–B(9)	1·859 (7)
Rh(2)–S	2·351 (1)	C(11)–C(12)	1·422 (7)
Rh(2)–B(6)	2·226 (6)	C(11)–C(15)	1·412 (6)
Rh(2)–B(7)	2·195 (6)	C(11)–C(111)	1·496 (7)
Rh(2)–B(8)	2·310 (4)	C(12)–C(13)	1·430 (7)
Rh(2)–C(21)	2·277 (5)	C(12)–C(121)	1·456 (8)
Rh(2)–C(22)	2·215 (5)	C(13)–C(14)	1·443 (7)
Rh(2)–C(23)	2·183 (5)	C(13)–C(131)	1·503 (8)
Rh(2)–C(24)	2·196 (4)	C(14)–C(15)	1·416 (7)
Rh(2)–C(25)	2·270 (4)	C(14)–C(141)	1·507 (7)
Cl–B(8)	1·793 (4)	C(15)–C(151)	1·503 (7)
S–B(2)	2·014 (7)	C(21)–C(22)	1·415 (9)
S–B(5)	2·076 (5)	C(21)–C(25)	1·397 (6)
S–B(6)	2·104 (7)	C(21)–C(211)	1·552 (11)
B(1)–B(2)	1·782 (8)	C(22)–C(23)	1·421 (9)
B(1)–B(3)	1·769 (8)	C(22)–C(221)	1·528 (9)
B(1)–B(4)	1·764 (8)	C(23)–C(24)	1·411 (6)
B(1)–B(5)	1·740 (10)	C(23)–C(231)	1·513 (10)
B(1)–B(9)	1·769 (8)	C(24)–C(25)	1·406 (8)
B(2)–B(3)	1·772 (10)	C(24)–C(241)	1·513 (8)
B(2)–B(5)	1·851 (8)	C(25)–C(251)	1·505 (8)
B(2)–B(6)	1·837 (8)		

Discussion. Our analysis establishes that the compound present in the sample crystals is 7-chloro-2,3-bis-(η-pentamethylcyclopentadienyl)-1-thia-2,3-dirhoda-dodecaborane(9), $[\{(\eta\text{-}C_5Me_5)Rh\}_2(SB_9H_8Cl)]$ (III) (Fig. 1). The mechanism of the formation of (III) is at

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[*] Lists of structure factors, anisotropic thermal parameters, bond angles and hydrogen-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39488 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

present unclear but the reaction has the formal stoichiometry

$$\underset{\text{(I)}}{\mathrm{Cs[SB_9H_{12}]}} + \underset{\text{(II)}}{[\mathrm{RhCl_2}(\eta\text{-}\mathrm{C_5Me_5})]_2} \longrightarrow$$

$$\underset{\text{(III)}}{[\{(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Rh}\}_2(\mathrm{SB_9H_8Cl})]} + \mathrm{CsCl} + 2\mathrm{HCl} + \mathrm{H_2}.$$

The basic structural unit of (III) is a distorted icosahedral $[Rh_2SB_9]$ framework (Fig. 1). From a formal point of view (III) can be considered as being constructed by the addition of a pair of $[Rh(\eta\text{-}C_5Me_5)]^{2+}$ vertices to *arachno*-$[SB_9H_8Cl]^{4-}$. The latter is a chlorine-substituted derivative of the hypothetical *arachno*-$[SB_9H_9]^{4-}$ which would be generated by the addition of two electron pairs to the known *closo*-[1-SB_9H_9] (Pretzer & Rudolph, 1976). To our knowledge, a complex formulated as $[2,4\text{-}\{Co(\eta\text{-}C_5H_5)\}_2\text{-}(1\text{-}SB_9H_9)]$ (IV) is the only previously reported example of a compound containing an $[SB_9H_9]^{4-}$ ligand. Details of the synthesis and structural characterization of (IV) were not described in the published report (Plzak, Plesek & Stibr, 1979). If the structure reported there is correct, the $[SB_9H_9]^{4-}$ ligand in (IV) is not isostructural with the related ligand in (III). An analogous selenaborane complex, $[\{Co(\eta\text{-}C_5H_5)\}_2(SeB_9H_9)]$, of unknown molecular architecture has been isolated from the base-induced degradation of $[Se_2B_9H_9]$ followed by reaction of the product with cobalt(II) chloride, triethylamine and cyclopentadiene (Friesen, Barriola, Daluga, Ragatz, Huffman & Todd, 1980).

The two rhodium atoms in (III) occupy adjacent vertices in the icosahedron and are each bound to three boron atoms, sulphur and one another. The Rh—Rh separation lies towards the upper end of the range established for bonds between adjacent rhodium atoms in polynuclear clusters and is similar to the unbridged Rh^{II}–Rh^{II} distance in $[Rh_2I_2(p\text{-}CNC_6H_4CH_3)_8]\,[PF_6]_2$ [2·785 (2) Å] (Felthouse, 1982). Each rhodium is also coordinated by an η-pentamethylcyclopentadienide ligand.

An unexpected feature of the structure of (III) is the presence of a terminal halogen atom on boron [B—Cl 1·793 (4) Å]. The boron atom in the precursor [6-SB_9H_{12}]$^-$ (I) bears two terminal hydrogen atoms (Guggenberger, 1974); in the course of the formation of (III) both of these are lost and replaced by a chlorine atom which must migrate to boron from one of the rhodium atoms in (II).

Molecule (III) with mean B—B 1·79 (4) Å compares closely with the isostructural isoelectronic $(CoC_5H_5)_2\text{-}(C_2B_8H_{10})$ (Callahan, Strouse, Sims & Hawthorne, 1974) with a mean B—B distance of 1·78 (3) Å and with $[(C_2B_9H_{11})_2Co_2C_2B_8H_{10}]^{2-}$ (Saint Clair, Zalkin & Templeton, 1969) with mean B—B 1·79 (2) Å.

The two C_5Me_5 ligands are in close proximity and are distorted from planarity by mutual repulsion. The dihedral angle between the two rings is 74·2 (3)° and the bonding to Rh is asymmetric, the longest distances being to C(11), C(15) and C(21) (Fig. 1) which are most affected by Me···Me interactions between the two rings. In each ring all the methyl carbon atoms are displaced out of the C_5 ring plane in the same direction on the opposite side to rhodium, with the largest displacements by C(111) [0·228 (6) Å] and C(211) [0·222 (8) Å].

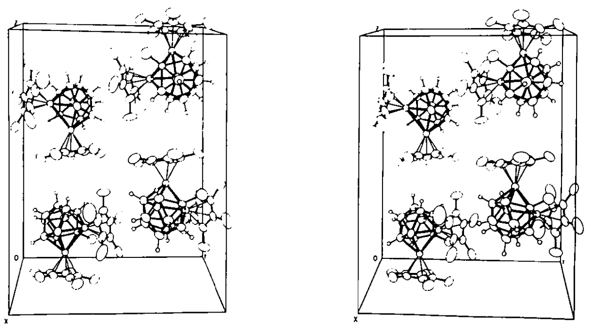

Fig. 2. A stereoview of the unit-cell contents of (III). (Origin rear lower-left corner, *c* vertical, *b* horizontal, *a* towards the reader.)

In the crystal structure (Fig. 2) molecules of (III) show no untoward intermolecular contacts and are separated by normal van der Waals distances.

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