

$[\mu\text{-}6,9\text{-Cl-}8\text{-(OMe)-}6,9\text{-(}\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{-}arachno\text{-}6,9,5\text{-Rh}_2\text{SB}_7\text{H}_7]$

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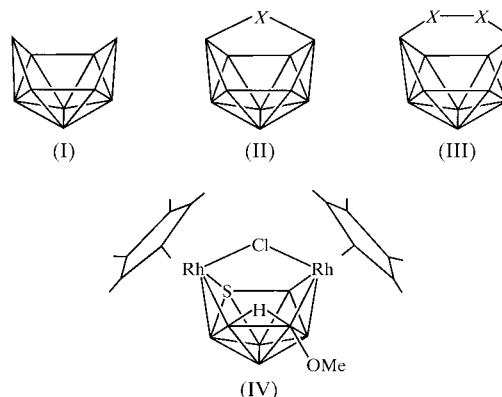
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The title compound, $\mu\text{-}6,9\text{-chloro-}8\text{-methoxy-}6,9\text{-bis}(\eta^5\text{-penta-}methylcyclopentadienyl)\text{-}6,9\text{-dirhoda-}5\text{-thia-}arachno\text{-}deca\text{-}borane(7)$, $[\text{Rh}_2(\text{CH}_{10}\text{B}_7\text{OS})(\text{C}_{10}\text{H}_{15})_2\text{Cl}]$, has a single Cl atom bridging the two remote rhodium 'prow' vertices of an *arachno* ten-vertex dirhodathiadecaborane cluster, with Rh—Cl distances of 2.3475 (11) and 2.3536 (11) Å, and an Rh—Cl—Rh angle of 106.82 (4)°.

Comment

Since the initial structural elucidation of the *arachno* and *nido* ten-vertex skeletons in borane cluster chemistry diagrammatically depicted in (I) (Van der Mass Reddy & Lipscomb, 1959; Kasper *et al.*, 1950), there has been a fascination with bridging the 6,9 positions across the open face, either with a single atom as in (II) or with a two-atom unit as in (III), but instances of both have been surprisingly rare. Several examples of structurally characterized one-atom bridges of the *arachno* skeleton have been reported. These include a phosphorus-bridged unit as in the $[\text{B}_{10}\text{H}_{12}\text{-}\mu\text{-}6,9\text{-(PPh}_2\text{)}]^-$ anion (Thornton-Pett *et al.*, 1986), a sulfur-bridged unit as in the $[\text{B}_{10}\text{H}_{12}\text{-}\mu\text{-}6,9\text{-(SMe)}]^-$ anion and related species (Binder & Hein, 1997, and references therein). Bridged *nido* skeletons have been structurally characterized containing an aluminium-bridged unit, $[\text{6,9-C}_2\text{B}_8\text{H}_{12}\text{-}\mu\text{-}6,9\text{-Al(OEt)Me}]$ (Schubert *et al.*, 1987), a tin bridge in $[\text{6,9-C}_2\text{B}_8\text{H}_{12}\text{-}\mu\text{-}6,9\text{-SnMe}_2]$ and related species (Kennedy *et al.*, 1992; Nestor *et al.*, 1993), as well as a nitrogen-bridged cluster in $[\text{5,10-C}_2\text{B}_8\text{H}_{12}\text{-}\mu\text{-}6,9\text{-(NH}^t\text{Bu)}]$ and related species (Janoušek *et al.*, 1992; Dörfler *et al.*, 2000). In this paper, we now report a chlorine bridge for the *arachno*-6,9,5-dimetallathiadecaborane cluster compound $[\mu\text{-}6,9\text{-Cl-}8\text{-(OMe)-}6,9\text{-(}\eta^5\text{-C}_5\text{Me}_5\text{)}_2\text{-}arachno\text{-}6,9,5\text{-Rh}_2\text{SB}_7\text{H}_7]$, (IV) (Fig. 1). A chlorine-bridged rhodium pair has been noted previously in the 11-vertex dimetallathiaborane $[\text{2,3-(PPh}_3\text{)}_2\text{-}3\text{-Cl-}\mu\text{-}2,3\text{-Cl-}\mu\text{-}2^P,7^C\text{-(Ph}_2\text{P-}2\text{-C}_6\text{H}_4\text{)-}closo\text{-}2,3,1\text{-Rh}_2\text{SB}_9\text{H}_8]$ (Ferguson *et al.*, 1990), although the bridged Rh atoms are adjacent in the contiguous $[\text{RhS}_2\text{B}_9]$ cluster $[\text{Rh}\cdots\text{Rh}$ distance

2.6307 (9) Å], rather than apart, as in the present compound $[\text{Rh}\cdots\text{Rh}$ distance 3.7748 (5) Å]. There is a bromine-bridged metals-apart example reported in $[\mu\text{-Br(CO)}_6(\text{B}_3\text{H}_8)\text{Mn}_2]$ (Chen *et al.*, 1980).



The asymmetric unit contains approximately 0.1 molecules of disordered CH_2Cl_2 solvent. The cluster structure is seen to be of the basic ten-vertex *nido/arachno* boat-shaped geometry, with a rhodium centre at each of the two 6,9 'prow' positions. The two Rh atoms are linked by a bridging Cl atom. An S atom occupies one of the open-face 'gunwale' positions, and there is a hydrogen bridge at the opposing interboron 'gunwale' position, consistent with the general *arachno* ten-vertex character that is also apparent from the formal Wadlan (Wade, 1976) 16-electron $\{2n + 6\}$ *arachno* electron count. The compound could also be regarded as of 11-vertex 'remote *arachno*' cluster constitution (Porterfield *et al.*, 1990). Using simple electron counting rules, each of the formal octahedral rhodium(III) centres has two two-electron bonding vectors which are contributed to the cluster (Kennedy, 1998; Bould *et al.*, 1999) and three which are directed towards the $\{\eta^5\text{-C}_5\text{Me}_5\}$ group. The sixth vector constitutes a two-electron bond with the bridging Cl atom, and one such from each rhodium generates the bridge. The two rhodium–chlorine distances of 2.3475 (11) and 2.3536 (11) Å are similar to those in the *closo* 12-vertex species mentioned above [2.437 (2) and

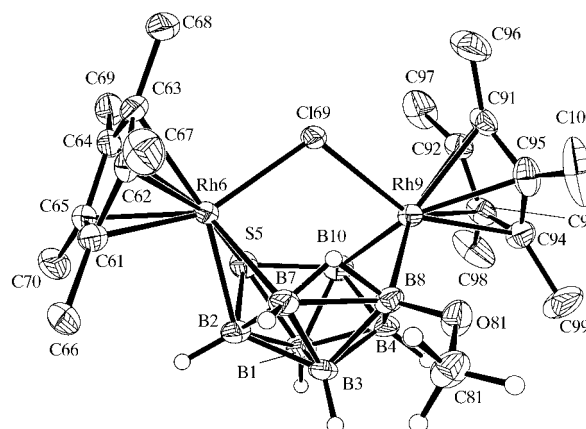


Figure 1

Perspective view of a single molecule of (IV) drawn with 40% probability ellipsoids and with H atoms shown as small circles of artificial radius. The H atoms on the C_5Me_5 methyl groups have been omitted for clarity.

2.448 (2) Å], and shorter than those in the doubly-bridged rhodium dimer $[(\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5))_2]$ from which compound (IV) was prepared [2.401 (4) Å] (Hoard & Sharpe, 1993).

Experimental

The title compound was isolated, along with its 10-methoxy isomer, (V), from the reaction between $[(\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5))_2]$ (100 mg, 162 μmol) and the $[\text{tmndaH}]^+$ salt of the $[\text{SB}_8\text{H}_{11}]^-$ anion (Jones *et al.*, 1989) [136 mg, 394 μmol ; tmnda is 1,8-bis(dimethylamino)-naphthalene] in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (1:1, 30 ml) for 30 min. Filtration and repeated thin-layer chromatography (silica gel G) on the filtrate mixture, using $\text{CH}_2\text{Cl}_2/\text{hexane}$ mixtures, revealed a mixture of several coloured components, from which it was possible to separate dark-red (IV) (4 mg, 6 μmol , 4%) and amber (V) (10 mg, 15 μmol , 9%) in pure form (R_F 0.28 and 0.35, respectively, liquid-phase $\text{CH}_2\text{Cl}_2/\text{hexane}$ 8:2). Crystals of compound (IV) were obtained by diffusion of hexane into a solution in CH_2Cl_2 . Selected NMR data for CDCl_3 solutions at 300 K {cluster resonances ordered as: assignment $\delta(^{11}\text{B})/\text{p.p.m.}$ [$\delta(^1\text{H})/\text{p.p.m.}$ for directly attached *exo*-hydrogen]}. [μ -6,9-CI-8-(OMe)-6,9-($\eta^5\text{-C}_5\text{Me}_5$)₂-*arachno*-6,9,5-Rh₂SB₇H₇], (IV): BH1 +8.9 [+3.64], BH2 -21.3 [+1.34], BH3 +5.7 [+3.54], BH4 -26.7 [+1.44], BH7 +1.5 [+3.19], B8 +27.4 [OMe substituted] and BH10 +14.4 [+3.97], with $\delta(^1\text{H})(\mu\text{-}7,8)$ -0.19, $\delta(^1\text{H})(\text{C}_5\text{Me}_5)$ at +1.69 and +1.56, $\delta(^1\text{H})(\text{OMe})$ at +3.61; [μ -6,9-CI-10-(OMe)-6,9-($\eta^5\text{-C}_5\text{Me}_5$)₂-*arachno*-6,9,5-Rh₂SB₇H₇], (V): BH1 +9.5 [+4.08], BH2 -23.5 [+1.55], BH3 +6.7 [+3.63], BH4 -26.0 [+1.45], BH7 +3.9 [+3.30], BH8 +26.0 [+1.45] and B10 +9.5 [OMe substituted], with $\delta(^1\text{H})(\mu\text{-}7,8)$ -1.71, $\delta(^1\text{H})(\text{C}_5\text{Me}_5)$ at +1.71 and +1.62, $\delta(^1\text{H})(\text{OMe})$ at +3.42; mass spectrometry (70 eV EI): each had a weak *m/e*(max) isotopomer envelope centred at 657 corresponding to the calculated molecular ion, $[\text{C}_{21}\text{H}_{40}\text{B}_7\text{ClORh}_2\text{S}]^+$, with a principal fragmentation involving loss of Cl.

Crystal data

$[\text{Rh}_2(\text{CH}_{10}\text{B}_7\text{OS})(\text{C}_{10}\text{H}_{15})_2\text{Cl}]$	Mo $K\alpha$ radiation
$M_r = 657.53$	Cell parameters from 37770 reflections
Tetragonal, $P4$	$\theta = 1.00\text{--}27.48^\circ$
$a = 18.1926(2) \text{ \AA}$	$\mu = 1.365 \text{ mm}^{-1}$
$c = 8.44420(10) \text{ \AA}$	$T = 150(2) \text{ K}$
$V = 2794.78(5) \text{ \AA}^3$	Prism, dark red
$Z = 4$	$0.60 \times 0.19 \times 0.15 \text{ mm}$
$D_x = 1.563 \text{ Mg m}^{-3}$	

Data collection

Nonius KappaCCD area-detector diffractometer	5465 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{\text{int}} = 0.079$
$T_{\text{min}} = 0.495$, $T_{\text{max}} = 0.822$	$\theta_{\text{max}} = 26^\circ$
50782 measured reflections	$h = -22 \rightarrow 22$
2956 independent reflections (plus 2532 Friedel reflections)	$k = -22 \rightarrow 22$
	$l = -9 \rightarrow 10$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.003$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
$wR(F^2) = 0.080$	$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$
$S = 1.143$	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
5488 reflections	Extinction coefficient: 0.0086 (6)
310 parameters	Absolute structure: Flack (1983)
H atoms: see below	Flack parameter = -0.02 (4)
$w = 1/[\sigma^2(F_o^2) + (0.0358P)^2 + 4.4768P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (Å, °).

Rh6—B2	2.238 (5)	B1—S5	1.971 (6)
Rh6—B7	2.259 (5)	B2—B3	1.702 (8)
Rh6—S5	2.2831 (12)	B2—B7	1.725 (8)
Rh6—Cl69	2.3475 (11)	B2—S5	1.998 (7)
Rh9—B10	2.066 (6)	B3—B7	1.736 (8)
Rh9—B4	2.156 (5)	B3—B4	1.750 (8)
Rh9—B8	2.195 (5)	B3—B8	1.760 (8)
Rh9—Cl69	2.3536 (11)	B4—B10	1.733 (9)
B1—B4	1.691 (9)	B4—B8	1.764 (8)
B1—B3	1.723 (10)	S5—B10	1.863 (6)
B1—B2	1.786 (9)	B7—B8	1.820 (7)
B1—B10	1.808 (9)	B8—O81	1.351 (6)
Rh6—Cl69—Rh9	106.82 (4)		

The final difference Fourier map showed two areas of diffuse electron density. Attempts to model these meaningfully as disordered solvent molecules were entirely unsuccessful. The contribution of these solvent 'voids' was therefore 'subtracted' from the measured data using the *SQUEEZE* routine of *PLATON* (van der Sluis & Spek, 1990). This program indicated an approximate total of 23 electrons in the two sites which, assuming both voids contain disordered hexane molecules, corresponds to approximately $0.11\text{C}_6\text{H}_{14}$. However, an accurate determination of the stoichiometric quantity of solvent in the crystal is not possible, so no contribution from the solvent has been included in the calculations of molecular formula, $F(000)$ value and calculated density. Methyl-associated H atoms were constrained to calculated positions with isotropic displacement parameters equal to $1.5U_{\text{eq}}$ of the parent C atom. Cluster-associated H atoms were either located *via* Fourier difference syntheses (open face; H7, H10 and H78) or positioned in calculated positions (five-connected vertices) and assigned isotropic displacement parameters equal to $1.2U_{\text{eq}}$ of the parent B atom. Although parameters associated with these atoms were used in structure-factor calculations they were not included in refinement.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1996); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *PLATON* (Spek, 2000) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *WC* (Thornton-Pett, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1000). Services for accessing these data are described at the back of the journal.

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