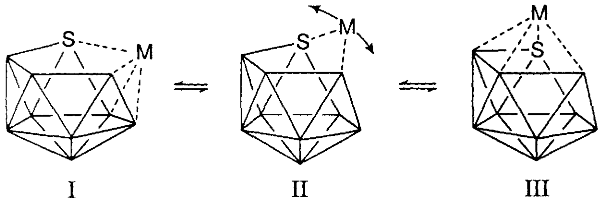
Novel Rhodathiaborane Complexes Derived from [$(PPh_3)_2RhSB_9H_{10}$]

George Ferguson,[a] Michael C. Jennings,[a] Alan J. Lough,[a] Siobhan Coughlan,[b] Trevor R. Spalding,[b] John D. Kennedy,[c] Xavier L. R. Fontaine,[c] and Bohumil Štíbr[c,d]

[a] *Chemistry Department, University of Guelph, Guelph, Ontario, Canada N1G 2W1*
[b] *Chemistry Department, University College, Cork, Ireland*
[c] *School of Chemistry, University of Leeds, Leeds LS2 9JT, UK*
[d] *Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 25068 Řež, Prague, Czechoslovakia*

The compound [8,8-$(PPh_3)_2$-8,7-$RhSB_9H_{10}$], (**1**), has a formal *closo* electron count but a *nido* structure, exhibits unusual fluxional behaviour in solution and reacts to give both *closo* and *nido* compounds, *e.g.*, *closo*-[2,3-$(PPh_3)_2$-3-(Cl)-μ-2; 3-(Cl)-2-($Ph_2PC_6H_4$)-2,3,1-$Rh_2SB_9H_8$], (**2**), and *nido*-[8,8-$(PPh_3)_2$-μ-8;9-(S_2CH)-8,7-$RhSB_9H_9$], (**3**); the structures of (**1**), (**2**), and (**3**) were determined by *X*-ray crystallographic methods.

Reaction between Cs[*arachno*-6-SB_9H_{12}] and [$Rh(PPh_3)_3Cl$] in ethanol at room temperature for 2 h affords air-stable, orange [8,8-$(PPh_3)_2$-8,7-$RhSB_9H_{10}$], (**1**), in 81% yield. Recrystallisation from CH_2Cl_2 solution gave crystals suitable for *X*-ray diffraction analysis (Figure 1 and Table 1). The *nido* structure of (**1**) is similar in its gross cage geometry to the known *nido* compounds [8-(η^6-MeC_6H_5)-8,7-$FeSB_9H_{11}$],[1] and [8-(η^5-C_5Me_5)-8,7-$IrSB_9H_{11}$][2] but in contrast to these compound (**1**) has a formally unsaturated 16-electron metal



Scheme 1

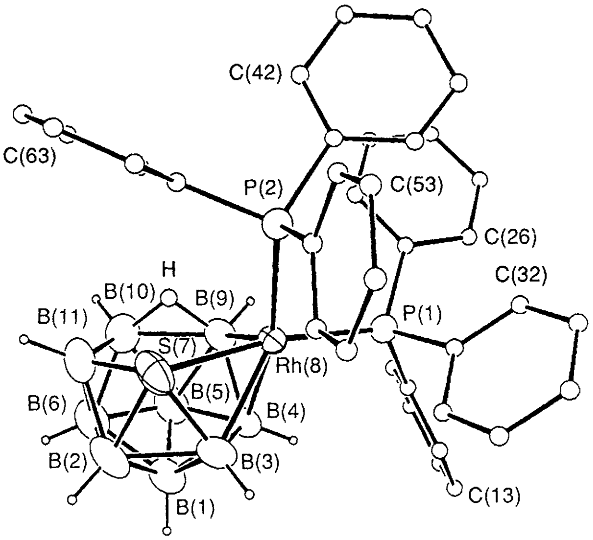


Figure 1. General view of one enantiomer of (1), [8,8-$(PPh_3)_2$-8,7-$RhSB_9H_{10}$] showing numbering scheme. For clarity all phenyl ring carbon atoms are shown as spheres of an arbitrary size. Bond lengths (Å); Rh(8)–S(7) 2.3769(6), Rh(8)–P(1) 2.2906(5), Rh(8)–P(2) 2.4197(5), Rh(8)–B(3) 2.242(4), Rh(8)–B(4) 2.236(3), Rh(8)–B(9) 2.146(3), S(7)–B(2) 1.986(4), S(7)–B(3) 2.035(4), S(7)–B(11) 1.908(4). Boron–boron distances range from 1.713(6) for B(6)–B(11) to 1.887(5) for B(2)–B(3) and the hydrogen bridged B(9)–B(10) distance is 1.863(7) (Å). Bond angles (°) around Rh(8); P(1)–Rh(8)–P(2) 98.50(2), S(7)–Rh(8)–P(1) 170.05(3), S(7)–Rh(8)–P(2) 85.88(3), S(7)–Rh(8)–B(9) 92.30(9), P(1)–Rh(8)–B(9) 93.07(9), Rh(8)–S(7)–B(11) 107.5(1).

Table 1. Crystallographic data.[a,b]

Compound	(**1**)·CH_2Cl_2	(**2**)·0.5(CH_2Cl_2)	(**3**)·C_6H_6
M	851.9	1242.5	921.2
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$Pbca$	$P\bar{1}$
a/Å	11.340(4)	18.610(5)	13.100(2)
b/Å	22.090(4)	23.183(10)	16.772(2)
c/Å	16.209(4)	26.853(10)	12.120(2)
α/°	—	—	107.91(1)
β/°	99.01(2)	—	117.16(1)
γ/°	—	—	93.73(1)
D_c/g cm^{-3}	1.41	1.42	1.40
U/Å^3	4010(3)	11585(12)	2187(1)
Z	4	8	2
Total no. ref'ns	8732	12242	9791
No. observed ref'ns [$I > 3\sigma(I)$]	6194	5610	7209
No. parameters	473	652	527
R	0.030	0.045	0.027
R_w	0.039	0.058	0.035
μ/cm^{-1}	7.09	8.5	6.2
abs (min.)	0.80	0.74	0.83
abs (max.)	0.91	1.20	0.94

[a] Data were collected on a CAD4 diffractometer at ambient temperature (20 ± 2 °C). After correction for Lorentz, polarisation, and absorption effects, the structures were solved by the Patterson heavy-atom method and refined by full-matrix least-squares calculations. Hydrogen atoms were located from difference maps and included as riding atoms (C–H 0.95 Å, B–H 1.08 Å) in the final round of refinement. All non-hydrogen atoms were allowed anisotropic motion. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1. [b] The solvent molecules were well behaved except for compound (**2**), dichloromethane solvate in which CH_2Cl_2 was only present with 0.5 occupancy.

centre. The effect of this on the cluster bonding is not entirely clear but in this context the ^{11}B and ^1H NMR shielding patterns† seem quite different to those reported for the more conventional *nido*-[8,7-MSB_9]-cluster types that have the {SB_9H_{11}} fragment.[1,2] However the shielding pattern in (**1**) appears more like that of the *nido*-{SB_9H_{11}} fragment than the *arachno*-{SB_9H_{12}}$^-$ moiety. An additional novel feature is that compound (**1**) is fluxional between enantiomers, the NMR coalescence behaviour indicating that this arises *via* a transfer of the {$(PPh_3)_2Rh$}-unit (with a corresponding reverse transfer of the B–B-bridging hydrogen atom) from one side to the other of the *nido*-structured {SB_9H_9} fragment (*i.e.*, I $\rightleftharpoons$ III in Scheme 1).

The activation energy $\Delta G^‡$ for this process is *ca.* 58 kJ mol^{-1}. It is reasonable to suggest that the interconversion I $\rightleftharpoons$ III passes through an eleven-vertex conventionally *closo*-structured species {II in Scheme 1 which would perhaps be [1,1-$(PPh_3)_2$-1-(H)-1,2-$RhSB_9H_9$]} and for which an unstable structural congener, *closo*-[1-(η^5-C_5Me_5)-1,2-$IrSB_9H_9$], has been recently characterised.[2a]

The unusual constitution of (**1**) implies enhanced reactivity, and in accord with this we have observed facile reactions of (**1**) with both electrophilic and nucleophilic centres. Several of these products also have novel structural or bonding features.

The *closo* compound [2,3-$(PPh_3)_2$-3-(Cl)-μ-2;3-(Cl)-2-($Ph_2PC_6H_4$)-2,3,1-$Rh_2SB_9H_8$], (**2**), was isolated in 74.5% yield from the reaction of equimolar amounts of (**1**) and [$Rh(PPh_3)_3Cl$] in dichloromethane at room temperature for 4 h in the presence of added [Me_4N]Cl. Recrystallisation from CH_2Cl_2 : cyclohexane solution gave crystals which analysed as (**2**)·0.5CH_2Cl_2 (Figure 2 and Table 1). Compound (**2**) is a *closo* twelve-vertex {Rh_2SB_9} compound with the sulphur and two rhodium atoms occupying one triangular face. The analogous compounds [2,3-(η^5-C_5Me_5)$_2$-7-(Cl)-2,3,1-$Rh_2SB_9H_8$],[3] and [2,3-(η^5-C_5H_5)$_2$-7-(I)-2,3,1-$Co_2SB_9H_8$][4] have been reported previously. In (**2**) however, the metal atoms are bridged by a chlorine atom which is a feature unique in any contiguous metallaborane-type cluster as far as we are aware. The rhodium to bridging chlorine distances are similar [Rh(2)–Cl(1) 2.437(2), Rh(3)–Cl(1) 2.448(2) Å] and the Rh(2)–Rh(3) distance is 2.6307(9) Å. In formal electron counting terms the bridging chlorine atom is acting as a three-electron donor and the metal units in (**2**) may be assessed as {$(PPh_3)_2Rh(Cl)$} and {(PPh_3)(μ-Cl)RhCl} which are both Wadian equivalents to {BH}. In addition to the bridging chlorine atom, (**2**) contains a terminal chlorine ligand and an *ortho*-cycloboronated site at B(7), Figure 2. This latter site is of interest since it is the only boron atom bound to both

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† *Measured NMR data* for compound (**1**) in CD_2Cl_2 at 294—297 K: BH data {tentative assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm]} as follows: B–H(3) +16.3 [+4.14], B–H(9) +12.6 [+3.59], B–H(1) +6.0 [+3.26], B–H(11) +4.5 [+2.32], B–H(4) +2.5 [2.38], B–H(5) −9.3 [+1.78], B–H(6) −18.6 [+1.56], B–H(10) −21.1 [+1.24], and B–H(2) −27.5 [+1.28]; $\delta(^1H)$(μ-9,10) −1.32 ppm; $\delta(^{31}P)$ (at 223 K) +43.0 [$^1J(^{103}Rh–^{31}P)$ 160 Hz] and +20.3 ppm [$^1J(^{103}Rh–^{31}P)$ 128 Hz]. $^2J(^{31}P–^{31}P)$ 35.5 ± 2.5 Hz; at higher temperatures (T_c *ca.* 338 K) $^{11}B(3)$ and $^{11}B(11)$, $^{11}B(1)$ and $^{11}B(6)$, together with $^{11}B(4)$ and $^{11}B(10)$ coalesce in these respective pairs, implying $\Delta G^‡$ *ca.* 58 ± 3 kJ mol^{-1} for the fluxional process at this temperature. Contrast B–H shielding for [8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{11}$] {data from ref. 2a; assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm]}: B–H(5) +7.7 [+4.80], B–H(3) +1.1 [+2.52], B–H(9) −2.6 [+2.90], B–H(11) −12.9 [+2.57], B–H(4) −13.8 [+1.20], B–H(2) −17.0 [+2.61], B–H(6) −18.2 [+3.91], B–H(1) −22.1 [+1.46], B–H(10) −23.0 [+1.64]; $\delta(^1H)$ (μ-10,11) −4.52, (μ-8,9) −11.4 ppm. The above assignment for compound (**1**) is perhaps more like that of the ten-vertex *nido*-6-SB_9H_{11} fragment than the *arachno*-6-$SB_9H_{12}^-$ fragment (see SB_9 fragment data in ref. 2b).

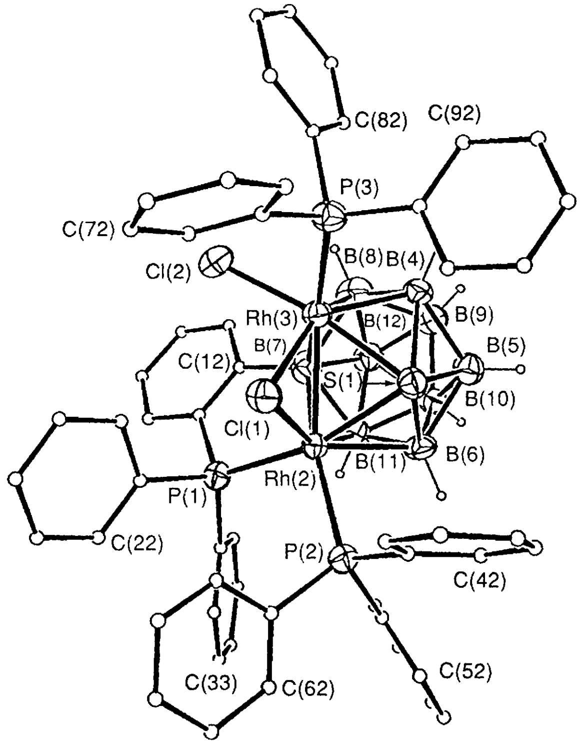

Figure 2. General view of (**2**) showing numbering scheme. For clarity all phenyl ring carbon atoms are shown as spheres of an arbitrary size. Bond lengths (Å); Rh(2)–Rh(3) 2.6307(9), Rh(2)–S(1) 2.434(2), Rh(2)–P(1) 2.329(2), Rh(2)–P(2) 2.404(2), Rh(2)–Cl(1) 2.437(2), Rh(2)–B(7) 2.293(10), Rh(2)–B(6) 2.300(9), Rh(2)–B(11) 2.219(9); Rh(3)–S(1) 2.325(2), Rh(3)–P(3) 2.360(2), Rh(3)–Cl(1) 2.448(2), Rh(3)–Cl(2) 2.356(2), Rh(3)–B(7) 2.337(10), Rh(3)–B(4) 2.223(9), Rh(3)–B(8) 2.186(10), S(1)–B(4) 2.159(9), S(1)–B(5) 1.963(10), S(1)–B(6) 2.057(9). Intercage B–B distances range from 1.716(14) for B(7)–B(12) to 1.905(13) Å for B(4)–B(5). The Rh(2)–Cl(1)–Rh(3) angle is 65.16(5)°.

metals, suggesting that it is activated during the formation of compound (**2**), and it is noteworthy that the related $[Rh_2SB_9]$[3] and $[Co_2SB_9]$[4] compounds contain substituents at B(7) also. The ^{11}B and ^{1}H NMR nuclear shielding patterns of (**2**)‡ are consistent with the *closo*-formulation and are similar to those of the species *closo*-$[(\eta^5\text{-}C_5Me_5)_2Rh_2B_9H_9PPh]$.[5]

Reaction between (**1**) and CS_2 in refluxing CS_2 solvent for 36 h afforded a *nido* complex, (**3**), in 37.0% yield. The compound, *nido*-$[8,8\text{-}(PPh_3)_2\text{-}\mu\text{-}8;9\text{-}(S_2CH)\text{-}8,7\text{-}RhSB_9H_9]$, was recrystallised from benzene solution. An *X*-ray diffraction study (Figure 3 and Table 1) revealed a unique S_2CH metal–boron bridging feature which may conceivably be formed by the addition of a C=S bond across the B(9)–H(9) in (**1**) (or across the equivalent position in the enantiomer). The dihedral angle between the plane containing the atoms in the open face of the cluster {S(7), Rh(8), B(9), B(10), B(11)} and that containing the atoms in the adjacent ring {Rh(8), S(1), C(1), S(2), B(9)} is 7.2°. Whereas in (**1**), the phosphine ligand P(1) is *trans* to S(7), in (**3**) it is *trans* to B(9) and the S(1) atom is *trans* to S(7). These different *trans* ligands induce significantly different Rh(8)–S(7) distances [2.3769(6) and 2.3561(4) Å respectively]. In general the comparable intercage distances in (**1**) and (**3**) are all remarkably similar except for those in the Rh(8)–S(7)–B(3) face. The S(7)–B(3) and Rh(8)–B(3) distances are 2.035(4), 2.242(4) Å for (**1**) and 2.072(3), 2.277(2) Å for (**3**) respectively. These distances could be expected to be most affected by the difference in the ligands *trans* to S(7) in (**1**) and (**3**). The ^{11}B and ^{1}H NMR shielding patterns for (**3**) appear to be very similar to those in (**1**).§

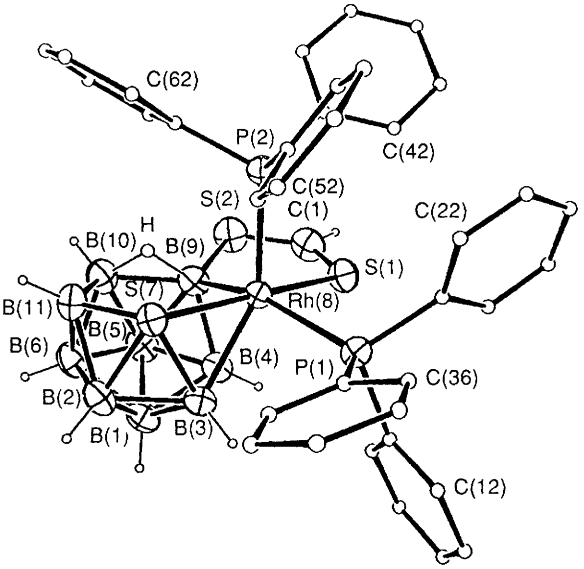

Figure 3. General view of (**3**) showing numbering scheme. For clarity all phenyl ring carbon atoms are shown as spheres of an arbitrary size. Bond lengths (Å); Rh(8)–S(7) 2.3561(4), Rh(8)–S(1) 2.2905(5), Rh(8)–P(1) 2.5599(7), Rh(8)–P(2) 2.4141(6), Rh(8)–B(9) 2.159(3), Rh(8)–B(3) 2.277(2), Rh(8)–B(4) 2.247(3), S(7)–B(2) 1.988(3), S(7)–B(3) 2.072(3), S(7)–B(11) 1.920(3), C(1)–S(1) 1.643(3), C(1)–S(2) 1.682(2), and S(2)–B(9) 1.894(2). Boron–boron distances range from 1.740(5) Å for B(6)–B(11) to 1.889(3) Å for B(2)–B(3). The B(9)–B(10) distance is 1.842(3) Å.

The remarkable similarities in general of the $RhSB_9$-cage dimensions and NMR parameters of (**1**) and (**3**) suggests the involvement of extra electron density originating from the rhodium atom in (**1**). The implications of this are presently under investigation.

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‡ *Measured NMR data* for compound (**2**) in CD_2Cl_2 at 294—297 K; B–H and B–X data {$\delta(^{11}B)$/ppm {comments} [$\delta(^{1}H)$/ppm of directly bound H atoms]}: +71.3 {broader, B(7)} [no H; *ortho*-cyclophenylated site], +15.3 {sharper} [+4.14], *ca.* +8 {broader, B(4) or (6)}, [+3.43, doublet splitting 21 Hz], +6.2 {sharper} [+3.92], +2.4 {sharper} [+3.53], *ca.* −2.8 {broader, B(4) or B(6)} [+2.40], −4.7 {intermediate line width} [+2.74], −6.6 {intermediate line width} [+1.61], and −27.7 {broader, B(5)} [+0.31]; aromatic ^{1}H region exhibited apparent triplet δ +6.44, apparent doublet δ +7.88, flanking the main agglomeration of aromatic resonances, arising from the *ortho*-cycloboronated $\{Ph_2PC_6H_4\}$ moiety. Additionally (CD_2Cl_2 at 223 K) $\delta(^{31}P_A)$ +49.8 [$^{1}J(^{103}Rh\text{–}^{31}P)$ 139 Hz], $\delta(^{31}P_B)$ +33.0 [$^{1}J(^{103}Rh\text{–}^{31}P)$ 104 Hz], $\delta(^{31}P_C)$ *ca.* +25.2 Hz [$^{1}J(^{103}Rh\text{–}^{31}P)$ 104 Hz, with additional splitting {?$^{2}J(^{103}Rh\text{–}^{31}P)$} of 5 Hz]. Compare B–H and B–X data for $[(C_5Me_5)_2Rh_2B_9H_8PPh]$ {data from ref. 5: assignment {comments} $\delta(^{11}B)$/ppm [$\delta(^{1}H)$/ppm]}: B(7) {T_1 changes markedly on substitution} +41.4 [+4.66], B(8,11) +8.7 [+2.87], B(9,10) +1.8 [+3.65, doublet splitting *ca.* 18 Hz], B(4,6) −6.5 {broad} [+2.11], B(12) −10.9 [+2.13], and B(5) −29.5 {broad} [+1.55].

§ *Measured NMR data* for (**3**) in CD_2Cl_2 solution at 293—297 K; B–H/B–X data: tentative provisional assignment $\delta(^{11}B)$/ppm [$\delta(^{1}H)$/ppm] as follows: B(9)–S(2) +22.7 [−], B–H(3) +10.0 [+3.87], B–H(1) +6.2 [+3.22], B–H(11) +3.4 [+2.37], B–H(4) −2.1 [2.88], B–H(5) −8.8 [+2.34], B–H(6) and B–H(10) −20.9 [+0.97] and −23.2 [+1.53], B–H(2) −30.0 [+1.15]; other data: $\delta(^{1}H)$ (μ-9,10) −0.67 ppm; $\delta(^{1}H)(HCS_2)$ (^{1}H-{^{31}P} spectrum) +9.90 ppm broad [probably from $^{3}J(^{11}B\text{–}^{1}H)$], $w_{1/2}$ (293 K) 13 Hz {at 243 K $\delta(^{1}H)$ +9.89 ppm [$J(^{31}P\text{–}^{1}H)$ 5.9 Hz and $J(^{103}Rh\text{–}^{1}H)$ 5.0 Hz]}; $\delta(^{31}P)$ +34.5 (sharper) and +12.7 (broader) ppm; assignments based on parallels of ^{11}B and ^{1}H shielding patterns and lineshapes with those of compound (**1**).

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