

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

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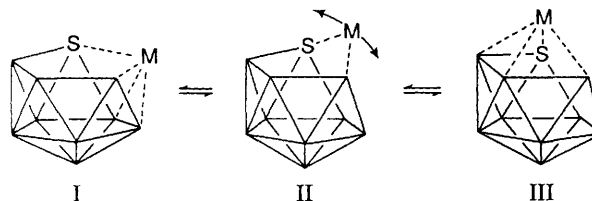
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The compound $[8,8-(PPh_3)_2-8,7-RhSB_9H_{10}]$, (**1**), has a formal *closo* electron count but a *nido* structure, exhibits unusual fluxional behaviour in solution and reacts to give both *closo* and *nido* compounds, e.g., *closo*- $[2,3-(PPh_3)_2-3-(Cl)-\mu-2; 3-(Cl)-2-(Ph_2PC_6H_4)-2,3,1-Rh_2SB_9H_8]$, (**2**), and *nido*- $[8,8-(PPh_3)_2-\mu-8;9-(S_2CH)-8,7-RhSB_9H_9]$, (**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 $[8-(\eta^6-MeC_6H_5)-8,7-FeSB_9H_{11}]$,¹ and $[8-(\eta^5-C_5Me_5)-8,7-IrSB_9H_{11}]$ ² but in contrast to these compound (**1**) has a formally unsaturated 16-electron metal



Scheme 1

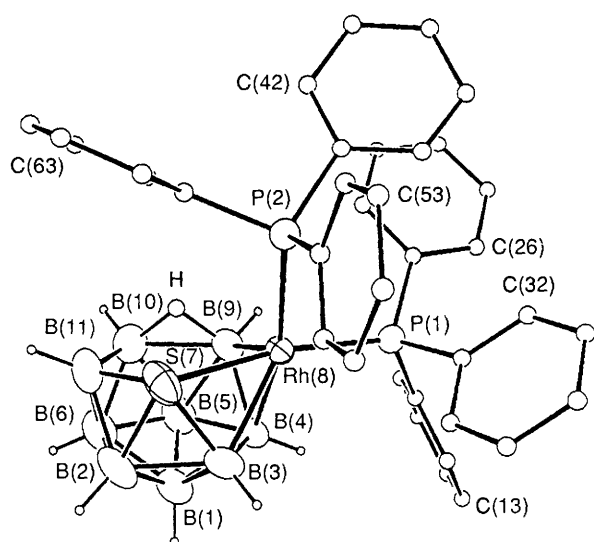


Figure 1. General view of one enantiomer of (1), [8,8-(PPh₃)₂-8,7-RhSB₉H₁₀] showing numbering scheme. For clarity all phenyl ring carbon atoms are shown as spheres of an arbitrary size. Bond lengths (Å): Rh(8)–S(7) 2.3769(6), Rh(8)–P(1) 2.2906(5), Rh(8)–P(2) 2.4197(5), Rh(8)–B(3) 2.242(4), Rh(8)–B(4) 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).

centre. The effect of this on the cluster bonding is not entirely clear but in this context the ¹¹B and ¹H NMR shielding patterns† seem quite different to those reported for the more conventional *nido*-[8,7-MSB₉]-cluster types that have the {SB₉H₁₁} fragment.^{1,2} However the shielding pattern in (1) appears more like that of the *nido*-{SB₉H₁₁} fragment than the *arachno*-{SB₉H₁₂}⁻ 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 {(PPh₃)₂Rh}-unit (with a corresponding reverse transfer of the B–B-bridging hydrogen atom) from one side to the other of the *nido*-structured {SB₉H₉} fragment (*i.e.*, I ⇌ III in Scheme 1).

The activation energy ΔG[‡] for this process is *ca.* 58 kJ mol⁻¹. It is reasonable to suggest that the interconversion I ⇌ III passes through an eleven-vertex conventionally *closo*-structured species {II in Scheme 1 which would perhaps be

† Measured NMR data for compound (1) in CD₂Cl₂ at 294–297 K: BH data (tentative assignment δ(¹¹B)/ppm [δ(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]; δ(¹H)(μ-9,10) –1.32 ppm; δ(³¹P) (at 223 K) +43.0 [¹J(¹⁰³Rh–³¹P) 160 Hz] and +20.3 ppm [¹J(¹⁰³Rh–³¹P) 128 Hz]. ²J(³¹P–³¹P) 35.5 ± 2.5 Hz; at higher temperatures (*T*_c *ca.* 338 K) ¹¹B(3) and ¹¹B(11), ¹¹B(1) and ¹¹B(6), together with ¹¹B(4) and ¹¹B(10) coalesce in these respective pairs, implying ΔG[‡] *ca.* 58 ± 3 kJ mol⁻¹ for the fluxional process at this temperature. Contrast B–H shielding for [8-(η⁵-C₅Me₅)-*nido*-8,7-IrSB₉H₁₁] {data from ref. 2a; assignment δ(¹¹B)/ppm [δ(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]; δ(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-SB₉H₁₁ fragment than the *arachno*-6-SB₉H₁₂⁻ fragment (see SB₉ fragment data in ref. 2b).

Table 1. Crystallographic data.^{a,b}

Compound	(1)·CH ₂ Cl ₂	(2)·0.5(CH ₂ Cl ₂)	(3)·C ₆ H ₆
<i>M</i>	851.9	1242.5	921.2
Crystal system	monoclinic	orthorhombic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> 1
<i>a</i> /Å	11.340(4)	18.610(5)	13.100(2)
<i>b</i> /Å	22.090(4)	23.183(10)	16.772(2)
<i>c</i> /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)
<i>D</i> _c /g cm ⁻³	1.41	1.42	1.40
<i>U</i> /Å ³	4010(3)	11585(12)	2187(1)
<i>Z</i>	4	8	2
Total no. refs	8732	12242	9791
No. observed refs [<i>I</i> > 3σ(<i>I</i>)]	6194	5610	7209
No. parameters	473	652	527
<i>R</i>	0.030	0.045	0.027
<i>R</i> _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 CH₂Cl₂ was only present with 0.5 occupancy.

[1,1-(PPh₃)₂-1-(H)-1,2-RhSB₉H₉] and for which an unstable structural congener, *closo*-[1-(η⁵-C₅Me₅)-1,2-IrSB₉H₉], 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-(PPh₃)₂-3-(Cl)-μ-2,3-(Cl)-2-(Ph₂PC₆H₄)-2,3,1-Rh₂SB₉H₈], (2), was isolated in 74.5% yield from the reaction of equimolar amounts of (1) and [Rh(PPh₃)₃Cl] in dichloromethane at room temperature for 4 h in the presence of added [Me₄N]Cl. Recrystallisation from CH₂Cl₂:cyclohexane solution gave crystals which analysed as (2)·0.5CH₂Cl₂ (Figure 2 and Table 1). Compound (2) is a *closo* twelve-vertex {Rh₂SB₉} compound with the sulphur and two rhodium atoms occupying one triangular face. The analogous compounds [2,3-(η⁵-C₅Me₅)₂-7-(Cl)-2,3,1-Rh₂SB₉H₈],³ and [2,3-(η⁵-C₅H₅)₂-7-(1)-2,3,1-Co₂SB₉H₈]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 {(PPh₃)₂Rh(Cl)} and {(PPh₃)₂(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

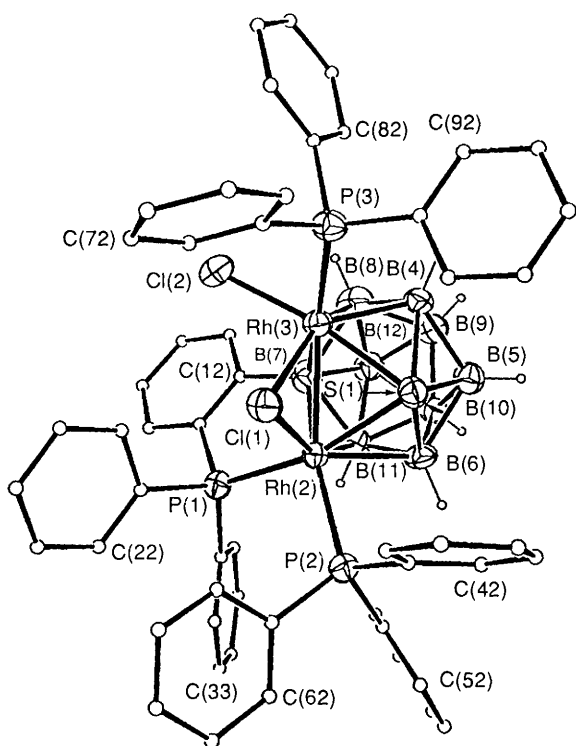


Figure 2. General view of (2) showing numbering scheme. For clarity all phenyl ring carbon atoms are shown as spheres of an arbitrary size. Bond lengths (Å): Rh(2)–Rh(3) 2.6307(9), Rh(2)–S(1) 2.434(2), Rh(2)–P(1) 2.329(2), Rh(2)–P(2) 2.404(2), Rh(2)–Cl(1) 2.437(2), Rh(2)–B(7) 2.293(10), Rh(2)–B(6) 2.300(9), 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 $[\text{Rh}_2\text{SB}_9]^3$ and $[\text{Co}_2\text{SB}_9]^4$ compounds contain substituents at B(7) also. The ^{11}B and ^1H NMR nuclear shielding patterns of (2)† are consistent with the *closo*-formulation and are similar to those of the species *closo*- $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2\text{B}_9\text{H}_9\text{PPh}]$.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-(PPh_3)₂- μ -8;9-(S_2CH)-8,7-RhSB₉H₉],

† Measured NMR data for compound (2) in CD_2Cl_2 at 294–297 K; B–H and B–X data $\{\delta(^{11}\text{B})/\text{ppm} \{\text{comments}\} [\delta(^1\text{H})/\text{ppm} \text{ of directly bound H atoms}]\}$: +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 ^1H region exhibited apparent triplet δ +6.44, apparent doublet δ +7.88, flanking the main agglomeration of aromatic resonances, arising from the *ortho*-cycloboronated ($\text{Ph}_2\text{PC}_6\text{H}_4$) moiety. Additionally (CD_2Cl_2 at 223 K) $\delta(^{31}\text{P}_\text{A})$ +49.8 [$^1J(^{103}\text{Rh}-^{31}\text{P})$ 139 Hz], $\delta(^{31}\text{P}_\text{B})$ +33.0 [$^1J(^{103}\text{Rh}-^{31}\text{P})$ 104 Hz], $\delta(^{31}\text{P}_\text{C})$ *ca.* +25.2 Hz [$^1J(^{103}\text{Rh}-^{31}\text{P})$ 104 Hz, with additional splitting ($^2J(^{103}\text{Rh}-^{31}\text{P})$) of 5 Hz]. Compare B–H and B–X data for $[(\text{C}_5\text{Me}_5)_2\text{Rh}_2\text{B}_9\text{H}_9\text{PPh}]$ {data from ref. 5: assignment {comments} $\delta(^{11}\text{B})/\text{ppm} [\delta(^1\text{H})/\text{ppm}]$: 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].

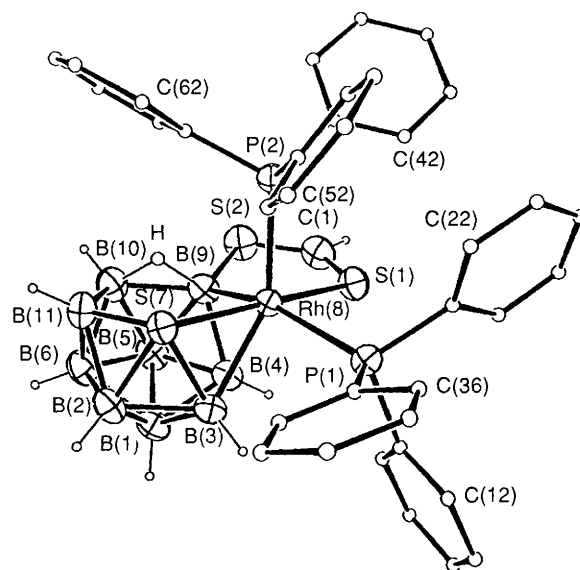


Figure 3. General view of (3) showing numbering scheme. For clarity all phenyl ring carbon atoms are shown as spheres of an arbitrary size. Bond lengths (Å): Rh(8)–S(7) 2.3561(4), Rh(8)–S(1) 2.2905(5), Rh(8)–P(1) 2.5599(7), Rh(8)–P(2) 2.4141(6), Rh(8)–B(9) 2.159(3), Rh(8)–B(3) 2.277(2), Rh(8)–B(4) 2.247(3), 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.

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 ^1H NMR shielding patterns for (3) appear to be very similar to those in (1).[§]

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.

§ Measured NMR data for (3) in CD_2Cl_2 solution at 293–297 K; B–H/B–X data: tentative provisional assignment $\delta(^{11}\text{B})/\text{ppm} [\delta(^1\text{H})/\text{ppm}]$ 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: $\delta(^1\text{H})$ (μ -9,10) –0.67 ppm; $\delta(^1\text{H})(\text{HCS}_2)$ ($^1\text{H}-^{31}\text{P}$) spectrum +9.90 ppm broad [probably from $^3J(^{11}\text{B}-^1\text{H})$], $w_{1/2}$ (293 K) 13 Hz [at 243 K $\delta(^1\text{H})$ +9.89 ppm [$^1J(^{31}\text{P}-^1\text{H})$ 5.9 Hz and $^1J(^{103}\text{Rh}-^1\text{H})$ 5.0 Hz]]; $\delta(^{31}\text{P})$ +34.5 (sharper) and +12.7 (broader) ppm; assignments based on parallels of ^{11}B and ^1H shielding patterns and lineshapes with those of compound (1).

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