Metallaheteroborane Chemistry. Part 10.[1] Synthesis and Characterisation of *closo*-Structured Rhodathiaborane Complexes [1-(CO)-1-L-3-L′-1,2-$RhSB_9H_8$] (L = L′ = PPh_3; L = PMe_2Ph, L′ = PMe_2Ph or PPh_3)†

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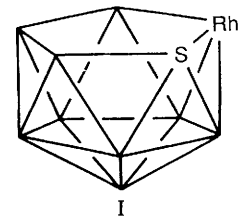
The reaction of CO with [8,8-$(PPh_3)_2$-8,7-$RhSB_9H_{10}$] **1** in benzene yields [8-(CO)-8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] **3** in 98% yield. Refluxing a benzene solution of **3** produces [1-(CO)-1,3-$(PPh_3)_2$-*closo*-1,2-$RhSB_9H_8$] **4** in 46% yield. The reaction between **4** and excess of PMe_2Ph in refluxing benzene affords [1-(CO)-1-(PMe_2Ph)-3-L-*closo*-1,2-$RhSB_9H_8$] [L = PMe_2Ph **5** (25%) or PPh_3 **6** (46%)]. NMR data (^1H, ^{11}B and ^{31}P) confirm the *nido* nature of **3** and the *closo* structures of compounds **4**–**6**. X-Ray diffraction studies of **4**, **4′** (= **4**·1.5C_6H_5Me), and **5** showed that there was conformational disorder in all three cases. The structure of **5** was solved in space group $P2_1/n$ with unit cell dimensions of a = 9.626(2), b = 23.714(5), c = 11.595(2) Å, β = 109.00(2)°, and Z = 4. The final R factor was 0.027 for 4472 observed reflections. Principal interatomic distances are Rh(1)–S(2) 2.3736(7), Rh(1)–P(1) 2.3090(7), Rh(1)–C(1) 1.855(3), Rh(1)–B(3) 2.101(3), Rh(1)–B (4, 5, 6, 7) 2.380(3)–2.444(3), S(2)–B 1.923(3)–1.989(4), B–B 1.719(4)–1.897(4) and B(3)–P(2) 1.895(3) Å. The geometry of the $RhSB_9$ cage in **5** was used as a template in the final refinement of the structures of **4** and **4′** which were more disordered: **4**, space group $C2/c$, a = 37.529(11), b = 10.749(5), c = 19.536(5) Å, β = 101.96(2)°, Z = 8, R 0.051 for 3970 observed reflections; **4′**, space group $P\bar{1}$, a = 11.933(2), b = 14.157(2), c = 14.190(2) Å, α = 79.25(1), β = 83.27(1), γ = 87.32(1)°, Z = 2, R 0.041 for 6959 observed reflections.

We recently reported the characterisation of a rhodathiaborane [$(PPh_3)_2RhSB_9H_{10}$] **1** which had a formal *closo* electron count but a *nido* cluster structure.[2] This compound had a five-membered $RhSB_3$ open face **I** and thereby contravened the structure electron-counting rules known as Wade's rules.[3] A survey of the literature shows that although eleven-atom *nido*-structured/*nido*-count metallaheteroboranes with heteroatoms from the chalcogen Group 16, for example the platinathiaborane *nido*-[$(PEt_3)_2HPtSB_9H_{10}$],[4] have been established for some time, eleven-atom *closo*-structured compounds are notably absent. Certainly, no eleven-atom *closo*-structured platinathiaboranes appear to have been characterised unambiguously.[5–7] Recently, an iridium complex [1-(η^5-C_5Me_5)-1,2-$IrSB_9H_9$] **2**, which appeared to have a *closo* structure, has been synthesised.[8] However, no structural work was reported. In the present work we describe the synthesis and characterisation by spectroscopic and X-ray diffraction techniques of three stable *closo*-structured rhodathiaboranes of the general type [1-(CO)-1-L-3-L′-*closo*-1,2-$RhSB_9H_8$] with ligands L, L′ being phosphines.

Results and Discussion

When carbon monoxide is passed through a solution of [$(PPh_3)_2RhSB_9H_{10}$] **1**, in benzene at room temperature, the yellow solid [8-(CO)-8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] **3** is immediately produced in 98% yield, reaction (1). This



I

$$\underset{\mathbf{1}}{[8,8\text{-}(PPh_3)_2\text{-}8,7\text{-}RhSB_9H_{10}]} + CO \longrightarrow \underset{\mathbf{3}}{[8\text{-}(CO)\text{-}8,8\text{-}(PPh_3)_2\text{-}8,7\text{-}RhSB_9H_{10}]} \quad (1)$$

compound was characterised spectroscopically. The infrared spectrum showed BH stretching absorption band maxima at 2573s, 2565(sh), 2543(sh), 2536vs, 2524(sh), 2518(sh), 2498vw and 2487s cm^{-1}, and a CO stretching band at 2030vw cm^{-1}. The 128 MHz ^{11}B-{^1H} NMR spectrum consisted of six peaks in the intensity ratio 1:2:2:2:1:1, but there was accidental overlapping which could be resolved with line-narrowing techniques to establish nine different boron positions, and selective ^1H-{^{11}B} decoupling experiments on the ^1H spectrum established each of the nine cage ^{11}B–^1H related signals. Specific assignments were not attempted, but the chemical shifts of the resonances were within the range δ +15.6 to −27.3 (compare δ +16.3 to −27.5 for **1**) and the overall pattern was also

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Measured NMR parameters of [1-(CO)-1,3-$(PPh_3)_2$-*closo*-1,2-$RhSB_9H_8$] **4**, [1-(CO)-1,3-$(PMe_2Ph)_2$-*closo*-1,2-$RhSB_9H_8$] **5**,[a] [1-(CO)-1-(PMe_2Ph)-3-(PPh_3)-*closo*-1,2-$RhSB_9H_8$] **6**,[a] [1-(η^5-C_5Me_5)-1,2-*closo*-$IrSB_9H_9$] **2**,[b] and [1-(η^6-$MeC_6H_4Pr^i$-4)-1,2-*closo*-$RuNB_9H_{10}$] **7**[c] at 294–297 K

	Compound **4**				Compound **5**		Compound **6**
Assignment[d]	$\delta(^{11}B)^e$	$^1J(^{11}B-^1H)$	$\delta(^1H)$	$\delta(^{11}B)^f$	$\delta(^{11}B)$	$\delta(^1H)$	$\delta(^{11}B)$
3	+36.8(sp)	$[145]^g$	—	+36.8	$+37.2^{k,l}$	—	+35.8
9	+28.1(msp)	143	$+3.97^h$	+30.0	$+26.1^{m,n}$	$+4.12^{p,u}$	+27.4
4, 5	+4.6(mbr)	*i*	+2.61	+6.8	+3.0	$+2.29^r$	+2.7
	+0.3(mbr)	*i*	+1.34	+1.3	−1.9	$+1.64^{s,t}$	−1.1
8	−6.3(br)	*i*	+2.63	−4.5	−7.1	$+2.68^q$	−6.3
6, 7	−15.8(msp)	*ca.* 140	+0.70	−14.2	-18.1^k	$+0.64^s$	−17.1
	−19.9(msp)	*ca.* 145	+0.77	−18.0	-23.2^l	$+0.29^r$	−21.5
10, 11	−26.6(sp)	145	+0.19	-24.5^j	$-28.6^{m,o}$	$+0.13^{q,t,u}$	−28.6
	−28.7(sp)	145	+0.12	-26.7^j	$-31.5^{n,o}$	$+0.10^{q,t,u}$	−31.1

	Compound **2**, $CDCl_3$		Compound **7**, CD_2Cl_2	
	$\delta(^{11}B)$	$\delta(^1H)$	$\delta(^{11}B)$	$\delta(^1H)$
3	+50.1	+7.68	+53.2	+7.68
9	+21.6	+6.22	+19.6	+3.92
4, 5	+5.8	+2.68	+0.6	+2.54
8	−18.2	+2.05	−13.8	+2.50
6, 7	−19.5	−0.54	−22.5	+0.15
10, 11	−23.7	−0.80	−25.7	+0.09

[a] This work; δ values in ppm and *J* in Hz. Solvent CD_2Cl_2 unless stated otherwise. Additional data: for **4** (213 K): $\delta(^{31}P)$ +36.5(s), $^1J(^{103}Rh-^{31}P)$ 131 Hz and +4.3(br); for **5** (211 K), $\delta(^{31}P)$ +1.5 [d, $^1J(^{103}Rh-^{31}P)$ 126] and *ca.* −6.6 [q, $^1J(^{11}B-^{31}P)$ *ca.* 155 Hz]; for **6**, $\delta(^{31}P)$ −2.4 (d, Rh–P) and +3.2 (q, B–P). [b] Data from ref. 8. [c] Data from ref. 9 assigned by COSY experiments. [d] See text. [e] sp = Sharp, br = broad and m = medium. [f] In $CD_3C_6H_5$ at 363 K. [g] Refers to $^1J(^{31}P-^{11}B)$. [h] $^3J(^{31}P-^1H)$ 16 Hz. [i] The ^{11}B peaks are too broad for accurate estimation. [j] [$^{11}B-^{11}B$]-COSY correlation observed only between these two peaks. [k–o] [$^{11}B-^{11}B$]-COSY correlated pairs. [p] Doublet structure splitting 25 Hz. [q–u] [$^1H-^1H$]-COSY correlated pairs.

remarkably similar to that for **1**. In addition, a bridging B–*H*–B proton resonance occurred at δ −3.85 and two phosphorus signals were observed in the ^{31}P NMR spectrum at δ +23.6 (sharp) and +14.8 (br), both being coupled to rhodium with $^1J(^{103}Rh-^{31}P)$ 122 ± 5 and 74 ± 5 Hz respectively.

Heating a solution of compound **3** in benzene at reflux temperature for 5 h produced an orange solution which contained only one product in any significant amount. This was recrystallised from toluene–light petroleum (b.p. 100–120 °C) to afford yellow crystals of *closo*-structured [1-(CO)-1,3-$(PPh_3)_2$-1,2-$RhSB_9H_8$] **4** in 46% yield, reaction (2).

$$\underset{\mathbf{3}}{[8\text{-(CO)-}8,8\text{-}(PPh_3)_2\text{-}8,7\text{-}RhSB_9H_{10}]} \xrightarrow{80\ ^\circ C} H_2\uparrow + \underset{\mathbf{4}}{[1\text{-(CO)-}1,3\text{-}(PPh_3)_2\text{-}1,2\text{-}RhSB_9H_8]} \quad (2)$$

The reaction between compound **4** and an eight-fold excess of PMe_2Ph in refluxing benzene solution for 4 d gave two yellow products, reaction (3). One was identified by spectroscopic and X-ray diffraction techniques as [1-(CO)-1,3-$(PMe_2Ph)_2$-1,2-$RhSB_9H_8$] **5** and the other was shown by spectroscopic methods to be the closely related *closo*-structured mixed-phosphine congener [1-(CO)-1-(PMe_2Ph)-3-(PPh_3)-1,2-$RhSB_9H_8$] **6**. Their yields were 25 and 46% respectively. The

$$\underset{\mathbf{4}}{[1\text{-(CO)-}1,3\text{-}(PPh_3)_2\text{-}1,2\text{-}RhSB_9H_8]} + PMe_2Ph(\text{excess}) \xrightarrow{80\ ^\circ C} \underset{\mathbf{5}}{[1\text{-(CO)-}1,3\text{-}(PMe_2Ph)_2\text{-}1,2\text{-}RhSB_9H_8]} + \underset{\mathbf{6}}{[1\text{-(CO)-}1\text{-}(PMe_2Ph)\text{-}3\text{-}(PPh_3)\text{-}1,2\text{-}RhSB_9H_8]} \quad (3)$$

infrared spectra (KBr) of **4**–**6** showed strong absorptions due to BH [ν_{max} 2550s, 2522s, 2504s(sh) for **4**; 2560s(sh), 2518s, 2470s for **5**; and 2575w(sh), 2562s, 2535s, 2523s, 2497s and 2484s for **6** respectively]. All three contained very strong CO absorption bands (ν_{max} 1990, 1975 and 1985 cm^{-1} respectively).

The ^1H, ^{11}B and ^{31}P NMR spectroscopic data for compounds **4**–**6** are in Table 1. Relevant data from the comparable *closo*-structured compounds [1-(η^5-C_5Me_5)-1,2-$IrSB_9H_9$] **2**[8] and [1-(η^6-$MeC_6H_4Pr^i$-4)-1,2-$RuNB_9H_{10}$] **7**[9] are included. Assignments were made on the basis of chemical shift values, coupling to ^1H or ^{31}P nuclei, the width of signals at half height, and by comparison with data from **2** and **7**. For these latter compounds [$^{11}B-^{11}B$] correlation spectroscopy (COSY) experiments had been used to assign the peaks and establish the connectivities.[8,9] Since most data were in the first instance obtained for **4**, discussion of this compound is given in full. Data from **5** and **6** were entirely consistent and reasonably assigned by comparison with **4**.

The spectra of compound **4** were assigned as follows. The incidence of coupling $^1J(^{31}P-^{11}B)$ assigns $^{11}B(3)$, with the incidence of $^3J(^{31}P-^1H)$(cisoid) of *ca.* 16 Hz assigning the position 9 (compare 17–33 Hz in, *e.g.*, refs 10–12). The broadness[7,13–15] of the ^{11}B NMR resonance at $\delta(^{11}B)$ −6.3 assigns it to the isolated position 8 adjacent to sulfur, with the relative ^{11}B peak widths (mbr, ms, s) assigning the others into the pairs indicated in Table 1. For these the 4,5 positions are assignable on the basis of chemical shift similarities to the other two (COSY-assigned) species **2** and **7**,[8,9] with the $^{11}B(4,5)$ assignments being supported further by the broadness of the resonances, short T_1 values being generally associated[7,13–15] with ^{11}B positions adjacent to chalcogen cluster constituents. The remaining two pairs are assigned on the basis of chemical shift parallels to the species **2** and **7**, the assignment being confirmed by the one observed [$^{11}B-^{11}B$]-COSY correlation, between $^{11}B(10)$ and $^{11}B(11)$. The ^{11}B lines were too broad, even at higher temperatures, to permit the observation of other

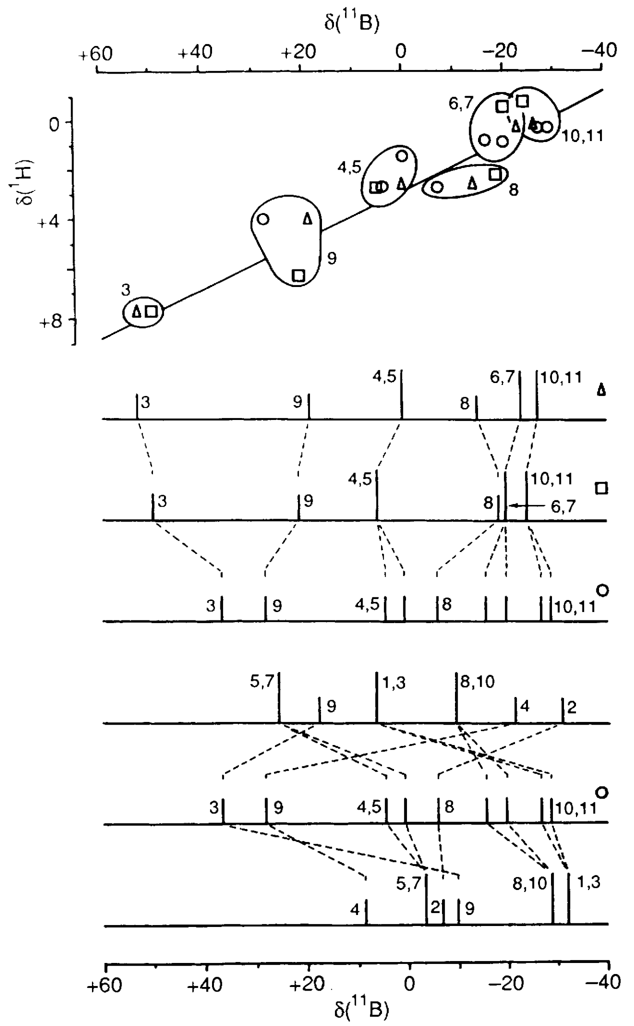
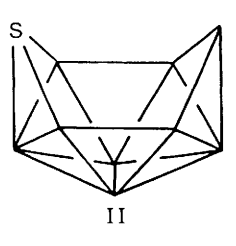
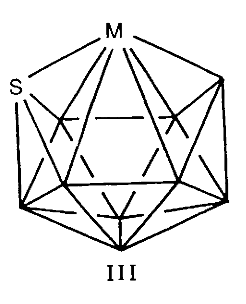


Fig. 1 NMR data for [1-(CO)-1,3-$(PPh_3)_2$-*closo*-1,2-$RhSB_9H_8$] **4** and for selected comparison species. The top diagram is a plot of δ(¹H) *versus* δ(¹¹B) for **4** (○), *closo*-structured [1-(η⁵-C_5Me_5)-1,2-$IrSB_9H_9$] **2** (□, data from ref. 8) and *closo*-structured [1-(η⁶-$MeC_6H_4Pr^i$-4)-1,2-$RuNB_9H_{10}$] **7** (△, data from ref. 9). The line drawn has slope δ(¹¹B):δ(¹H) 10:1, intercept +2.50 in δ(¹H). The centre diagrams are stick representations of the chemical shifts and relative intensities in the ¹¹B NMR spectra of compounds **4**, **2** and **7**, and the lowest diagrams are stick representations of the chemical shifts and relative intensities in the ¹¹B NMR spectra of (top to bottom) *nido*-6-SB_9H_{11},[13] compound **4**, and the *arachno*-[6-SB_9H_{12}]⁻ anion.[13] Hatched lines connect equivalent cluster positions



II



III

COSY correlations, and practicable [¹H–¹H]-COSY work was precluded by low solubility (but see data for compound **5**, Table 1). The small ¹¹B chemical shift differences (of up to *ca.* 6 ppm) within each of the (4,5), (6,7) and (10,11) pairs arises from the differential *trans* effects of rhodium-bound CO *versus* PPh_3; individual assignments within these pairs is not possible on present evidence, but in view of the small differences this is not important. There was no evidence of any high-temperature exchange within these three pairs, showing that the compound was not fluxional in the sense that the $Rh(CO)(PPh_3)$ group does not rotate *vis-à-vis* the $SB_9H_8(PPh_3)$ moiety. This contrasts to the very ready fluxional behaviour of the quasi-isoelectronic species [1,1-$(PMe_2Ph)_2$-2-Me-1,2,3-$PtC_2B_8H_9$].[16] However, in the rhodium compound the bulk of the $B(3)PPh_3$ substituent would constitute a severe steric inhibition to rotation. It may be noted in this context that the observed cluster structure for compound **4** constitutes the transition-state cluster structure proposed elsewhere for the fluxional enantiomerisation of the quasi-isoelectronic but *nido*-structured compound [8,8-$(PPh_3)_2$-8,7-$RhSB_9H_{10}$].[2]

Fig. 1 compares graphically the ¹¹B and ¹H chemical shifts of compound **4** with those of some related species containing {SB_9} fragments, and also with [1-(η⁶-$MeC_6H_4Pr^i$-4)-1,2-$RuNB_9H_{10}$] **7**[8] which contains the equivalent {$RuNB_9$} fragment. The top trace plots δ(¹H) *versus* δ(¹¹B) for compound **4**, for [1-(η⁵-C_5Me_5)-1,2-$IrSB_9H_9$] **2** and for **7**. Clearly, this (¹¹B,¹H) and the δ(¹¹B) behaviour are both very similar for all three species, confirming similarities in electronic structure. The drawn (¹¹B,¹H) correlation line is steep [δ(¹H):δ(¹¹B) *ca.* 1:10], as found also for 12-vertex *closo*-2,1-metallachalogenadodecaboranes,[7,14,15] but in contrast to more openly structured species.[2,13,17] The lowest parts of Fig. 1 compare the ¹¹B shieldings of compound **4** with those of **7** and with the *nido* and *arachno* species 6-SB_9H_{11} and [6-SB_9H_{12}]⁻.[13] These last two both have the schematic cage structure **II**, from which the {MSB_9} structures **III** are derived by a simple capping process. Interestingly, it can be seen that the ¹¹B shielding in the two {MSB_9} species is very much more akin to that of the *arachno* residue than the *nido* one, the most significant changes from *arachno*-[6-SB_9H_{12}]⁻ being at the B(9) position which becomes the four-connected B(3) position adjacent to the metal (hatched lines in Fig. 1), and at the B(4) position antipodal to sulfur [B(9) in the metal-containing species]. In particular it is noteworthy that the *arachno/nido* {SB_9} ¹¹B chemical shift sequencing inversion[13] does not occur when *arachno*-[6-SB_9H_{12}]⁻ is compared to the two metal-containing species.

In order to obtain solid-state structural data for these *closo*-structured eleven-atom rhodathiaboranes, crystals of **5** which were suitable for an X-ray diffraction study were grown from CH_2Cl_2 solution. During the X-ray analysis it became clear that there was some slight disorder (3%) of the structure corresponding to a rotation of the molecule about an axis such that the two phosphorus atom sites are interchanged. The effect of this rotation is to move the rhodium atom from position Rh(1) to position Rh(X). The small extent of this disorder precluded the observation of any of the lighter atoms of the minor component in difference maps since their electron density would be < 0.2 e Å^{-3}. Fig. 2 is a general view of **5** which shows both rhodium sites in that molecule. The occupancy factors for Rh(1) and Rh(X) were 0.97 and 0.03 respectively. In attempts to circumvent the disorder problem crystals of **4** were grown from both dichloromethane and toluene solutions. However, these systems, **4** and **4′**, were found to have an even worse disorder problem than **5**, with the rhodium present at two sites in **4** (occupancy factors 0.935 and 0.065) and three sites in **4′** (occupancy factors 0.92, 0.06 and 0.02). Fig. 3 shows the positions of the Rh(1), Rh(X) and Rh(Y) atoms with respect to the rhodathiaborane cage of the principal component in **4′**. It is noteworthy that this disorder occurred even though the three separate systems, **4**, **4′** and **5**, had crystallised in three different space groups. On refinement, compound **5** produced the structure with the 'cleanest' disorder and consequently the thiaborane cage geometry from this model was used during the (constrained) refinement of the structures of **4** and **4′**.

In the first instance compound **5**, Fig. 2, could be described as being derived from the *closo*-$[B_{11}H_{11}]^{2-}$ deltahedral species with C_{2v} symmetry, **IV**. This formally requires the {$Rh(CO)(PR_3)$}, {$B(PR_3)$}, and S cluster units to replace $[BH]^+$, $[BH]^-$, and $[BH]^{2-}$ borane units. The conversion of **1** *via* **3**

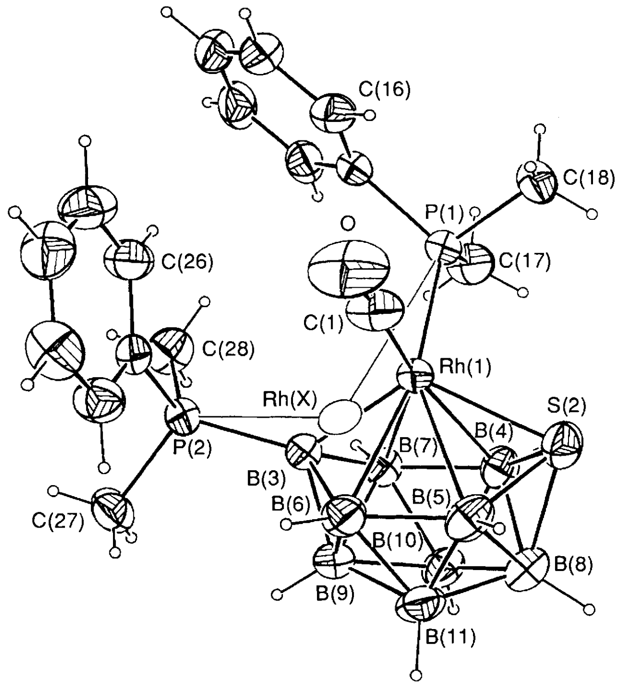


Fig. 2 A view of $[1\text{-}(CO)\text{-}1,3\text{-}(PMe_2Ph)_2$-*closo*-$1,2\text{-}RhSB_9H_8]$ **5** with the atom numbering scheme. The position of the rhodium atom, Rh(X), in the minor disordered component in the crystal is included

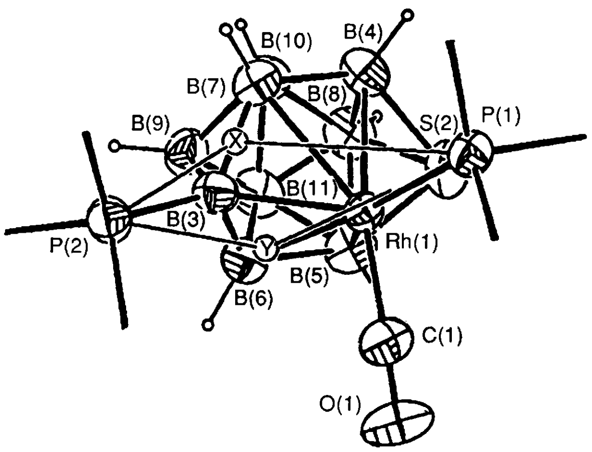
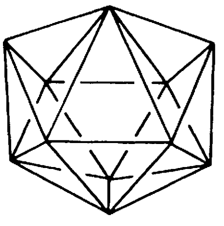
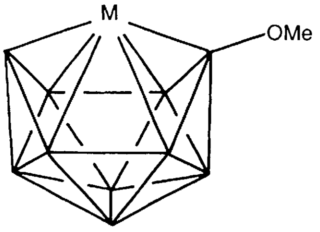


Fig. 3 A view of $[1\text{-}(CO)\text{-}1,3\text{-}(PPh_3)_2$-*closo*-$1,2\text{-}RhSB_9H_8]\cdot 1.5C_6H_5Me$ **4'**. The numbering scheme is as in Fig. 2. The positions of the rhodium atoms in the disordered minor components are shown as X and Y



IV



V

into **4** has involved the replacement of a terminal hydride ligand by PR_3, the removal of the bridging H atom and an increase in the connectivity of the Rh atom to the cage from four to six.

Interatomic distances for adjacent cage atoms, the *exo*-cage B–P, Rh–P, Rh–C and C–O distances, and selected interatomic angles in compound **5** are given in Table 2. The Rh–S distance, 2.3736(7) Å, is almost unchanged from that reported in the isoelectronic, but *nido*-structured, compound $[8,8\text{-}(PPh_3)_2\text{-}8,7\text{-}RhSB_9H_{10}]$ **1**, 2.3769(6) Å. These distances are both longer than the cage Rh–S distance of 2.3561(4) Å in the derivative $[8,8\text{-}(PPh_3)_2\text{-}8,9\text{-}\mu\text{-}(S_2CH)$-*nido*-$8,7\text{-}RhSB_9H_9]$ **8** and are between the two values of 2.325(2) and 2.434(2) Å reported in the *closo* compound $[2,3\text{-}(PPh_3)_2\text{-}3\text{-}Cl\text{-}2,3\text{-}\mu\text{-}Cl\text{-}2\text{-}(Ph_2PC_6H_4)\text{-}2,3,1\text{-}Rh_2SB_9H_8]$ **9**.[2]

In compound **5** the Rh–B(3) distance is 2.101(3) Å, much less than the other Rh–B distances for which the mean values are 2.385(3) Å for rhodium to B(6) and B(7) and 2.437(3) Å for rhodium to B(4) and B(5). In the previously reported deltahedral complex $[1\text{-}(\eta^5\text{-}C_5Me_5)\text{-}1\text{-}RhB_{10}H_9(OMe)\text{-}2]$ **10**, which had the *closo* structure shown in diagram **V** but formally a sub-*closo* electron count,[18] the distances which are comparable with those mentioned above were 2.101(5) Å for Rh(1)–B(3), 2.123(5) Å for Rh(1)–B(2), and the four Rh–B(4) to B(7) distances had a mean value of 2.287 Å.

The B–S distances range from 1.923(3) to 1.989(4) Å in compound **5** and are comparable with values in **1**, **8** and **9** of 1.908(4)–2.035(4), 1.920(3)–2.072(3) and 1.963(10)–2.159(9) Å respectively.[2] In the last three compounds the longest S–B distances were those to the boron atoms which were also attached to rhodium atoms. In the *closo*-structured compounds described in this paper the reverse was true. For example in **5**, the S–B distances to B(5) and B(4) (also attached to Rh) were 1.923(3) and 1.947(3) Å whereas that to B(8) was 1.989(4) Å. A large range of interboron distances [1.719(4)–1.897(4) Å] was observed in **5**. The short distances of 1.719(4), 1.723(3) and 1.724(4) Å involved B(3) bonding to B(6), B(7) and B(9) respectively. The distances to B(8) are of interest in that there are two distinct pairs which are at opposite extremes of the observed B–B range. Thus the interactions of B(8) to B(10) or B(11) are short [1.721(5) and 1.730(4) Å respectively] but those between B(8) and B(4) or B(5) are long [1.894(5) and 1.897(4) Å]. However, even though the range of interboron distances is large, it is not exceptional in the general context of metallaborane structural chemistry.[19]

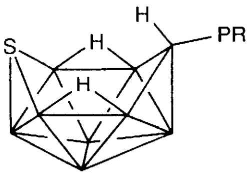
The length of the B–P bond in compound **5** is 1.895(3) Å. This is typical of such bonds which are usually in the range 1.87–1.93 Å.[19] The Rh–P distance of 2.3090(7) Å is notably short compared with the reported values from **8**, **9** and the twelve-vertex species $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H$-*closo*-$2,1\text{-}RhTeB_{10}H_{10}]$ **11**,[14] where the Rh–P distances ranged from 2.329(2) Å in **8** to 2.5599(7) Å in **9**.[2] In **1** the Rh–P bond *trans* to the sulfur atom was shorter [2.2906(5) Å] than that in **5** but that positioned with the rhodium–phosphorus vector perpendicular to the plane containing the $RhSB_3$ face was considerably longer at 2.4197(5) Å.

The rhodium–carbon and carbon–oxygen distances in the Rh–C–O linkage in compound **5** were 1.855(3) and 1.131(3) Å respectively. These values compare with distances of 1.845(4) and 1.122(5) Å observed in the dinuclear *closo* complex $[(PPh_3)(CO)Rh_2Te_2B_{20}H_{20}]$ **12**.[20] The weaker C–O bonding in **5** is confirmed by the carbonyl stretching frequencies which were at 1975 and 2062 cm^{-1} respectively.

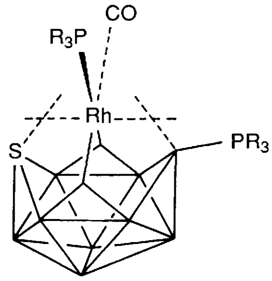
The process by which the *nido* compound **3** is converted into *closo* compound **4** is clearly complex and numerous questions remain to be answered before a possible mechanism can be formulated. However, it would seem likely that the boron atom which is bonded to the phosphine in **4** is the one adjacent to the rhodium in the open $RhSB_3$ face of **3** (or **1**). Some additional support for this suggestion comes from the formation of **5** in reaction (3). While the substitution of the rhodium-bound PPh_3 in **4** by the more basic and less sterically demanding PMe_2Ph ligand, giving **6**, may not be surprising, the substitution of the boron-bound PPh_3 to give **5** is an unusual reaction. This suggests that (*a*) the B–P bond is labile and (*b*), once formed, the *closo*-structured compounds **4**–**6** may be inherently unreactive towards the addition of a two-electron ligand at the metal. This

Table 2 Selected interatomic distances (Å) and angles (°) in [1-(CO)-1,3-(PMe$_2$Ph)$_2$-*closo*-1,2-RhSB$_9$H$_8$] **5**

Rh(1)–S(2)	2.3736(7)	B(3)–B(6)	1.719(4)	B(6)–B(11)	1.788(4)	P(1)–C(17)	1.815(3)
Rh(1)–P(1)	2.3090(7)	B(3)–B(7)	1.723(3)	B(7)–B(9)	1.812(4)	P(1)–C(18)	1.814(3)
Rh(1)–C(1)	1.855(3)	B(3)–B(9)	1.724(4)	B(7)–B(10)	1.801(4)	P(2)–C(21)	1.809(3)
Rh(1)–B(3)	2.101(3)	B(4)–B(7)	1.831(4)	B(8)–B(10)	1.721(5)	P(2)–C(27)	1.796(3)
Rh(1)–B(4)	2.430(3)	B(4)–B(8)	1.894(5)	B(8)–B(11)	1.730(4)	P(2)–C(28)	1.795(3)
Rh(1)–B(5)	2.444(3)	B(4)–B(10)	1.763(5)	B(9)–B(10)	1.766(3)	Rh(X)–B(7)	2.355(6)
Rh(1)–B(6)	2.380(3)	B(5)–B(6)	1.843(4)	B(9)–B(11)	1.779(5)	Rh(X)–P(1)	3.303(6)
Rh(1)–B(7)	2.389(3)	B(5)–B(8)	1.897(4)	B(10)–B(11)	1.821(4)	Rh(X)–P(2)	2.589(6)
S(2)–B(4)	1.947(3)	B(5)–B(11)	1.752(5)	P(2)–B(3)	1.895(3)	Rh(X)–Rh(1)	1.279(6)
S(2)–B(5)	1.923(3)	B(6)–B(9)	1.801(4)	O–C(1)	1.131(3)		
S(2)–B(8)	1.989(4)			P(1)–C(11)	1.818(2)		
S(2)–Rh(1)–P(1)	104.01(2)	Rh(1)–B(3)–B(6)	76.4(2)	B(6)–B(5)–B(11)	59.6(2)	B(11)–B(8)–B(10)	63.7(2)
S(2)–Rh(1)–C(1)	114.59(9)	Rh(1)–B(3)–B(7)	76.6(1)	B(8)–B(5)–B(11)	56.4(2)	B(6)–B(9)–B(3)	58.3(2)
S(2)–Rh(1)–B(5)	47.04(6)	P(2)–B(3)–B(6)	123.2(2)	Rh(1)–B(6)–B(5)	69.4(1)	B(6)–B(9)–B(11)	59.9(2)
S(2)–Rh(1)–B(3)	120.18(8)	P(2)–B(3)–B(7)	129.6(2)	Rh(1)–B(6)–B(3)	59.1(1)	B(3)–B(9)–B(7)	58.3(2)
S(2)–Rh(1)–B(4)	47.80(7)	P(2)–B(3)–B(9)	119.6(2)	B(5)–B(6)–B(11)	57.7(2)	B(7)–B(9)–B(10)	60.4(2)
P(1)–Rh(1)–C(1)	91.27(9)	B(6)–B(3)–B(9)	63.1(2)	B(3)–B(6)–B(9)	58.6(2)	B(11)–B(9)–B(10)	61.8(2)
B(5)–Rh(1)–B(6)	44.9(1)	B(7)–B(3)–B(9)	63.4(2)	B(11)–B(6)–B(9)	59.4(2)	B(7)–B(10)–B(4)	61.8(2)
B(6)–Rh(1)–B(3)	44.6(1)	Rh(1)–B(4)–S(2)	64.58(8)	Rh(1)–B(7)–B(3)	58.8(1)	B(7)–B(10)–B(9)	61.0(2)
B(3)–Rh(1)–B(7)	44.54(8)	Rh(1)–B(4)–B(7)	66.5(1)	Rh(1)–B(7)–B(4)	68.91(1)	B(4)–B(10)–B(8)	65.9(2)
B(7)–Rh(1)–B(4)	44.69(9)	S(2)–B(4)–B(8)	62.4(1)	B(3)–B(7)–B(9)	58.3(2)	B(8)–B(10)–B(11)	58.4(2)
Rh(1)–S(2)–B(5)	68.4(1)	B(7)–B(4)–B(10)	60.1(2)	B(4)–B(7)–B(10)	58.1(2)	B(11)–B(10)–B(9)	59.5(2)
Rh(1)–S(2)–B(4)	67.61(8)	B(8)–B(4)–B(10)	56.0(2)	B(9)–B(7)–B(10)	58.5(2)	B(5)–B(11)–B(6)	62.7(2)
B(5)–S(2)–B(8)	58.0(1)	Rh(1)–B(5)–S(2)	64.6(1)	S(2)–B(8)–B(5)	59.3(1)	B(5)–B(11)–B(6)	62.7(2)
B(4)–S(2)–B(8)	57.5(1)	Rh(1)–B(5)–B(6)	65.7(1)	S(2)–B(8)–B(4)	60.1(1)	B(8)–B(11)–B(11)	57.9(2)
Rh(1)–C(1)–O	178.2(3)	S(2)–B(5)–B(8)	62.7(1)	B(5)–B(8)–B(11)	57.6(2)	B(5)–B(11)–B(8)	66.0(2)
Rh(1)–B(3)–P(2)	128.8(2)			B(4)–B(8)–B(10)	58.1(2)	B(9)–B(11)–B(10)	57.9(2)



VI



VII

unreactivity inhibits the opening up of the cluster and the formation of *nido* derivatives related to **3** which could have possibly contained Rh(PPh$_3$)(PR$_3$)(CO) units. Comparison of the structures of the *closo* compounds **4**–**6** with that of **1** suggests that the presence of the bridging 8,9-μ-H atom in **1** is a major factor in the stabilisation of the *nido* structure of **1**. Moreover, it appears to be significant that the rhodium-based cluster unit in **1** is {Rh(PPh$_3$)$_2$} and not {RhH(PPh$_3$)$_2$} since the latter group is the most commonly found rhodium-based unit in rhodium–carbaborane[21] and -heteroborane[22] compounds. However, it should not be forgotten that alternative structures may be close in energy. For example, in the eleven-vertex {RhC$_2$B$_8$} compounds which are closely related to **4**–**6**, there is in solution a *closo* structure $\rightleftharpoons$ *nido* structure equilibrium between [(PPh$_3$)$_2$HRhC$_2$B$_8$H$_{10}$] and [(PPh$_3$)$_2$RhC$_2$B$_8$H$_{11}$].[23]

Finally the cluster electron-counting formalism associated with compounds **4**–**6** merits brief discussion in the light of the similarities of their ^{11}B NMR spectra and those of {*arachno*-SB$_9$} species (see Fig. 1). Compounds **4**–**6** may be described as *closo* species in terms of the conventional Wade–Williams approach[3] as discussed above which implies a formal rhodium(I) metal centre bonding to a *nido*-type [SB$_9$H$_{10}$]$^-$ ligand. However, the ^{11}B shielding parameters are markedly similar to those of *arachno* ten-vertex species such as the [6-SB$_9$H$_{12}$]$^-$ anion, Fig. 1, and the neutral 9-(PR$_3$)-6-SB$_9$H$_{11}$ adduct whose schematic structure is shown in diagram **VI**.[13] Hence, it is tempting to consider the metal–ligand interactions in **4**–**6** to involve a substantial or even dominant [SB$_9$H$_{10}$]$^{3-}$ ligand/rhodium(III) contribution. In this model the three *endo* and bridging hydrogen atoms are replaced by bonds to the rhodium(III) centre, diagram **VII**.

Experimental

General.—All preparative experiments and crystallisations were carried out in an inert atmosphere. Both [RhCl(PPh$_3$)$_3$][24] and the caesium salt of the *arachno*-[6-SB$_9$H$_{12}$]$^-$ anion[25] were prepared by literature methods. Infrared spectra were recorded from KBr discs on a Mattson Polaris Ir 10410 FT spectrometer. Chemical elemental analyses were performed at University College, Cork.

Synthesis of [8,8-(PPh$_3$)$_2$-8,7-RhSB$_9$H$_{10}$] **1**.—A solution of [RhCl(PPh$_3$)$_3$] (0.25 g, 0.27 mmol) in ethanol (10 cm^3) was added to a solution of Cs[6-SB$_9$H$_{12}$] (0.074 g, 0.27 mmol) in ethanol (15 cm^3). After stirring at room temperature for 2 h the reaction mixture was filtered, yielding an orange *solid* which was crystallised from CH$_2$Cl$_2$ affording [8,8-(PPh$_3$)$_2$-8,7-RhSB$_9$H$_{10}$]·CH$_2$Cl$_2$ **1** (0.162 g, 81.0%) (Found: C, 52.20; H, 5.00. C$_{37}$H$_{42}$B$_9$Cl$_2$P$_2$RhS requires C, 52.20; H, 4.95%) which was characterised spectroscopically and by X-ray crystallography. IR: ν_{max} 2560s, 2533s, 2518s and 2506s (all BH) cm^{-1}; NMR data are given in ref. 1.

Reaction of Compound **1** *with* CO.—Carbon monoxide gas was bubbled through a solution of compound **1** (0.20 g, 0.26 mmol) in benzene (25 cm^3) at room temperature for 30 min. The solvent was removed and the remaining yellow solid was crystallised from CH$_2$Cl$_2$ to yield yellow *crystals* of [8-(CO)-8,8-(PPh$_3$)$_2$-*nido*-8,7-RhSB$_9$H$_{10}$] **3** (0.202 g, 97.7%). IR: ν_{max} 2030w(CO) cm^{-1}; ^{11}B-{^{1}H} NMR (CD$_2$Cl$_2$, 294–297 K) {ordered as: δ(^{11}B) (peak shape and relative intensity) [δ(^{1}H)]}: +15.6 (s, 1 B) [+3.76], +10.1 (s, 1 B) [+2.66], *ca.* +9.6 (br, 1 B) [+3.42], +4.5 (s, 1 B) [+3.85], *ca.* +4.0 (br, 1 B) [2.91], *ca.* −13.8 (s, 1 B) [+1.01], −14.4 (s, 1 B) [+1.75], −18.3 (s, 1 B) [1.90], *ca.* −27.3 (br, 1 B) [+1.14]; in addition, δ(^{1}H) −3.85 (B–H–B).

Table 3 Details of data collection and refinement for compounds **4**, **4′** and **5**

	4	**4′**	**5**
Crystal size/mm	0.08 × 0.44 × 0.20	0.21 × 0.35 × 0.16	0.18 × 0.20 × 0.55
Crystal colour and shape	Yellow platelet	Yellow block	Yellow block
Range of orienting reflections/°	$7 < \theta < 15$	$10 < \theta < 14$	$7 < \theta < 20$
Range of *hkl* collected	0–48, 0–13, −25 to 25	0–15, −18 to 18, −18 to 18	0–12, 0–30, −14 to 14
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan width	$0.80 + 0.35 \tan\theta$	$0.60 + 0.35 \tan\theta$	$0.60 + 0.35 \tan\theta$
2θ limits/°	4–50	4–54	4–54
Reflections collected	7289	10 111	5924
Independent reflections	7109	10 111	5761
Observed reflections [$I > 3\sigma(I)$]	3970	6959	4472
Maximum and minimum transmission factors	0.96, 0.79	0.94, 0.87	1.11, 0.91
Least-squares parameters	401	471	291
R	0.051	0.041	0.027
R'	0.056	0.044	0.040
Goodness of fit	0.91	1.40	1.57
$g\,\{w = [\sigma^2(F_o) + g(F_o)^2]^{-1}\}$	0.006	0.001	0.001
Maximum shift/error	<0.04	<0.02	<0.01
Maximum (minimum) $\Delta\rho$/e Å^{-3}	1.34 (0.61)	0.78 (0.45)	0.52

Thermolysis of Compound **3**.—A solution of compound **3** (0.387 g, 0.487 mmol) in benzene (25 cm^3) was refluxed for 5 h yielding a brown solution. The solvent was removed to afford a dark yellow solid which was washed with CH_2Cl_2. Crystallisation from toluene–light petroleum (b.p. 100–120 °C) yielded yellow *plates* of [1-(CO)-1,3-$(PPh_3)_2$-*closo*-1,2-$RhSB_9H_8$] **4** (0.179 g, 46.2%) which were identified spectroscopically and by X-ray crystallography; NMR data are given in Table 1.

Reaction of Compound **4** *with* PMe_2Ph.—An excess of PMe_2Ph (0.25 cm^3, 1.75 mmol) was added to a solution of compound **4** (0.167 g, 0.21 mmol) in benzene (20 cm^3) and then refluxed for 4 d. The yellow solution was concentrated under reduced pressure and subjected to preparative TLC [CH_2Cl_2–heptane (7:3)]. The two major bands were collected. Crystallisation of these bands from toluene–light petroleum (b.p. 100–120 °C) yielded (*a*) yellow *crystals* which were identified spectroscopically as [1-(CO)-1-(PMe_2Ph)-3-(PPh_3)-*closo*-1,2-$RhSB_9H_8$] **6** (0.064 g, 45.8%) (Found: C, 48.55; H, 5.20. $C_{27}H_{34}B_9OP_2RhS$ requires C, 48.50; H, 5.10%) (NMR data are given in Table 1) and (*b*) yellow *crystals* which were identified spectroscopically and by X-ray crystallography as [1-(CO)-1,3-$(PMe_2Ph)_2$-*closo*-1,2-$RhSB_9H_8$] **5** (0.02 g, 25%) (Found: C, 38.60; H, 5.60. $C_{17}H_{30}B_9OP_2RhS$ requires C, 37.50; H, 5.55%) (NMR data are given in Table 1).

Crystal Structure Analyses for Compounds **4**, **4′** *and* **5**.—*Crystal Data.* [(CO)(PPh_3)Rh$(SB_9H_8)$$(PPh_3)$] **4**, $C_{37}H_{38}B_9OP_2RhS$, $M = 792.9$, monoclinic, $a = 37.529(11)$, $b = 10.749(5)$, $c = 19.536(5)$ Å, $\beta = 101.96(2)°$, $U = 7709(8)$ Å^3, $Z = 8$, $D_c = 1.37$ g cm^{-3}, $F(000) = 3232$, λ(Mo-Kα) = 0.71073 Å, $\mu = 6.0$ cm^{-1}, space group $C2/c$ determined uniquely from systematic absences (*hkl* absent if $h + k = 2n + 1$; *h*0*l* absent if $l = 2n + 1$).

[(CO)(PPh_3)Rh$(SB_9H_8)$$(PPh_3)$]·1.5$C_6H_5Me$ **4′**, $C_{37}H_{38}B_9OP_2RhS\cdot1.5C_7H_8$, $M = 931.1$, triclinic, $a = 11.933(2)$, $b = 14.157(2)$, $c = 14.190(2)$ Å, $\alpha = 79.25(1)$, $\beta = 83.27(1)$, $\gamma = 87.32(1)°$, $U = 2238(1)$ Å^3, $Z = 2$, $D_c = 1.33$ g cm^{-3}, $F(000) = 958$, λ(Mo-Kα) = 0.71073 Å, $\mu = 5.0$ cm^{-1}, space group $P\bar{1}$ determined by cell reduction and subsequent successful refinement.

[(CO)(PMe_2Ph)Rh$(SB_9H_8)$$(PMe_2Ph)$] **5**, $C_{17}H_{30}B_9OP_2RhS$, $M = 544.64$, monoclinic, $a = 9.626(2)$, $b = 23.714(5)$, $c = 11.595(2)$ Å, $\beta = 109.00(2)°$, $U = 2503(2)$ Å^3, $Z = 4$, $D_c = 1.45$ g cm^{-3}, $F(000) = 1104$, λ(Mo-Kα) = 0.71073 Å, $\mu = 8.9$ cm^{-1}, space group $P2_1/n$ determined uniquely from systematic absences (*h*0*l* absent if $h + l = 2n + 1$; 0*k*0 absent if $k = 2n + 1$).

Structure determination. All three compounds were analysed in a similar way (details of data collection and structure determination are summarised in Table 3). Accurate cell dimensions and the crystal orientation matrix were determined by a least-squares treatment of the setting angles of 25 reflections. Data were collected on a CAD4 diffractometer using graphite-monochromated (Mo-Kα) radiation. Intensities of three reflections measured every 2 h showed no decay. Data were corrected for Lorentz, polarisation and absorption effects. The coordinates of the heavy atoms were determined from analyses of the three-dimensional Patterson functions and those of the remaining non-hydrogen atoms were found *via* the heavy-atom method. Refinement was by full-matrix least-squares calculations, initially with isotropic then with anisotropic thermal parameters. At an intermediate stage in the refinement it became obvious that there was slight (2–6%) disorder in the packing of the molecules; this revealed itself by the presence of additional unexpected peaks in electron-density maps consistent with the disorder of the entire molecules but only the rhodium contribution could be clearly discerned and accounted for (see Figs. 2 and 3).

Molecule **5** had the 'cleanest' disorder and the disordered rhodium site did not appear to affect the thiaborane cage atoms markedly. Refinement of the structure proceeded smoothly and led to occupancy factors of 0.97 and 0.03 for Rh(1) and Rh(X) sites. The effect of rotating the molecule so that the two phosphine sites are interchanged is to move the Rh atom of the principal site to position Rh(X) in Fig. 2. Since only a small percentage of the system is disordered, the non-rhodium disordered sites had too small an electron density to be detected (3.0% of 45 electrons = 1.35 electrons compared with the lighter atoms, *e.g.* for boron, 3.0% of 5 electrons = 0.15 electrons). In **5** the disordered Rh(X) site was clearly located above the B(3)–B(6)–Rh(1) face. In compounds **4** and **4′** the sites corresponding to the disordered Rh atom (one additional site in **4**, two in **4′**) were very close to the boron atoms B(3)–B(6)–B(7) in the B_9S cage. For refinement of these two structures we used the geometry details determined for molecule **5** with the DFIX options in SHELX 76[26] (with bond constraints of 0.001 Å for Rh–S, 0.003 Å for all other non-hydrogen distances in each molecule and 0.01 Å for the toluene of solvation in **4′**). In final difference maps there were no chemically significant features.

The occupancy factors for the rhodium atom sites in compound **4** were 0.935 and 0.065, and for **4′**, 0.92, 0.06 and 0.02 (Fig. 3). Solvent of crystallisation was present in **4′** with one toluene disordered over three sites with occupancies of 0.45, 0.35 and 0.20 for the three orientations and a second toluene was disordered about an inversion centre. The toluene molecules

Table 4 Positional parameters and their estimated standard deviations for compound **5**

Atom	*x*	*y*	*z*
Rh(1)	0.122 68(2)	0.162 49(1)	0.082 30(1)
S(2)	0.064 43(8)	0.215 58(3)	−0.100 87(6)
P(1)	−0.102 03(6)	0.147 42(3)	0.108 67(5)
P(2)	0.343 22(6)	0.048 15(3)	0.251 48(5)
O	0.228 9(3)	0.231 4(1)	0.309 6(2)
C(1)	0.186 5(3)	0.205 2(1)	0.223 9(2)
C(11)	−0.095 9(2)	0.121 5(1)	0.257 8(2)
C(12)	−0.124 6(3)	0.065 4(1)	0.277 2(2)
C(13)	−0.114 6(3)	0.046 6(1)	0.392 4(3)
C(14)	−0.074 3(3)	0.083 5(1)	0.490 2(2)
C(15)	−0.046 1(3)	0.138 9(1)	0.472 5(2)
C(16)	−0.057 3(3)	0.158 3(1)	0.357 2(2)
C(17)	−0.224 5(3)	0.098 5(1)	0.003 0(2)
C(18)	−0.214 1(3)	0.210 4(1)	0.091 2(3)
C(21)	0.405 5(3)	0.088 3(1)	0.391 6(2)
C(22)	0.541 3(3)	0.114 6(1)	0.426 8(2)
C(23)	0.590 7(3)	0.144 8(1)	0.534 4(3)
C(24)	0.504 2(4)	0.149 4(1)	0.607 8(3)
C(25)	0.367 2(3)	0.124 7(1)	0.572 0(3)
C(26)	0.317 1(3)	0.094 3(1)	0.464 4(2)
C(27)	0.497 6(3)	0.007 0(1)	0.246 1(3)
C(28)	0.212 6(3)	−0.002 3(1)	0.269 1(2)
B(5)	0.273 2(3)	0.206 2(1)	−0.026 9(3)
B(6)	0.365 0(3)	0.148 6(1)	0.076 2(3)
B(3)	0.268 1(3)	0.093 9(1)	0.110 8(2)
B(7)	0.137 2(3)	0.078 6(1)	−0.027 2(2)
B(4)	0.041 8(3)	0.134 8(1)	−0.131 1(2)
B(8)	0.184 3(4)	0.173 0(1)	−0.182 4(3)
B(11)	0.349 2(3)	0.149 2(2)	−0.081 8(3)
B(9)	0.330 3(3)	0.084 3(1)	−0.011 4(2)
B(10)	0.196 1(3)	0.101 8(1)	−0.151 7(2)
Rh(X)	0.249 5(6)	0.140 9(3)	0.134 4(5)

Atoms Rh(1) and Rh(X) had occupancies 0.97 and 0.03 respectively.

were refined as rigid groups (planar hexagons for the aromatic rings) and hydrogen atoms were not included in these molecules.

Scattering factors and anomalous-dispersion corrections were taken from ref. 27. All calculations were performed on a PDP-11/74 computer using SDP-Plus[28] in conjunction with an IBM 3081-K mainframe computer using SHELX 76. Atomic coordinates of compound **5** are listed in Table 4 and principal details of the molecular geometry in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles for **5**, and complete sets of data for **4** and **4′**.

NMR Spectroscopy.—The NMR spectra were recorded at 9.35 T on a Bruker AM400 spectrometer. Details of the techniques used and the chemical shift standards are given in ref. 22. Data were recorded at 294–297 K for CD_2Cl_2 solutions unless otherwise indicated.

Acknowledgements

We thank Johnson Matthey plc for the generous loan of rhodium salts. The Department of Education of the Republic of Ireland is thanked for financial support (to S. C.). G. F. thanks the National Science and Engineering Research Council (Canada) for Grants in Aid of Research.

References

1 Part 9, M. McGrath, T. R. Spalding, X. L. R. Fontaine, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1991, 3223.

2 G. Ferguson, M. C. Jennings, A. J. Lough, S. Coughlan, T. R. Spalding, J. D. Kennedy, X. L. R. Fontaine and B. Štibr, *J. Chem. Soc., Chem. Commun.*, 1990, 891.

3 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1978, **18**, 1.

4 A. R. Kane, L. J. Guggenberger and E. L. Muetterties, *J. Am. Chem. Soc.*, 1970, **92**, 2571.

5 T. K. Hilty, D. A. Thompson, W. M. Butler and R. W. Rudolph, *Inorg. Chem.*, 1979, **18**, 2642.

6 A. R. Siedle, D. McDowell and L. J. Todd, *Inorg. Chem.*, 1974, **13**, 2735.

7 Faridoon, O. Ni Dhubhghaill, T. R. Spalding, G. Ferguson, X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1989, 1657.

8 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1991, 2657; K. Nestor, Ph.D. Thesis, University of Leeds, 1989.

9 K. Baše, M. Bown, B. Štibr, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1988, 1240.

10 J. Taylor, N. Alcock and M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1983, 1168.

11 J. Bould, J. E. Crook, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1984, 1903.

12 K. Nestor, B. Štibr, T. Jelinek, K. Baše, X. L. R. Fontaine, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1990, 2887.

13 M. Bown, X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1988, 1467.

14 Faridoon, O. Ni Dhubhghaill, T. R. Spalding, G. Ferguson, B. Kaitner, X. L. R. Fontaine, J. D. Kennedy and D. Reed, *J. Chem. Soc., Dalton Trans.*, 1988, 2739.

15 G. Ferguson, J. D. Kennedy, X. L. R. Fontaine, Faridoon and T. R. Spalding, *J. Chem. Soc., Dalton Trans.*, 1988, 2555.

16 J. D. Kennedy, M. Thornton-Pett, B. Štibr and T. Jelinek, *Inorg. Chem.*, 1991, **30**, 4481.

17 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1987, 1573.

18 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 2417.

19 J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519; 1986, **34**, 211 and refs. therein.

20 G. Ferguson, A. J. Lough, Faridoon, M. McGrath, T. R. Spalding, J. D. Kennedy and X. L. R. Fontaine, *J. Chem. Soc., Dalton Trans.*, 1990, 1831.

21 R. T. Baker, M. S. Delaney, R. E. King, C. B. Knobler, J. A. Long, T. B. Marder, T. E. Paxon, R. G. Teller and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 2965 and refs. therein.

22 Faridoon, O. Ni Dhubhghaill, T. R. Spalding, G. Ferguson, B. Kaitner, X. L. R. Fontaine, J. D. Kennedy and D. Reed, *J. Chem. Soc., Dalton Trans.*, 1988, 2739; X. L. R. Fontaine, J. D. Kennedy, M. McGrath and T. R. Spalding, *Magn. Reson. Chem.*, 1991, **29**, 711.

23 C. W. Jung and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1980, **102**, 3024.

24 J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1990, **28**, 77.

25 R. W. Rudolph and W. R. Pretzer, *Inorg. Synth.*, 1983, **22**, 226.

26 G. Sheldrick, SHELX 76, A program for crystal structure analysis, University of Cambridge, 1976.

27 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

28 SDP-Plus Program system, B. A. Frenz and Associates, College Station, TX and Enraf-Nonius, Delft, 1983.

Received 20*th March* 1992; *Paper* 2/01474B