A Novel Rh–B σ Bond. Crystal Structure of $[N(CH_3)_4][RhCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{–}C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{–}C_2B_9H_9\}]$

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The complex $[N(CH_3)_4][RhCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{–}C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{–}C_2B_9H_9\}]$ is an octahedral Rh(III) complex; the sixth coordination site is occupied by a σ-bond B–Rh in this first example of B(3)–Rh coordination.

Three general modes of *nido* ion $[7,8\text{-}C_2B_9H_{12}]^{1-}$ to Rh bonding have been reported: η^5 coordination to the open pentagonal C_2B_3 face[1] as in *closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$;[2] *exo-nido* coordination as in *exo-nido*-$[(PPh_3)_2Rh][7,8\text{-}\mu\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]$[3] and a mixed mode composed of η^5 coordination and one Rh–H–B bridge $[Rh(PPh_3)C_2B_9H_{11}]_2$.[4]

Besides these three types of Rh–C_2B_9 interaction, a less common M–B σ bond is also known, *e.g.* a B(10)–Ru σ bond is found in $[N(PPh_3)_2][RuW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_8\text{-}Me_2)(CO)_3(\eta\text{-}C_5H_5)]$.[5] All B–H–M or B–M bonds reported in the literature for derivatives of $[7,8\text{-}C_2B_9H_{12}]^{1-}$ involve one boron atom of the open face. When *exo-nido* coordination takes place, the boron atom of the second B–H → M interaction belongs to the carbaborane's second layer. However, an interaction in which the participating boron atom is connected to both carbaborane carbon atoms[6] has not been found.

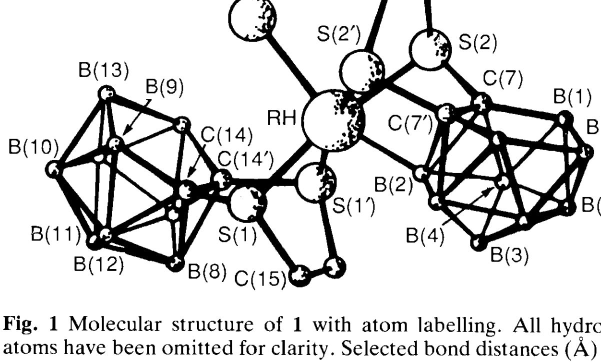

Fig. 1 Molecular structure of **1** with atom labelling. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Rh–Cl 2.525(2), Rh–S(1) 2.357(2), Rh–S(2) 2.330(2), Rh–B(2) 2.115(14) Å; S(1)–Rh–S(1)′ 77.3(1), S(1)–Rh–S(2)′ 110.8(1), S(2)–Rh–S(2)′ 79.4(1), Cl–Rh–S(2) 89.2(1), Cl–Rh–S(1) 100.9(1), B(2)–Rh–S(1) 96.7(3), B(2)–Rh–S(2) 73.6(3).

In the course of our investigations on the coordination chemistry of macrocyclic derivatives of *exo*-dithiocarbaborane[7–12] we have observed a dependence of the *w* angle [defined as the angle subtended by lines drawn from the midpoint of the S · · · S vector to the atom M and to the midpoint of the C(carb) · · · C(carb) vector respectively] and the *exo*-cluster chain length[13] (Fig. 1). The shorter the *exo*-cluster chain, the smaller the *w* angle. This led to the hypothesis that using short *exo*-cluster chains such as those in $[7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}]^{1-}$ a B–H–M interaction could be found with the boron atom bonded directly to both carbaborane carbon atoms.

$RhCl_3\cdot3H_2O$ (22.4 mg, 0.085 mmol) was added to deoxygenated ethanol solution (20 cm^3) containing 50 mg (0.17 mmol) of $[N(CH_3)_4][7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}]$. The mixture was refluxed under N_2 for 4 h. The resulting yellow solid was removed by filtration. Acetone (20 cm^3) was added to the precipitate and the resulting suspension was filtered. Upon addition of diethyl ether to the filtrate an analytically pure solid was obtained in 65% yield.[†]

The ^{11}B NMR spectrum displays ten signals with intensities 2 : 3 : 2 : 2 : 2 : 2 : 1 : 2 : 1 : 1[†] indicating a non-equivalence of the two carbaborane cages. This could be due to the existence of the expected B–H–Rh interaction in one of the cages, however, the diamagnetism of the compound suggested a Rh(III) complex, which implies a direct B–Rh interaction.[‡] The observed ^{11}B NMR spectrum is similar to that of the free ligand 2 : 1 : 2 : 2 : 1 : 1[13] and can be interpreted as the sum of

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[†] *Data* for $[N(CH_3)_4][RhCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_9\}]$: IR (KBr) ν(B-H) 2224 cm^{-1}. ^{11}B-NMR{^1H} NMR (in acetone; chemical shifts, referenced to external $BF_3.OEt_2$, upfield of the reference are designated as negative) −5.6, −6.7, −14.3, −17.4, −20.5, −22.6, −31.6, −32.2, −34.16, −37.8 with relative intensities 2:3:2:2:2:2:1:2:1:1. Anal. Calcd for $C_{12}H_{39}B_{18}NS_4Rh$: C, 21.85; H, 5.98; N, 2.12. Found: C, 21.42; H, 5.78; N, 2.11.

[‡] A magnetic susceptibility measurement at room temperature indicated that the compound was diamagnetic.

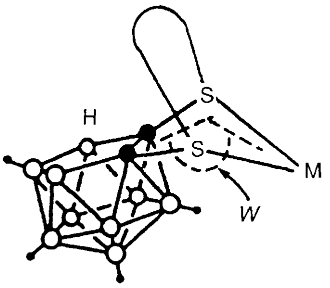

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Fig. 2

two such sequences except for the important fact that the resonance due to the boron atom, B–Rh is shifted *ca.* 25 ppm upfield. This upfield shift corroborates the direct B–Rh interaction since a downfield shift in the range 5–20 ppm is expected in three-centre two-electron B–H → M interactions.[14]

The molecular structure of this compound was clearly determined by an X-ray diffraction study§ and confirms the presence of this new type of B–Rh bond.

The molecular structure of **1** consists of a rhodium(III) chloride moiety attached to two ligands [7,8-μ-S(CH$_2$CH$_2$)S-C$_2$B$_9$H$_{10}$] through the sulphur atoms. One of the ligands is further coordinated to the Rh atom *via* a B–Rh σ bond (w angle = 108°). This distance is similar to the Ru–B(10) in [N(PPh$_3$)$_2$][RuW(μ-CC$_6$H$_4$Me-4)(μ-σ,η^5-C$_2$B$_9$H$_8$Me$_2$)(CO)$_3$-(η-C$_5$H$_5$)][6] (2.12 *vs.* 2.15 Å). Because of this bond the carbaborane fragments do not behave equivalently in the complex. The carbaborane fragment on the right-hand side of Fig. 2 displays an *anti* disposition of the C$_2$B$_3$ open face with regard to the metal. The carbaborane fragment on the left-hand side displays for the first time a *syn* disposition in these complexes.

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§ A yellow parallelepiped crystal suitable for X-ray analysis was grown from acetone by vapour diffusion. Orthorhombic, *Pnma*; a = 17.209(3) Å, b = 12.118(6) Å, c = 16.360(5) Å; V = 3412 Å^3; Z = 4; D_{calc} = 1.40 g cm^{-3}; μ(Mo-$K\alpha$) = 8.2 cm^{-1}. An automated diffractometer (ENRAF–NONIUS CAD4) was used to collect 1536 reflections with $I > 3\sigma(I)$ at 293 K. The structure was solved by multisolution direct methods using the Ω tangent formula (J. Rius and C. Miravitlles, *Acta Crystallogr. Sect. A*, 1989, **45**, 490), Fourier and least-squares techniques (G. M. Sheldrick, SHELX/76, University of Cambridge, England 1976) and refined to residuals of R = 0.050 and R_w = 0.054 with a 'goodness-of-fit' index of 2.6 ($w = k/(\sigma^2(F) + 0.00427^*F^2)$; 'goodness of fit' = $[\Sigma(w(|F_o| - |F_o|)^2/(N_{obs} - N_{parameters}))^{1/2}]$ and with max and min heights in final F-synthesis 0.55 and -0.40 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 H. F. Dare, J. A. K. Howard, M. U. Pilotti, F. G. A Stone and J. Szameitat, *J. Chem. Soc., Chem. Commun.*, 1989, 1409.

2 P. E. Behnken, J. A. Belmont, D. C. Busby, M. S. Delaney, R. E. King, III, C. W. Kreimendahl, T. B. Marder, J. J. Wilczynski and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 3011, R. T. Baker, M. S. Delaney, R. E. King III, C. B. Knobler, J. A. Long, T. B. Marder, T. E. Paxson, R. G. Teller and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 2965.

3 J. A. Long, T. B. Marder, P. E. Behnken and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 1979; C. B. Knobler, T. B. Marder, E. A. Mizusawa, R. G. Teller, J. A. Long and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 2990.

4 P. E. Behnken, T. B. Marder, R. T. Baker, C. B. Knobler, M. R. Thompson and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1985, **107**, 932.

5 M. Green, J. A. K. Howard, A. N. de M. Jelfs, O. Johnson and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 73.

6 J. D. Hewes, C. W. Kreimendhal, T. B. Marder and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 5757.

7 F. Teixidor and R. W. Rudolph, *J. Organomet. Chem.*, 1983, **241**, 301.

8 C. Viñas, W. M. Butler, F. Teixidor and R. W. Rudolph, *Organometallics*, 1984, **3**, 503.

9 C. Viñas, W. M. Butler, F. Teixidor and R. W. Rudolph, *Inorg. Chem.*, 1986, **25**, 4369.

10 F. Teixidor, A. M. Romerosa, J. Rius, C. Miravitlles, J. Casabó, C. Viñas, E. Sanchez and L. Escuiche, *Inorg. Chim. Acta*, 1990, **176**, 287.

11 F. Teixidor, A. M. Romerosa, J. Rius, C. Miravitlles, J. Casabó, C. Viñas and E. Sánchez, *J. Chem. Soc., Dalton Trans.* 1990, 525.

12 F. Teixidor, C. Viñas, J. Rius, C. Miravitlles and J. Casabó, *Inorg. Chem.*, 1990, **29**, 149.

13 (*a*) C. Viñas, PhD Thesis, Universitat de Barcelona, 1990; (*b*) F. Teixidor, J. Casabó, C. Viñas, E. Sanchez and R. Kivekäs, *Inorg. Chem.*, in the press.

14 P. E. Behnken, T. B. Marder, R. T. Baker, C. B. Knobler, M. R. Thompson and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1985, **107**, 932.