Novel Phosphonium-betaine Ligands $[SC(H)PPh_3$-*C,S*$]^-$ and $[S(H)C{=}C(PPh_3)S$-*S,S′*$]^-$ Stabilised in Rhodacarborane Complexes

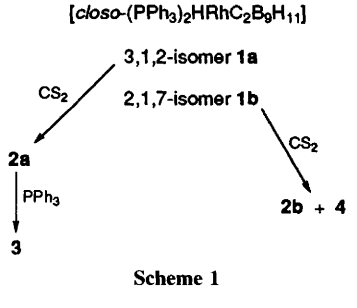
George Ferguson,[*a] **John F. Gallagher,**[a] **Michael C. Jennings,**[a] **Siobhan Coughlan,**[b] **Trevor R. Spalding,**[*b] **John D. Kennedy**[c] **and Xavier L. R. Fontaine**[c]

[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, UK LS2 9JT*

Two novel phosphonium-betaine ligands $[SC(H)PPh_3]^-$ and $[S(H)C{=}C(PPh_3)S]^-$ are stabilised in the twelve-vertex *closo*-type rhodacarborane complexes $[3\text{-}\{\eta^2\text{-}SC(H)PPh_3\}\text{-}3\text{-}(PPh_3)\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ and $[2\text{-}\{\eta^2\text{-}S(H)C{=}C(PPh_3)S\}\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$ which are characterised spectroscopically and by X-ray diffraction methods.

Several ligands containing S–C–P fragment donor sites have been the subjects of much recent interest.[1] Some of these ligands, including R_3PCS_2[1a–c] and $[Ph_2PCS_2]^-$,[1d] have been synthesised in reactions between CS_2 and phosphines. Others have been obtained from reactions between phosphines and dithioformato ligands attached to metals, *e.g.* $[S_2C(H)PR_3]^-$[1e,f] and $[SC(H)SCPh_3]$.[1g] We now report the synthesis of two novel, anionic, phosphonium-betaine ligands $[SC(H)PPh_3]^-$ and $[S(H)C{=}C(PPh_3)S]^-$ which are stabilised in rhodacarborane complexes. The former ligand is bonded to the metal *via* C and S atoms. The latter ligand is bonded *via* both sulfur atoms and can be considered to be a novel derivative of the dithiolene system $S(X)C{=}C(Y)S$,[2] related to the recently reported $S(O)C{=}C[P(NMe_2)_3]S$[2e] and $S(S)C{=}C[P(C_6H_{11})_3]S$[2f] ligands. Dithiolate complexes have been studied for many years with particular attention being paid to their ability to stabilise unusual metal oxidation states.[2a–c] The dithiolate complex described below may be regarded as an unusual *closo*-type cluster containing a 16-electron rhodium(III) centre and thereby formally has a 'sub-*closo*' electron count.

The major product of the reaction of $[3,3\text{-}(PPh_3)_2\text{-}3\text{-}H\text{-}$*closo*$\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ **1a** with carbon disulfide in a CS_2 solution, heated at reflux for 3 days, was $[3\text{-}(\eta^2\text{-}S_2CH)\text{-}3\text{-}(PPh_3)\text{-}$*closo*$\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ **2a** (31% yield). Reaction between **2a** and excess PPh_3 in dichloromethane solution at room temperature afforded the novel complex $[3\text{-}\{\eta^2\text{-}SC(H)PPh_3\}\text{-}3\text{-}(PPh_3)\text{-}$*closo*$\text{-}3,1,2\text{-}RhC_2B_9H_{11}]$ **3** (80% yield based on **2a**, see Scheme 1). Satisfactory analytical and spectroscopic data were obtained for **2a** and **3**,† and single crystals of both **2a**[3a] and **3**‡ have been the subjects of X-ray diffraction studies. Fig. 1 is a general view of **3** with important interatomic distances and angles noted. The structure contains an unusual RhCS ring. The Rh–S distance, 2.348(1) Å, is not significantly different from those in the rhodadithioformato group in **2a**, 2.352(1) and 2.356(1) Å, and it is between the values observed in $[2\text{-}(\eta^2\text{-}S_2CH)\text{-}2\text{-}(PPh_3)\text{-}$*closo*$\text{-}2,1\text{-}RhSeB_{10}H_{10}]$,[3b] 2.328(1) and 2.406(1) Å. The Rh–C distance, 2.134(4) Å, is somewhat longer than 2.085(14) Å in the RhCS ring in the cation $[Rh\{\eta^2\text{-}SC(S)\}(np)_3]^+$ {np$_3$ = tris[2-(diphenylphosphino)ethyl]amine}[4] or 2.035(14) Å in the RhC(S)SC(S)S ring of $[Rh(\eta^2\text{-}C_2S_4\text{-}$*C,S′*$)(PMe_3)(\eta^5\text{-}C_5H_5)]$.[5] The PC(H)S fragment in **3** is almost planar.



Scheme 1

When $[2,2\text{-}(PPh_3)_2\text{-}2\text{-}H\text{-}$*closo*$\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$ **1b** was allowed to react with CS_2 under the same conditions as for the 3,1,2-isomer **1a**, two products were isolated, each in 3% yield. One was the η^2-dithioformato complex $[2\text{-}(\eta^2\text{-}S_2CH)\text{-}2\text{-}(PPh_3)\text{-}$*closo*$\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$ **2b**[3c] and the other was a second *closo*-type species $[2\text{-}\{\eta^2S(H)C{=}C(PPh_3)S\}\text{-}2,1,7\text{-}RhC_2B_9H_{11}]$ **4**, Scheme 1. This latter compound gave a satisfactory elemental analysis and was characterised by spectroscopic§ and X-ray crystallographic data;¶ it contains an anionic, dithiolene-based, phosphonium-betaine ligand attached to the rhodium atom of a RhC_2B_9 cage, Fig. 2. The ligand skeleton PC(1S)S(1)C(2S)S(2) is essentially planar with torsion angles S(1)–C(1S)–C(2S)–S(2) −0.6(0)° and P–C(1S)–C(2S)–S(2) −175.8(3)°. The angles at C(1S) and C(2S) all approached 120°, Fig. 2 legend. The C(1S)–C(2S) distance is 1.349(5) Å which is typical of dithiolene ligands.[2d,6] The P–C(1S) single-bond distance is 1.785(3) Å. The C–S distances are slightly different at the 3 e.s.d. level being C(1S)–S(1) 1.733(3) and C(2S)–S(2) 1.706(3). The Rh–S distances [mean 2.238(1) Å] are notably shorter than any of the Rh–S distances in **2a**, **2b**, **3**, or $[2\text{-}(\eta^2\text{-}S_2CH)\text{-}2\text{-}(PPh_3)\text{-}$*closo*$\text{-}2,1\text{-}RhSeB_{10}H_{10}]$, which are in the range 2.328(1)[3b] to 2.432(1),[3c] or the mean Rh–S distance of 2.308 Å reported for rhodium [SC(R)C(R′)S]-thiolene complexes.[6] The plane containing the rhodium atom and the PC(1S)S(1)C(2S)S(2) atoms of the

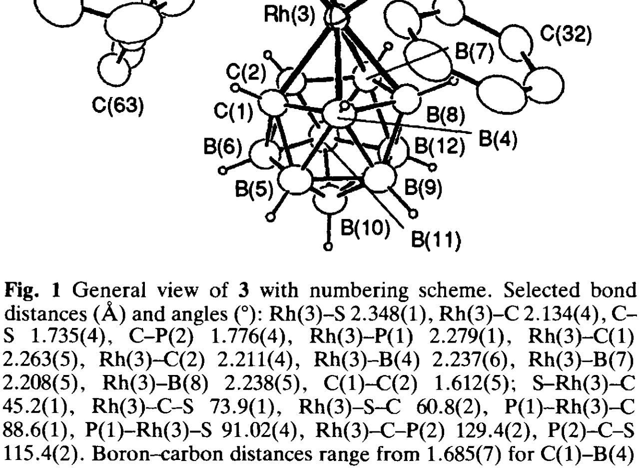


Fig. 1 General view of **3** with numbering scheme. Selected bond distances (Å) and angles (°): Rh(3)–S 2.348(1), Rh(3)–C 2.134(4), C–S 1.735(4), C–P(2) 1.776(4), Rh(3)–P(1) 2.279(1), Rh(3)–C(1) 2.263(5), Rh(3)–C(2) 2.211(4), Rh(3)–B(4) 2.237(6), Rh(3)–B(7) 2.208(5), Rh(3)–B(8) 2.238(5), C(1)–C(2) 1.612(5); S–Rh(3)–C 45.2(1), Rh(3)–C–S 73.9(1), Rh(3)–S–C 60.8(2), P(1)–Rh(3)–C 88.6(1), P(1)–Rh(3)–S 91.02(4), Rh(3)–C–P(2) 129.4(2), P(2)–C–S 115.4(2). Boron–carbon distances range from 1.685(7) for C(1)–B(4) to 1.728(8) for C(2)–B(6) and B–B distances 1.743(8) for B(6)–B(10) to 1.849(7) for B(4)–B(8).

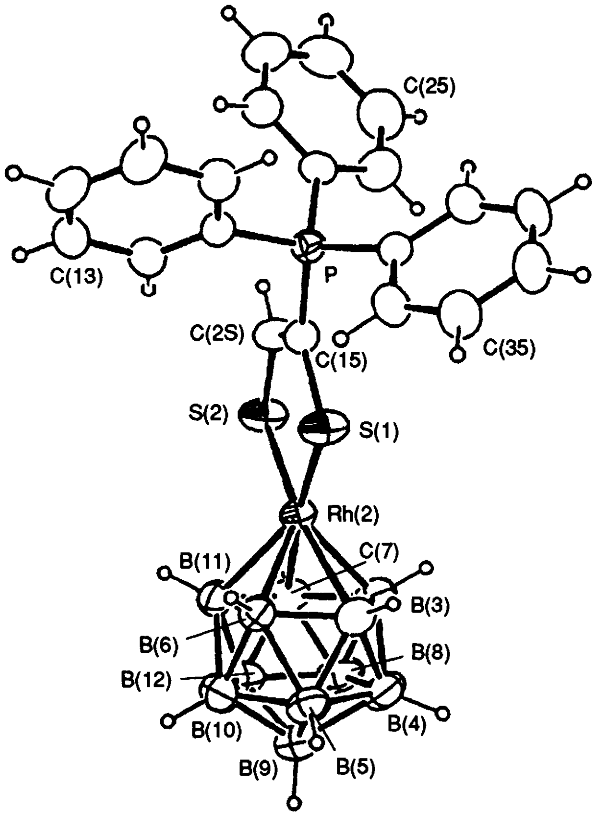


Fig. 2 General view of **4** with numbering scheme. Selected bond distances (Å) and angles (°): Rh(2)–S(1) 2.2414(10), Rh(2)–S(2) 2.2352(10), C(1S)–S(1) 1.733(3), C(2S)–S(2) 1.706(4), C(1S)–C(2S) 1.349(5), C(1S)–P(1) 1.785(3), Rh(2)–C(1) 2.198(4), Rh(2)–C(7) 2.191(4), Rh(2)–B(3) 2.126(4), Rh(2)–B(6) 2.166(4), Rh(2)–B(11) 2.145(4); S(1)–Rh(2)–S(2) 87.74(4), Rh(2)–S(1)–C(1S) 105.35(12), Rh(2)–S(2)–C(2S) 105.61(13), P(1)–C(1S)–S(1) 119.89(20), P(1)–C(1S)–C(2S) 120.2(3), C(1S)–C(2S)–S(2) 121.5(3), C(2S)–C(1S)–S(1) 119.8(3). Boron–carbon distances range from 1.678(6) for C(7)–B(11) to 1.747(6) for C(1)–B(3) and B–B distances 1.755(7) for both B(4)–B(5) and B(5)–B(9) to 1.852(6) for B(6)–B(11).

phosphonium-betaine ligand is almost coincident with the plane containing the Rh, C(1) and C(7) atoms. Thus, the conformation of the RhS_2C_2 unit above the C_2B_3 carborane face is that expected for a *closo*-type compound with a sixteen-electron metal centre.[7] Although **4** formally has a sub-*closo* electron count, this does not appear to affect the *closo*-type cage structure significantly.

Finally, two points of general interest are noteworthy; (*a*) the rhodacarborane isomer (**1a** or **1b**) used affected both the number of products and their yields, and (*b*) during the present work no compounds were observed which were analogous with $[\{\eta^2:\eta'^1\text{-}S_2C(H)(PPh_3)\}RhXB_{10}H_{10}]_2$ (X = Se, Te).[1e]

Received, 16th March 1994; Com. 4/01587H

Footnotes

† Compound **3**. Measured ^{11}B and ^1H NMR data (CD_2Cl_2 at 294–297 K) as: assignment, $\delta(^{11}B)$ [δ ^1H]; BH(8) +2.9 [+2.17], BH(10) −1.9 [+2.87], BH(12) *ca.* −9.0 [+1.39], BH(9) *ca.* −9.4 [+1.49], BH(4) *ca.* −9.4 [+1.94], BH(7) *ca.* −9.4 [+2.25], BH(11) *ca.* −19.9 [+1.25], BH(5) *ca.* −19.9 [+0.90], BH(6) −23.8 [+1.05]. Additionally, $\delta(^1H)$ CH(2) +2.57, CH(1) +1.98 and SC*H*(PPh_3) +2.92 {d of d of d, $^1J(^{103}Rh{-}^1H)$ 1.2, $^3J(^{31}P_A{-}^1H)$ 6.3, $^2J(^{31}P_B{-}^1H)$ 13.7 Hz} $\delta(^{31}P)$ P_A +44.4 [$^2J(^{103}Rh{-}^{31}P)$ 173 Hz], P_B +23.5 [$^2J(^{103}Rh{-}^{31}P)$ 2.8 Hz], $^2J(^{31}P_A{-}^{31}P_B)$ 4.2 Hz. Selected IR data (KBr) ν_{max}/cm^{-1} (BH) 2595m, 2549s, 2524s and (SCH) 1180w and 900m.

‡ *Crystal data* for **3**·$2CH_2Cl_2$: $C_{41}H_{46}B_9Cl_4P_2RhS$, M = 974.85, monoclinic, space group $P2_1/n$, a = 13.239(3), b = 19.384(3), c = 18.883(3) Å, β = 108.68(1)°, D_c = 1.41 g cm^{-3}, U = 4590(3) $Å^3$, Z = 4, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 7.4 cm^{-1}, $F(000)$ = 1984. A total of 10401 reflections were measured in the range $2 < 2\theta < 54°$ with a CAD4 diffractometer using an orange crystal (0.22 × 0.25 × 0.44 mm). Of these reflections, 9972 were unique (R_{int} 0.022) and the 6237 with $I > 3\sigma(I)$ were labelled as 'observed' and used in the analysis. The intensity data were corrected for Lorentz, polarisation and absorption effects. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations using SDP-Plus[8] to R = 0.043, R_w = 0.057. All non-hydrogen atoms were refined anisotropically and H atoms were treated as 'riding' atoms.

§ Compound **4**. Measured ^{11}B and ^1H NMR data (CD_2Cl_2 at 294–297 K) as: intensity, $\delta(^{11}B)$ [$\delta(^1H)$]; 1BH +7.9 [+3.91], 2BH −2.7 [+3.15], 1BH −2.7 [+3.51], 2BH −12.0 [+1.79], 1BH −15.3 [+1.91], 2BH −18.0 [+1.85]. Additionally, $\delta(^1H)$ 2CH +3.31 and SC*H*C(PPh_3)S +8.20 {d of d, $^3J(^{103}Rh{-}^1H)$ 4.4, $^3J(^{31}P{-}^1H)$ 8.3 Hz} $\delta(^{31}P)$ +16.1 [$^3J(^{103}Rh{-}^{31}P)$ 12 Hz]. Selected IR data (KBr) ν_{max}/cm^{-1} (BH) 2570(sh), 2560(sh), 2541s, 2510s and (SCH) 1220w and 945m.

Crystal data for **4**: $C_{22}H_{27}B_9PRhS_2$, M = 586.74, monoclinic, space group $P2_1/c$, a = 12.352(2), b = 17.498(2), c = 12.421(2) Å, β = 97.62(1)°, D_c = 1.40 g cm^{-3}, U = 2661(1) $Å^3$, Z = 4, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 8.5 cm^{-1}, $F(000)$ = 1184. 5022 reflections were measured in the range $2 < 2\theta < 50°$ with a CAD4 diffractometer using a red needle shaped crystal (0.13 × 0.14 × 0.40 mm). Of these reflections, 4664 were unique (R_{int} 0.015) and the 3222 with $I > 2.5\sigma(I)$ were labelled as 'observed' and used in the analysis. The intensity data were corrected for Lorentz, polarisation and absorption effects. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations using NRCVAX[9] to R = 0.027, R_w = 0.031. All non-hydrogen atoms were refined anisotropically and H atoms were treated as 'riding' atoms. For both structures **3** and **4** atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 (*a*) D. Miguel, J. A. Perez-Martinez, V. Riera and S. Garcia-Granda, *Organometallics*, 1993, **12**, 1394; (*b*) J. Cuyas, D. Miguel, J. A. Perez-Martinez, V. Riera and S. Garcia-Granda, *Polyhedron*, 1992, **11**, 2713; (*c*) A. L. Hector and A. F. Hill, *J. Organomet. Chem.*, 1993, **447**, C7; (*d*) K-H. Yih, Y-C. Lin, M-C. Cheng and Y. Wang, *J. Chem. Soc., Chem. Commun.*, 1993, 1380; (*e*) Faridoon, T. R. Spalding, G. Ferguson, J. D. Kennedy and X. L. R. Fontaine, *J. Chem. Soc., Chem. Commun.*, 1989, 906; (*f*) D. Miguel, J. A. Miguel, V. Riera and X. Solans, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1014; (*g*) J. L. Moler, D. P. Eyman and L. M. Mallis, *Inorg. Chem.*, 1992, **31**, 1816.

2 (*a*) G. N. Schrauzer, *Acc. Chem. Res.*, 1969, **2**, 72; (*b*) R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 303; (*c*) S. P. Best, S. A. Ciniawsky, R. J. H. Clark and R. C. S. McQueen, *J. Chem. Soc., Dalton Trans.*, 1993, 2267; (*d*) C. Bianchini, C. Mealli, A. Meli and M. Sabat, *Inorg. Chem.*, 1984, **23**, 4125; (*e*) W. Petz and F. Weller, *Z. Naturforsch., Teil B*, 1991, **46**, 971; (*f*) B. Alvarez, S. Garcia-Granda, Jing Li, D. Miguel and V. Riera, *Organometallics*, 1994, **13**, 16.

3 (*a*) G. Ferguson, S. Coughlan, T. R. Spalding, X. L. R. Fontaine, J. D. Kennedy and B. Stibr, *Acta Crystallogr., Sect. C*, 1990, 1402; (*b*) G. Ferguson, Faridoon and T. R. Spalding, *Acta Crystallogr., Sect. C*, 1988, 1368; (*c*) G. Ferguson, S. Coughlan and T. R. Spalding, *Acta Crystallogr., Sect. C*, 1993, 957.

4 C. Bianchini, D. Masi, C. Mealli, A. Meli and M. Sabat, *Organometallics*, 1985, **4**, 1014.

5 H. Werner, O. Kolb, R. Feser and U. Schubert, *J. Organomet. Chem.*, 1980, **191**, 283.

6 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

7 D. M. P. Mingos, M. I. Forsyth and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1978, 1363.

8 B. A. Frenz and Associates Inc., College Station, Texas 77840, USA and Enraf-Nonius, Delft, 1983.

9 E. J. Gabe, Y. LePage, J-P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384.