Novel Bonding Mode and Reaction of a Phosphonium-betaine Ligand $S_2C(H)(PPh_3)$. Synthesis of the $[Rh(XB_{10}H_{10})\{S_2C(H)(PPh_3)\}]_2$ Dimers (X = Se, Te) and X-Ray Diffraction Study of the Te-compound

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The novel dimers $[Rh(XB_{10}H_{10})\{S_2C(H)(PPh_3)\}]_2$ (X = Se, Te), obtained from the reaction of *closo*-$[2,2-(PPh_3)_2-2-(H)-1,2-XRhB_{10}H_{10}]$ and CS_2, exist in equilibrium (dichloromethane solution) with monomeric $[2-(PPh_3)-2-(\eta^2-S_2CH)-1,2-XRhB_{10}H_{10}]$ species, and exhibit a unique *cis*-bis(phosphonium-betaine) intercluster linkage with each ligand having one S atom bridging both Rh atoms and the other S atom singly co-ordinating to a Rh atom.

There is a continuing interest in transition metal complexes containing ligands derived from CS_2.[1] It has been our intention to extend the study of complexes of CS_2-based ligands to include compounds containing polyborane ligands. An analysis of the literature shows that transition metal complexes with the carbon disulphide based ligands $S_2C(X)$ (X = H, OR, NR_2, *etc.*) and $S_2C(H)(PR_3')$ on the one hand,[2] and boranes and heteroboranes on the other,[3] are well established but separate fields. Our work on metal derivatives of Se- and Te-containing heteroboranes has recently produced a η^2-thioformato complex of rhodium (1a), *closo*-$[2-(PPh_3)-2-(\eta^2-S_2CH)-1,2-SeRhB_{10}H_{10}]$, which was structurally charac-

terised in an X-ray diffraction study.[4] This complex was obtained from the reaction between CS_2 and *closo*-$[2,2-(PPh_3)_2-2(H)-1,2-SeRhB_{10}H_{10}]$ in CS_2 as solvent and we have isolated the telluraborane analogue (1b) similarly. We now report that, at room temperature in dichloromethane solution, compounds (1a,b) exhibit an unprecedented reversible reaction which involves an interesting and substantial modification of the exo-polyhedral $\{(PPh_3), (S_2CH)\}$ rhodium ligands, Scheme 1. This results in approximately equimolar equilibrium concentrations of (1a,b) and the dimeric compounds $[Rh(XB_{10}H_{10})\{S_2C(H)(PPh_3)\}]_2$ (2a,b for X = Se, Te). The dimers contain intact rhodaheteroborane cages

(1a,b)   (2a,b)

a; X = Se
b; X = Te
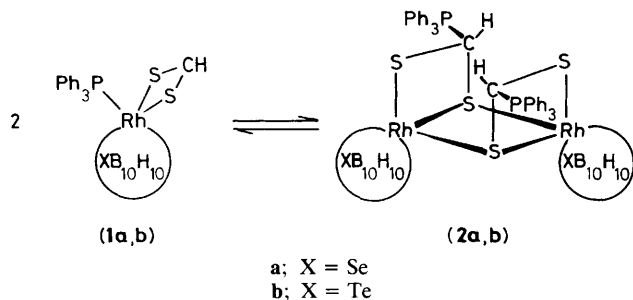
Scheme 1

which are linked rhodium-to-rhodium by two phosphonium-betaine ligands that exhibit a previously undescribed η^2,η^1-bridging co-ordination mode. These facts were established by i.r. and multi-element n.m.r. spectroscopy,† and single crystal X-ray diffraction analysis.

The equilibration reaction is sufficiently slow (several hours at room temp.) so that the red dimers may be separated in reasonable purity from the yellow monomers by preparative t.l.c. Moreover, crystals of (2b) suitable for an X-ray diffraction study were grown from dichloromethane solution.‡

A general view of the structure is shown in Figure 1. The dimer (2b) has two-fold crystallographic symmetry with each rhodium atom bound to a TeB_{10}-cage and a $S_2C(H)(PPh_3)$ ligand; the adjacent $RhTeB_{10}$ cages are bridged through two adjacent $S_2C(H)(PPh_3)$ ligands. The central Rh(2)–S(1)–

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† Measured ¹¹B and ¹H n.m.r. data (CD_2Cl_2 at 294—297 K) for the monomers are as follows {¹¹B, ¹H data for directly bound BH units being ordered as: assignment δ(¹¹B)/p.p.m.[δ(¹H)/p.p.m.]}: Se compound (1a) BH(12) +15.8[+4.21], BH(9) +13.1[+4.51], BH(3,6) ca. +12.5[+3.34], BH(7,11) +10.6[+3.40], BH(8,10) −11.6[+2.26], BH(4,5) −12.9[+1.95], δ(¹H)(RhS$_2$CH) +11.15, $^3J(^{103}Rh-^1H)$ 4.1 Hz, $^4J(^{31}P-^1H)$ 7.5 Hz; Te compound (1b) BH(12) +18.0[+5.36], BH(9) +13.8[+4.99], BH(3,6) +12.0[+3.74], BH(7,11) +11.9[+3.88], BH(8,10) −10.8[+2.87], BH(4,5) −14.5[+2.26], δ(¹H)(RhS$_2$CH) +11.02, $^3J(^{103}Rh-^1H)$ 3.9 Hz, $^4J(^{31}P-^1H)$ 7.2 Hz. Measured n.m.r. data for the dimers (CD_2Cl_2 at 294—297 K) are as follows {ordered as δ(¹¹B)/p.p.m.[δ(¹H)/p.p.m.] for directly bound BH units}: Se compound (2a) +15.7[+4.80], ca. +12[+3.27], +11.8[+3.85], +10.8[+4.62], ca. +10.5[+3.23], ca. +9[+2.89], −10.8[+2.60], −12.5[+2.58], ca. −14.5[+2.13], ca. −16[+2.10], δ(¹H)(RhS$_2$CHPPh$_3$) +9.99; Te compound (2b) ca. +16[+2.96], +13.8[+3.78], +10.2[+4.20], ca. +10[+3.38], +9.8[+2.76], ca. +8[+2.40], −11.7[+1.90], −12.5[+1.96], −13.2[+1.96], ca. −16[+1.84], δ(¹H)(RhS$_2$CHPPh$_3$) + 9.87. Selected i.r. data (cm⁻¹, KBr) (1a) ν_{BH}(max.) 2580vs, 2565w, 2535vs; ν_{HCS}(max.) 1220w. (1b) ν_{BH}(max.) 2560w, 2520s; ν_{HCS}(max.) 1220w. (2a) ν_{BH}(max.) 2560w, 2520vs. (2b) ν_{BH} (max.) 2540s 2440w.

‡ Crystal data for (2b): $C_{38}H_{72}B_{20}P_2S_4Rh_2Te_2$, M = 1396.4, monoclinic, space group $C2/c$, a = 19.833(2), b = 12.734(2), c = 23.317(2) Å, β = 103.55(1)°, D_c = 1.62 g cm⁻³, U = 5725 Å³, Z = 4, μ(Mo-K_α) = 17.9 cm⁻¹, λ(Mo-K_α) = 0.71073 Å, F(000) = 2752. Reflection data were measured with a CAD4 diffractometer using a deep-red plate crystal (0.03 × 0.42 × 0.45 mm). After an initial period of exposure, the crystal decomposed rapidly in the X-ray beam. 1305 reflections were measured, of which 1162 were unique, and the 852 with $I \geqslant 3\sigma(I)$ were retained as observed. After correction for Lorentz, polarization, and absorption effects, the structure was 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 rounds of refinement. The Te, Rh, S, and P atoms were allowed anisotropic motion and the C and B atoms constrained to isotropic motion. The final refinement cycle had 163 variables and converged with R = 0.063, R_w = 0.082. 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.

Figure 1. A general view of (2b), [Rh(TeB$_{10}$H$_{10}$){S$_2$C(H)(PPh$_3$)}]$_2$, looking approximately along the crystallographic two-fold axis; for clarity, atoms are shown as spheres of arbitrary size. The environment about Rh is pseudo-octahedral with angles (°) Te(1)–Rh(2)–S(1*) 175.3(2), S(1)–Rh(2)–B(7) 162.8(8), and S(2)–Rh(2)–B(11) 166.7(7). As expected the C(1)(sp³) bonds in (2b) are longer [C–S(1) 1.83(2), C–S(2) 1.79(2) Å] than the C(sp²)–S bonds in (1a) [1.669(4) and 1.650(5) Å].

Rh(2*)–S(1*) section is slightly folded (fold angle 17.3°) with Rh(2)–S(1) and Rh(2)–S(1*) distances of 2.394(7) and 2.461(7) Å and angles Rh(2)–S(1)–Rh(2*) 94.9(2)° and S(1)–Rh(2)–S(1*) 82.4(2)°. The Rh(2)–S(2) distance to the non-rhodium bridging S atom of the phosphonium-betaine ligand is 2.432(6) Å. Hence the three rhodium–sulphur distances in (2b) are very similar. They may be compared with values of 2.328(1) and 2.406(1) Å observed in (1a). The inter-rhodium linkage of (2a,b) could be viewed initially as resembling a $Rh_2S_4C_2$-based cubane-type structure with two edges broken. However only two of the angles in the Rh(2)–S(1)–C(1)–S(2) section of the molecule approach 90°; [*i.e.* Rh(2)–S(1)–C(1) 88.2(7), and C(1)–S(2)–Rh(2) 89.9(7)]. The others are 107(1)° for S(1)–C(1)–S(2) and 73.0(2)° for S(1)–Rh(2)–S(2) respectively.

The overall bonding of the $S_2C(H)(PPh_3)$ ligands in the dimers is novel and the *cis*-conformation of the phosphonium-betaine ligands with respect to the Rh_2S_2 section is a notable feature. It contrasts to the *trans*-disposition of the μ-YZ ligands in the complexes [(triphos)Rh(μ-YZ)$_2$Rh(triphos)]²⁺ [YZ = SO, S$_2$, Se$_2$; triphos = (Ph$_2$PCH$_2$)$_3$CMe] which were prepared from rhodium–Y$_2$C compounds.[5a–c] These *trans*-conformations may be dictated to a large extent by the steric demands of the pendant phenyl groups on the triphos ligand whereas the XB$_{10}$-cages in (2a,b) are apparently less sterically demanding. In this context it is also noteworthy that [(triphos)Rh{S$_2$C(H)(PEt$_3$)}]²⁺, prepared by protonation of [(triphos)RhCl{S$_2$C(PEt$_3$)}] in the presence of Na[BPh$_4$], was obtained as a monomeric species with no evidence for dimerisation. A *transoid* arrangement of two S$_4$-bridges has been recently reported in [Rh$_2$S$_8$(η⁵-C$_5$Me$_5$)$_2$].[5d]

Considerable changes occur in the RhTeB$_{10}$-cage with the change in the *exo*-cage ligands from the {(PPh$_3$)$_2$H} set in the

precursor complex *closo*-[2,2-(PPh$_3$)$_2$-2-(H)-1,2-TeRh-B$_{10}$H$_{10}$] (**3**)[6] to the {S(1),S(2),S*} set in (**2b**). Most notable are (i) the reduction in the rhodium–tellurium distance from 2.6172(4) Å in (**3**) to 2.537(3) Å in (**2b**); (ii) the increase in the range of boron–boron distances from 1.743(7)—1.962(7) Å in (**3**) to 1.57(4)—1.95(4) Å in (**2b**).

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