Progressive Cage-opening in d^6, d^8, d^{10}, and $d^{10}s^2$ Metallacarbaboranes: Crystal and Molecular Structures of 3-Triphenylphosphino-3-mercura-1,2-dicarbadodecaborane and Triphenylmethylphosphonium 3-Thalla-1,2-dicarbadodecaborate

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Summary *X*-Ray studies of the novel d^{10} metallacarbaborane 3-PPh$_3$-3,1,2-HgC$_2$B$_9$H$_{11}$ (I) and the $d^{10}s^2$ species [PPh$_3$Me]$^+$[3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$ (II) show that in (I) the mercury atom is bonded principally only to triphenylphosphine and to the unique boron atom of the C$_2$B$_3$ face, whereas in the anion of (II) the position of the thallium atom suggests an ion-pair formulation [Tl$^+$C$_2$B$_9$H$_{11}$$^{2-}$]$^-$; together with results for analogous d^6 and d^8 systems, these structures demonstrate progressive opening of the metallacarbaborane cage as electron density on the metal increases.

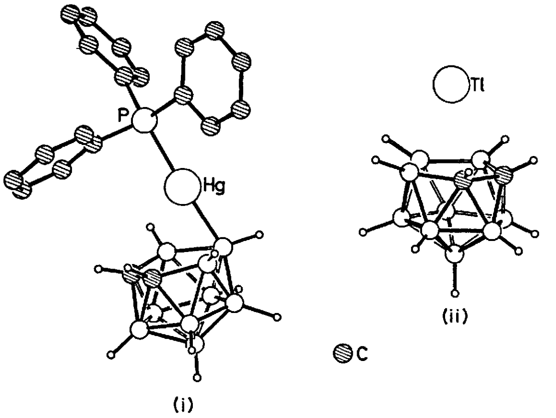

Figure 1. Molecular structures of (i) 3-PPh$_3$-3,1,2-HgC$_2$B$_9$H$_{11}$ (I) (phenyl hydrogen atoms are omitted) and (ii) [3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$ (II).

Structural studies on metallacarbaboranes derived from the 7,8-C$_2$B$_9$H$_{11}$$^{2-}$ ion have established the existence of two basic geometries, the symmetrically bonded *closo* structure observed for d^0–d^7 transition metal ions,[1,2] and the distorted *nido* or 'slipped' configuration adopted by complexes containing formal d^8 (refs. 3 and 4) and d^9 (ref. 5) ions. We now report the structures of related d^{10} (Hg$^{\text{II}}$) and $d^{10}s^2$ (Tl$^{\text{I}}$) complexes, and rationalise the structural variations observed for d^0–$d^{10}s^2$ metalladicarbadodecaboranes.

The d^{10} complex 3-PPh$_3$-3,1,2-HgC$_2$B$_9$H$_{11}$ (I), m.p. 165 °C (decomp.), was obtained in 60% yield from the reaction between [PPh$_3$HgCl$_2$]$_2$ and Tl$^+$[3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$ (CH$_2$Cl$_2$, 10 min, 25 °C). Recrystallisation from 1,4-dioxan–acetone–ether gave a dioxan solvate 3-PPh$_3$-3,1,2-HgC$_2$B$_9$H$_{11}$·(C$_4$H$_8$O$_2$)$_{0\cdot5}$, the structure of which was determined by a single crystal *X*-ray study at −60 °C.

Crystal data: PPh$_3$HgC$_2$B$_9$H$_{11}$·(C$_4$H$_8$O$_2$)$_{0\cdot5}$, M 639·3, triclinic, space group $P1$, a = 10·9135(17), b = 11·1883(19), c = 12·0071(18) Å, α = 83·50(1), β = 86·98(1), γ = 61·55(1)°, U = 1280·8(4) Å^3, D_c = 1·657 g cm^{-3}, μ (Mo-K_α) = 60·8 cm^{-1}, Z = 2. R is currently 0·037 for 2450 independent observed reflections.†

The molecule [Figure 1(i)] possesses approximate mirror symmetry, with the mercury atom co-ordinated almost linearly by triphenylphosphine and the unique boron atom (B′) of the open face [Hg–P = 2·39(3), Hg–B′ = 2·20(1) Å, ∠P–Hg–B = 172·5(4)°]. Additional, though relatively weak, bonding is suggested by the other Hg–B (facial) distances [2·50(2) and 2·53(2) Å] so that the complex is perhaps best described as *pseudo* σ-bonded. Consistent with a σ-bonded description, the hydrogen atom bonded to B′ is displaced downward from its normal radial position, and lies essentially in the plane of the C$_2$B$_3$ face. Mercury–carbon (facial) separations of 2·89(2) and 2·91(2) Å correspond to essentially non-bonded interactions, and the dioxan of solvation does not co-ordinate to mercury but merely stabilises the crystal lattice.

The [3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$ ion, originally reported by Spencer *et al.*,[6] was isolated as the air-sensitive triphenylmethylphosphonium salt [PPh$_3$Me]$^+$[3,1,2-TlC$_2$B$_9$H$_{11}$]$^-$·(THF)$_{0\cdot5}$ (II) and its structure [Figure 1(ii)] was determined from *X*-ray data at −100 °C.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Crystal data: $[PPh_3Me]^+[TlC_2B_9H_{11}]^- \cdot (C_4H_8O)_{0\cdot5}$, $M = 650\cdot16$, monoclinic, space group $P2_1/c$, $a = 12\cdot3755(17)$, $b = 14\cdot4518(18)$, $c = 15\cdot3769(16)$ Å, $\beta = 98\cdot42(1)$, $U = 2720\cdot5(7)$, $D_c = 1\cdot587$ g cm^{-3}, μ (Mo-K_α) $= 60\cdot7$ cm^{-1}, $Z = 4$. R is currently 0·030 for 3279 independent observed reflections.†

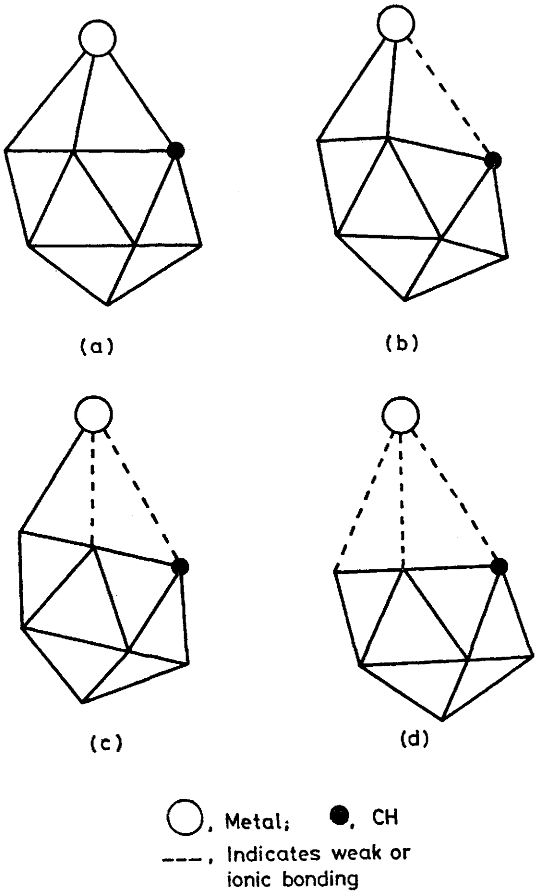

FIGURE 2. Metal–cage interactions in (a) $[3\text{-}(CO)_3\text{-}3,1,2\text{-}ReC_2B_9H_{11}]^-$ (d^6,Re$^{\text{I}}$), (b) $3\text{-}Et_2NCS_2\text{-}3,1,2\text{-}AuC_2B_9H_{11}$ (d^8,Au$^{\text{III}}$), (c) $3\text{-}PPh_3\text{-}3,1,2\text{-}HgC_2B_9H_{11}$ (d^{10}, Hg$^{\text{II}}$), and (d) $[3,1,2\text{-}TlC_2B_9H_{11}]^-$ ($d^{10}s^2$, Tl$^{\text{I}}$); projections are parallel to the cage C–C bond with all structures drawn to the same scale.

The thallium atom in (II) is more symmetrically located with respect to the cage than is the mercury atom in (I) [Tl–B′ = 2·664(7), Tl–B = 2·744(8) and 2·741(7), and Tl–C = 2·915(6) and 2·923(6) Å], but even the shortest thallium–cage distance considerably exceeds the sum of covalent radii‡ ($Tl\text{–}B_{calc} = 2\cdot36$ Å) so that the species may be formally regarded as an ion pair, $[Tl^+C_2B_9H_{11}{}^{2-}]^-$. Since both Tl^+ and $7,8\text{-}C_2B_9H_{11}{}^{2-}$ are colourless however, the pale yellow colour of the complex perhaps implies a slight degree of charge-transfer.

Comparison of the structures reported here with those previously described for d^6 (Re$^{\text{I}}$)[7] and d^8 (Au$^{\text{III}}$)[4] species reveals a progressive opening of the metallacarborane cage as electron density on the metal increases (Figure 2). Wade[8] has suggested that, in addition to the 'skeletal' electron pairs of a polyhedral framework ($n + 1$ pairs for a *closo* system, *etc.*), up to 3 electron pairs may be accommodated in the 'non-bonding' d-orbitals of a transition metal, implying that metal electron pairs in excess of this number must contribute to the total skeletal electron count. On this basis, $(n+1)$, $(n+2)$, $(n+3)$, and $(n+4)$ skeletal electron pairs ($n = 12$) can be associated with the presence of formal (d^0–d^6), d^8, d^{10}, and $d^{10}s^2$ ions respectively, leading to progressive opening of the metallacarbaborane cage. In M.O. terms the increasing electron density is assigned to metal–cage antibonding orbitals ($e_1{}^*$, $a_1{}^*$) located principally on the metal ($e_1{}^* \approx d_{xz,yz}$, $a_1{}^* \approx s$).[9] In the case of d^8 systems the observed deviations from a symmetrically bonded structure have been ascribed to the overlap of a filled cage e_1 orbital with a vacant metal s–p_z orbital;[10] this interaction also seems likely in (I). At the $d^{10}s^2$ configurations, however, both $e_1{}^*$ and $a_1{}^*$ are filled, and only ionic binding remains.

Since $[(CO)_3ReC_2B_9H_{11}]$, $Et_2NCS_2AuC_2B_9H_{11}$, $PPh_3HgC_2B_9H_{11}$ (I) and $[TlC_2B_9H_{11}]^-$ (II) are isoelectronic (18e) but not isostructural (Figure 2) we conclude that any attempt to predict metallacarborane structures on the basis of electron-counting rules must take into account the electron configuration of the metal in its formal oxidation state, at least for the heavier transition- and post-transition-elements.

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‡ The covalent radius of thallium(I) was estimated as 1.48 Å from the internuclear separation in gaseous molecular TlI (A. H. Barrett and M. Mandel, *Phys. Rev.*, 1958, **109**, 1572).

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