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Homobimetallic B-frame Species: an Interesting $(2 \times 11) \rightarrow (10 + 12)$ Cluster Disproportionation of an Eleven-vertex *nido*-Platinaundecaborane and the Molecular Structure of the Twelve-vertex *closo*-Diplatinadodecaborane $[1\text{-Cl-}1,2,2,4\text{-}(PMe_2Ph)_4\text{-}closo\text{-}1,2\text{-}Pt_2B_{10}H_9]$

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There is a growing interest in the use of polyhedral borane clusters as 'B-Frame' matrices on which to juxtapose two or more potentially reactive metal centres [1–3]. In this context we now wish to report preliminary findings about the reaction of the *nido*-7-platinaundecaborane $[(PMe_2Ph)_2PtB_{10}H_{12}]$ [4–6] with the tertiary phosphine $[PMe_2Ph]$. This appears to result in a novel (2×11)-vertex $\rightarrow (10 + 12)$-vertex $2\{PtB_{10}\} \rightarrow \{B_{10}\} + \{Pt_2B_{10}\}$ cluster disproprotionation to generate dimetallaborane clusters with metal atoms in adjacent sites. Thus reaction in refluxing toluene for 16 h yields a variety of novel *closo* twelve-vertex 1,2-diplatinadodecaborane compounds together with the previously unreported family of the more straightforward *closo* ten-vertex $[B_{10}H_8(PMe_2Ph)_2]$ isomers. Although the basis of the stoichiometry is represented in eqn. (1), the diplatinadodecaboranes are obtained in a variety of susbstituted and/or isomeric forms. This is perhaps not unexpected as the reaction must necessarily be a complex multistep process.

$$2[(PMe_2Ph)_2PtB_{10}H_{12}] + 2[PMe_2Ph] \longrightarrow [(PMe_2Ph)_4Pt_2B_{10}H_{10}] + [B_{10}H_8(PMe_2Ph)_2] + 3H_2 \tag{1}$$

Typical total yields of the ten- and twelve-vertex species isolated so far are both in the region of about 12% (as yet unoptimized). The predominant $[B_{10}H_8(PMe_2Ph)_2]$ isomer formed is the (1,10) species; a number of the other $[B_{10}H_8(PMe_2Ph)_2]$ isomers are also formed, but we have not yet been able to mutually separate and therefore to characterize them.

The more abundant of the diplatinadodecaborane products have so far not crystallized in forms suitable for single-crystal X-ray diffraction analysis, but multielement multiple resonance NMR spectroscopy indicates that all the diplatinum species are of the same structural type. The first of those that we have been able to characterize structurally is in fact a byproduct, $[(PMe_2Ph)_3ClPt_2B_{10}H_9(PMe_2Ph)]$, that contains chlorine as a substituent on one of the metal atoms (we have established that the halogen in this case originates from impurities in the free phosphine used in some of the initial experiments). Crystals of the air-stable orange compound were monoclinic, space group $P2_1/c$, with $a = 1187.6(3)$, $b = 2170.4(3)$ pm, $\beta = 97.93(2)^\circ$, $Z = 4$, and the structure (based on 6446 independent F_o having $I > 2\sigma(I)$, out of a total of 7053), was refined to $R = 0.0312$. A drawing of the molecule is given in Fig. 1.

The compound is seen to be based on a closed $\{Pt_2B_{10}\}$ icosahedron with the metal atoms in adjacent sites. Interestingly, there is no significant distortion to a *nido* or 'slipped *closo*' geometry, and the interplatinum distance is reasonably strongly bonding at 286.3 pm. A simplistic initial rationale of the electronic structure, in the absence of detailed MO treatment, would involve a basic *nido*-decaboranyl-type $\{B_{10}\}$ skeleton and two *tetrahapto* borane-to-platinum binding modes, each with a two-orbital metal contribution to the cluster. An additional two-electron two-centre platinum–platinum bond would then complete a formal $2n + 2$ *closo* cluster

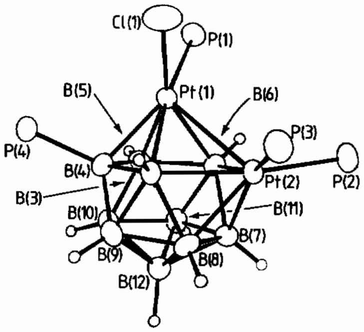

Fig. 1. Drawing of the molecular structure of $[(PMe_2Ph)_3ClPt_2B_{10}H_9(PMe_2Ph)]$ with organyl group atoms omitted for clarity. Cluster hydrogen atoms were located and *exo*-terminal hydrogen atoms for all boron atoms except B(4) were confirmed by $^1H\text{-}\{^{11}B\}$ NMR spectroscopy which also confirmed the absence of other cluster proton types. Selected interatomic distances are as follows: from Pt(1) to Pt(2) 286.3, to P(1) 231.7(4), to Cl(1) 238.9(4), to B(3) 233.2(8), to B(4) 219.3(8), to B(5) 217.1(8), and to B(6) 221.6(8); from Pt(2) to P(2) 232.2(3), to P(3) 233.2(4), to B(3) 230.3(8), to B(6) 235.5(8), to B(7) 221.2(9), and to B(8) 223.0(9) pm. Interboron distances among Pt-bound boron atoms are in the range 179.0(10)–187.4(10) pm, and other interboron distances are in the range 174.5(11)–180.0(11) pm. B(4)–P(4) is 192.4 pm.

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electron count and involve each platinum centre in overall *quasi*-conical three-orbital contribution to the cluster bonding. There would however be considerable delocalization within this formal scheme.

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References

1 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 949 (1983).
2 J. Bould, J. E. Crook, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 951 (1983).
3 M. Elrington, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1398 (1984).
4 S. K. Boocock, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 305 (1980).
5 J. D. Kennedy and B. Wrackmeyer, *J. Magn. Reson.*, *38*, 529 (1980).
6 S. K. Boocock, N. N. Greenwood, J. D. Kennedy, W. S. McDonald and J. Staves, *J. Chem. Soc., Dalton Trans.*, 2573 (1981).