

New Modes of Bonding in Some Platinum Derivatives of $B_{18}H_{22}$: X-Ray Crystal Structures of $[(Pt_2B_{18}H_{16})(PMe_2Ph)_4]$ and of Three Structural Isomers of $[(PtB_{18}H_{20})(PMe_2Ph)_2]^\dagger$

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Reaction of the deprotonated *anti*-isomer[†] of $B_{18}H_{22}$ with *cis*- $[PtCl_2(PMe_2Ph)_2]$ yields (in addition to the expected $[(Pt-\eta^4\text{-anti-}B_{18}H_{20})(PMe_2Ph)_2]$) a novel $\mu\text{-}\eta^1, \eta^2$ isomer in which the $Pt(PMe_2Ph)_2$ group bridges the two edge-linked B_{10} clusters, together with a more compact green diplatina derivative $[(Pt_2B_{18}H_{16})(PMe_2Ph)_4]$ in which the novel confacial *conjuncto*-borane unit $B_{18}H_{16}$ is η^4 -bonded to one $Pt(PMe_2Ph)_2$ unit and ($\eta^4 + \eta^2$)-bonded to the other; use of *syn*- $B_{18}H_{22}$ provides a third isomer of $[(PtB_{18}H_{20})(PMe_2Ph)_2]$.

We have isolated a number of polyhedral metallaboranes from the reaction of an approximately equimolar mixture of *syn*-

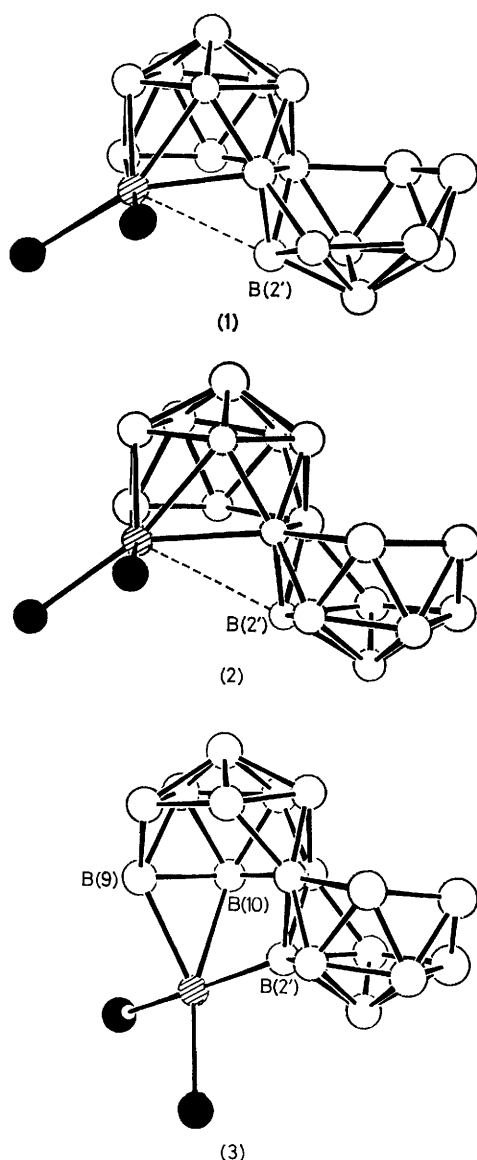


Figure 1. ORTEP drawings of $[(Pt-\eta^4\text{-syn-}B_{18}H_{20})(PMe_2Ph)_2]$ (1), $[(Pt-\eta^4\text{-anti-}B_{18}H_{20})(PMe_2Ph)_2]$ (2) and $[(Pt-\eta^4, \eta^2\text{-anti-}B_{18}H_{20})(PMe_2Ph)_2]$ (3). Distances from the Pt atom to the nearest neighbour B atoms in (1) are 231, 225, 224, and 235 pm, in (2) 236, 227, 224, and 234 pm, and in (3) 229 and 232 (η^2), and 212 (η^4) pm. The distances from the Pt atom to the next nearest B atom, B(2'), (dashed lines) in (1) and (2) are 296 and 304 pm respectively.

and *anti*- $B_{18}H_{22}$ [†] with *cis*- $[PtCl_2(PMe_2Ph)_2]$ in the presence of base, and have determined the molecular structures of four of these by single crystal X-ray diffraction analysis [compounds (1)–(4), Figures 1 and 2, and Table 1]. The yellow air-stable crystalline compounds $[(Pt-\eta^4\text{-syn-}B_{18}H_{20})(PMe_2Ph)_2]$ (1) and $[(Pt-\eta^4\text{-anti-}B_{18}H_{20})(PMe_2Ph)_2]$ (2) are the expected platina-borane derivatives of *syn*- and *anti*- $B_{18}H_{22}$ respectively. The structures are as originally predicted,¹ and in accord with this the mode of borane-to-metal bonding is as in simpler related species such as $[(Pt-\eta^4\text{-}B_{10}H_{12})(PMe_2Ph)_2]$.² In (1) and (2) the fairly close approach of B(2') to the Pt atom [296(1) and 304(1) pm respectively] is of additional interest, and presumably indicates an axial association of H(2') with the metal atom, similar to that often observed for *ortho*-hydrogen atoms of *P*-phenyl groups in metal complexes of phenyl-phosphine ligands.

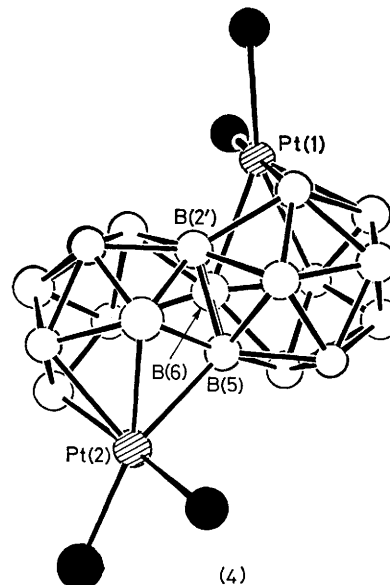


Figure 2. ORTEP drawing of $[(Pt_2-\eta^4, \eta^6\text{-anti-}B_{18}H_{16})(PMe_2Ph)_4]$ (4). Distances from the Pt(1) atom to neighbouring B atoms are given in Figure 3; distances from the Pt(2) atom to the nearest neighbour B atoms are 223, 223, 227, and 230 pm. The proposed heavy atom structure of $[(Pt-\eta^6\text{-anti-}B_{18}H_{16})(PMe_2Ph)_2]$ (5) can be derived from the ORTEP drawing of (4) by the omission of Pt(2) and its attached phosphine ligands.

[†] Throughout this communication we have used the descriptors *anti* and *syn* for compounds based on the centrosymmetric cluster structure of *nido*-decaborano-(6',7';5,6)-*nido*-decaborane and the C_2 structure of *nido*-decaborano-(6',7';6,7)-*nido*-decaborane, respectively; these are preferred to the trivial descriptors 'normal' and 'iso' which appear in the literature for historical reasons but are structurally uninformative.

Table 1. Crystallographic data.

	(1) (Pt- η^4 - <i>syn</i> -B ₁₈)	(2) (Pt- η^4 - <i>anti</i> -B ₁₈)	(3) (Pt- η^1, η^2 - <i>anti</i> -B ₁₈)	(4) (Pt ₂ - η^4, η^6 - <i>anti</i> -B ₁₈)
<i>a</i> /pm	1544.4(2)	968.3(1)	1120.9(2)	1430.0(3)
<i>b</i> /pm	1068.2(3)	3128.4(6)	1371.0(2)	1435.3(5)
<i>c</i> /pm	1981.9(3)	1055.9(1)	1048.4(2)	1314.3(3)
α /°	90	90	97.42(1)	103.63(3)
β /°	105.81(2)	110.40(1)	103.12(1)	96.85(2)
γ /°	90	90	77.11(1)	66.70(3)
<i>Z</i>	4	4	2	2
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
No. of <i>F</i> 's	3112	3224	3797	4760
<i>R</i> factor ^a	0.049	0.040	0.035	0.075

^a Pt and P were refined anisotropically, B and C isotropically.

The new yellow crystalline compound [(PMe₂Ph)₂(μ -Pt- η^1, η^2 -*anti*-B₁₈H₂₀)] (3) is isomeric with (1) and (2), but has a previously unobserved borane-to-metal bonding mode. The structure (Figure 1) derives from that of *anti*-B₁₈H₂₂ via the replacement of the bridging H(9, 10) and terminal H(2') atom (B₁₈H₂₂ numbering system used throughout) with bonds to the bridging Pt(PMe₂Ph)₂ moiety, the metal atom thereby providing an additional, and novel type of, link between the two constituent edge-fused ten-vertex cages of the octadecaborane cluster. The compound may thus be regarded as a 4-co-ordinate planar platinum(II) species, rare in polyhedral borane chemistry.

The bottle-green diplatina compound [Pt₂{ $\eta^4, (\eta^4 + \eta^2)$ -*anti*-B₁₈H₁₆}(PMe₂Ph)₄] [(4), Figure 2] also derives from *anti*-B₁₈H₂₂, but in this compound each Pt atom contributes 4 electrons to the cluster bonding as is more generally the case in polyhedral borane species. One of the metal atoms, Pt(2), is bonded η^4 to one of the two *anti* open faces of the octahedral cluster as found in the straightforward mono-platinum derivative (2). The other Pt atom, Pt(1), is of more interest. It has four closest neighbour boron atoms [Pt-B = 224–233(3) pm] (Figure 3) with the distances to the B(2') and B(3') atoms being somewhat longer at 269(3) and 254(3) pm respectively, but still within bonding distances. This is formally an η^6 borane-to-metal bonding mode, which may be regarded as a consequence of icosahedral η^5 -[B(6), B(7), B(8), B(9), B(2')] bonding to the Pt atom together with additional axial-type interaction with the B(3') and/or H(3') atoms.

The gross structure of (4) approximates to that of a combination of a *nido*-platinaundecaborane and a *closo*-platina-dodecaborane which are fused with a common B–B–B triangular face. This *confacial-conjuncto* feature is unique in metallaborane chemistry, and arises from the *formal* elimina-

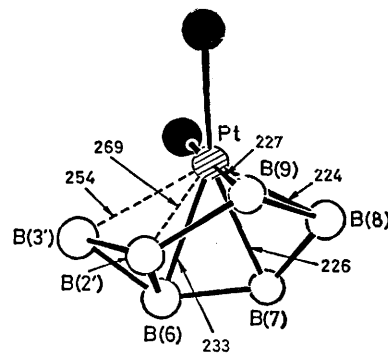


Figure 3. Distances from the Pt(1) atom of (4) to the nearest neighbour B atoms.

tion of the bridging H(9, 10) and terminal H(2') atoms of the *anti*-B₁₈H₂₂ structure to form a B(9)–B(10)–B(2') 3-centre bond, the new common triangular face being B(5)–B(6)–B(2'). The cluster closure seems to be facilitated by the second (η^4 -bonded) Pt atom in the molecule, as the otherwise expected compound [(Pt- η^6 -*anti*-B₁₈H₁₈)(PMe₂Ph)₂] (5) (see legend to Figure 2) does not appear to be present in the product mixture. Also it seems that the cluster closure does not originate from an η^4 -bonded face, since the heating of (2) at 120 °C for several hours appears, from preliminary experiments, to produce no significant decomposition. On the other hand, the heating of the η^1, η^2 -bonded compound (3) under the same conditions does produce a reasonably clean decomposition to give substantial quantities (ca. 60%) of a new orange-yellow crystalline compound which n.m.r. spectroscopy suggests may well be the η^6 -bonded compound (5). It may be significant in this context that the η^1, η^2 -bonding in (3) and the closure to produce (4) and (5) both involve B(9), B(10), and B(2').

Finally, we report that in addition to compounds (1)–(4) the initial reaction mixture contains a variety of other coloured metallaborane products. Preliminary examination by ³¹P n.m.r. spectroscopy shows a number of these have additional unique features which will be described in later communications.

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