Bis-μ-(2,3,4-η^3-*nido*-hexaboranyl)-bis(dimethylphenylphosphine)-diplatinum(Pt–Pt), [$Pt_2(\eta^3$-$B_6H_9)_2(PMe_2Ph)_2$], an Unexpected Product from the Reaction of $(B_{10}H_{13})_2O$ with [$PtCl_2$-$(PMe_2Ph)_2$]; Crystal and Molecular Structure

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Summary One of the products from the reaction of 6,6′-$(B_{10}H_{13})_2O$ with *cis*-[$PtCl_2(PMe_2Ph)_2$] is [$Pt_2(\eta^3$-$B_6H_9)_2$-$(PMe_2Ph)_2$], which is shown by *X*-ray crystallography to have a Pt–Pt bond with two bridging bidentate η^3-*nido*-hexaboranate ligands.

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nido-Decaboranyl oxide, 6,6′-$(B_{10}H_{13})_2O$, is relatively unreactive, and is inert to treatment with such reagents as $SOCl_2$, BCl_3, PBr_5, and Br_2, although in common with many boranes it is degraded by basic compounds.[1] We have now found that it reacts smoothly and readily with *cis*-[$PtCl_2(PMe_2Ph)_2$] in neutral dipolar solvents at room temperature to give a yellow solution which contains a number of components. We have isolated one of the major components chromatographically as yellow needles and have shown it to be [$Pt_2(\eta^3$-$B_6H_9)_2(PMe_2Ph)_2$] by single-crystal *X*-ray diffraction. Such a reaction is unprecedented.

Crystal data: monoclinic, space group $P2_1/c$, $Z = 2$, $a = 10{\cdot}140(2)$, $b = 5{\cdot}868(2)$, $c = 23{\cdot}169(6)$ Å, and $\beta = 91{\cdot}66(2)°$. The structure, based on 2234 independent F_o measurements with $I > 3\sigma(I)$, and refined with anisotropic temperature factors for non-hydrogen atoms, is shown in Figure 1. Not all hydrogen atoms were well defined, but ^1H-{^{11}B} n.m.r. experiments showed that each boron atom had a terminal hydrogen atom associated with it, and in addition there were two ^1H resonances of relative area 2 : 1 at $\delta(^1H) = -1{\cdot}01$ and $-1{\cdot}14$. (CD_2Cl_2 solution) which are reasonably ascribed to hydrogen atoms in the bridging positions (2,6)/(4,5) and (5,6), respectively. Peaks corresponding to these hydrogen positions appear in the final difference synthesis.†

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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.

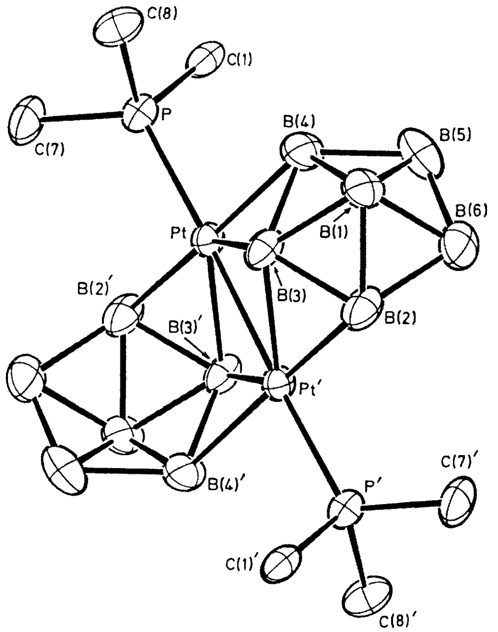

Figure 1. ORTEP drawing of $[Pt_2(\eta^3\text{-}B_6H_9)_2(PMe_2Ph)_2]$, with thermal ellipsoids shown at the 50% probability level. Hydrogen and the phenyl carbon atoms C(2)—C(6) are omitted for clarity. Primed atoms are related to the corresponding unprimed atoms by a centre of symmetry. Selected interatomic distances are: Pt'–B(2) 2·222(10), Pt'–B(3) 2·178(7), Pt–B(3) 2·224(9), Pt–B(4) 2·228(10), Pt–P 2·302(2), B–B 1·747—1·825(14) Å.

The molecule is seen to be a binuclear (Pt–Pt) compound with two bidentate bridging 2,3,4-η^3-*nido*-hexaboranate ligands. There is a crystallographic symmetry centre at the mid-point of the Pt–Pt bond (2·644 Å) and the P–Pt–Pt–P system is almost linear [∠Pt–Pt–P = 175·5(1)°]. Within each *nido*-$B_6H_9^-$ ligand the two non-hydrogen-bridged basal boron–boron bonds are adjacent and each of these bonds acts as a two-electron donor to a different platinum atom, resulting in approximately square planar geometry about each metal centre (see Figure 2). Alternatively the bonding may be described in terms of a 3-electron 'borallyl' radical ligand. Relative to each *nido*-hexaboranyl cluster, the platinum atoms are below the basal plane and take up bridging positions analogous to those of the bridging hydrogen atoms.

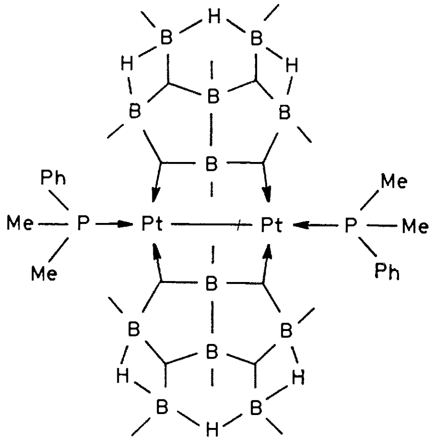

Figure 2. Schematic representation of the structure and proposed bonding in $[Pt_2(\eta^3\text{-}B_6H_9)_2(PMe_2Ph)_2]$; a number of canonical forms may be written for the cluster valency bond structure.

Examples of monodentate behaviour of the B_6H_{10}[2] and $B_6H_9^-$[3] ligands are known, but the *cis*-bidentate η^3-behaviour reported here is novel. The structure has similarities to the bis(2-methylallyl) compound $[Pd_2(C_3H_4Me)_2(PPr^i_3)_2]$, recently reported[4] by Werner and Kühn, in which both of the hydrocarbon ligands are believed to have a disposition about the palladium atoms similar to that found[5] by *X*-ray diffraction analysis for the related species $[Pd_2\mu\text{-}(C_5H_5)\mu\text{-}(C_3H_4Me)(PPh_3)_2]$; the platinum analogue of this latter compound is known,[4] but not that of the former. The unexpected formation of $[Pt_2(\eta^3\text{-}B_6H_9)_2(PMe_2Ph)_2]$ from $(B_{10}H_{13})_2O$ and the mononuclear complex $[PtCl_2(PMe_2Ph)_2]$ is of particular interest.

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