ORGANOMETALLICS

Polyhedral Platinaborane Chemistry. Interaction of PMe_2Ph with $[(PMe_2Ph)_2PtB_{10}H_{12}]$

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Supporting Information

ABSTRACT: In solution, $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (1) and PMe_2Ph exist in dynamic equilibrium with $[(PMe_2Ph)_3PtB_{10}H_{12}]$ (2). The activation energy for the dynamic process, ΔG^{\ddagger} , is ca. 63 kJ mol⁻¹ at +17 °C, with ΔS being ca. 335 J mol⁻¹ deg⁻¹ and ΔH ca. 105 kJ mol⁻¹ for the equilibrium. At low temperatures a rocking fluxionality of the {Pt(PMe_2Ph)_3} unit versus the { η^4 -B₁₀H₁₂} unit in **2** becomes apparent, with an activation energy ΔG^{\ddagger} of ca. 28 kJ mol⁻¹ at ca. -105 °C. Compound **2** is characterized by NMR spectroscopy and by a single-crystal X-ray diffraction analysis, for which the results suggest that, in contrast to the common view, the extra electron pair gained by the metal-atom center in going from **1** to **2** does not disrupt the cluster electron count proper nor the observed nido electronic structure and geometry.



INTRODUCTION

Gordon Stone and his co-workers at the University of Bristol pioneered an extensive and interesting chemistry of platinacarbaboranes, reporting families of new compounds such as $[(PR_3)_2PtC_2R_2B_4H_4]^1$, $[(PR_3)_2PtC_2R_2B_5H_5]^2$, $[(PR_3)_2PtC_2R_2B_6H_6]^3$, $[(PR_3)_2PtC_2R_2B_7H_9]^4$, $[(PR_3)_2PtC_2B_8H_{10}]^3$, $[(PR_3)_4PtC_2B_8H_{11}]^3$ $[(PR_3)_2PtC_2R_2B_9H_9]^5$, $[(PR_3)_2PtB_{10}H_{10}C(NMe_3)]^6$, and $[(PPh_3)-$ HPtCB₁₀H₁₁].⁷ This interesting new chemistry acted as inspiration and encouragement for many groups throughout the world. For our part in Leeds, this work formed part of a stimulus to examine platinum compounds based initially on borane residues, rather than on carbaborane residues, and these have included species such as on carbadorate restortes, and these have included species such as $[(PR_3)_2CIPtB_5H_8]_8^8 [(PR_3)_2Pt_2B_{12}H_{18}]_9^9 [(PR_3)_2PtB_8H_{12}]_1^{10} [(PR_2Ph)_2PtB_9H_{11}(PMe_2Ph)]_1^{11} [(PMe_2Ph)_2PtB_{10}H_{12}]_1^{12} [(PR_3)_2PtB_{18}H_{20}]_1^{13} [(PMe_2Ph)]_1^{14} [(PR_3)_2Pt_2B_8H_{14}]_1^{15} [(PR_3)_4Pt_3B_{14}H_{18}]_1^{14} [(PMe_2Ph)_2Pt_2B_{16}H_{15}(C_6H_4Me)(PMe_2Ph)]_1^{16} and [(PMe_2Ph)_2Pt_2B_{16}H_{15}(C_6H_4Me)(PMe_2Ph)]_1^{16} and [(PMe_2Ph)_2Pt_2B_{16}H_{26}(PMe_2Ph)]_1^{17} Of these, [(PMe_2Ph)_2PtB_{10}H_{12}] (1) is a$ particularly useful and interesting species. First, it can be used as a starting substrate for dimetallaborane syntheses,¹⁸ and in this area, the behavior of [(PMe2Ph)4Pt2B10H10] (3) and related species can be singled out for their remarkable propensity to reversibly sequester small molecules such as O_2 and CO at the dimetal site.^{18,19} Second, the molecule 1 exhibits a particular contrarotational fluxionality of the {Pt(PMe₂Ph)₂} unit relative to the { η^4 -B₁₀H₁₂} cluster unit.¹² Third, because of the 16electron transition-element coordination-sphere characteristics of the platinum center,²⁰ the cluster structure, though geometrically 11-vertex nido, has a formal 11-vertex closo cluster electron count.²¹ In view of this formal unsaturation of the metal center, it was of interest to examine for the addition of a third 2-electron ligand to the metal coordination sphere of compound 1. This would have the effect of conferring a formal nido electron count to the cluster and also be of relevance to understanding the addition of small molecules to dimetallic species such as $[(PMe_2Ph)_{4^-}Pt_2B_{10}H_{10}]$ (3) mentioned above, as well as being germane to the catalytic propensities of related 11-vertex formally nido compounds such as $[8,8-(PR_3)_2$ -*nido*-8,7-RhSB₉H₁₀],²² for which the mechanism is proposed to involve reversible ligand addition at the metal center and, for several of which, addition of a third ligand at the metal center has indeed recently been categorized.^{22b,23}

RESULTS AND DISCUSSION

The addition of 1 equiv of PMe_2Ph to a solution of yellow $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (1) in CH_2Cl_2 gave a color change from yellow to pale yellow, and fine very pale yellow crystals slowly dropped out of solution. Larger crystals were formed from a saturated solution of the compound in CH_2Cl_2 /hexane and were identified by a single-crystal X-ray diffraction analysis as $[(PMe_2Ph)_3PtB_{10}H_{12}]$ (2) (Figure 1).

Monitoring a solution of **2** by NMR spectroscopy over the ranges +70 to -50 °C (CDCl₃) and +30 to -100 °C (CD₂Cl₂) (Figure 2; numerical data in Table S1, Supporting Information) established that **2** was in equilibrium with **1** and PMe₂Ph (eq 1), with the ¹¹B and ¹H cluster spectra each showing resonances corresponding to a weighted mean of the amounts of the two platinaboranes present within the system, rather than

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Figure 1. Crystallographically determined molecular structures of (top) $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (1) (data from ref 12b) and of (bottom) $[(PMe_2Ph)_3PtB_{10}H_{12}]$ (2). Selected distances (in Å) for 2 (with equivalent distances for 1 in brackets) are as follows: Pt(7)-P(1) = 2.4132(5) [2.309(1)], Pt(7)-P(2) = 2.3988(5) [2.337(1)], Pt(7)-P(3) = 2.3905(5), Pt(7)-B(2) = 2.270(2) [2.214(5)], Pt(7)-B(3) = 2.252(2) [2.225(5)], Pt(7)-B(8) = 2.245(2) [2.279(6)], Pt(7)-B(11) = 2.269(2) [2.301(6)]. Selected angles (deg): P(1)-Pt(7)-P(2) = 95.542(19) [95.4(1)], P(3)-Pt(7)-P(1) = 96.767(13), P(3)-Pt(7)-P(1) = 96.296(12).



Figure 2. Variation with temperature of the μ -H ¹H NMR resonance of the {B₁₀H₁₂} residue for a 0.88 M sample of compound **2** in CDCl₃ (**•**), a 1.27 M sample of compound **2** in CD₂Cl₂ (×), and a sample of compound **1** in CDCl₃ (**•**). There is an approximately linear decrease in shielding with decreasing temperature for fully associated compound **2** (left-hand side of the CD₂Cl₂ data plot) and for fully dissociated compound **1** (uppermost data plot).

Table 1. Measured NMR Parameters for $[(PMe_2Ph)_3PtB_{10}H_{12}]$ (2) Together with Selected Values for $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (1) for Comparison

	compd 1 ^a		compd $2^{b,c}$	
assignt	$\delta(^{11}\text{B})$	$\delta(^{1}\text{H})$	$\delta(^{11}\text{B})$	$\delta({}^{1}\mathrm{H})^{d}$
1	+14.0	+3.52	+19.4	+4.33
2, 3	+14.5	+3.52	+9.5	+3.67
8, 11	+8.8	+2.98	+0.7	+1.94
9, 10	-4.0	+2.44	-11.6	+1.74
5	+1.5	+2.39	ca12	ca. +1.75
4, 6	-27.6	+1.12	-27.7	+0.95
μ -H		-2.12		-4.54

^aConditions: 233 K/CDCl₃. Also $\delta({}^{1}\text{H}) + 1.62$ ($N({}^{31}\text{P}{-}^{1}\text{H}) = 10.5$ Hz, PMe₂), +1.86 ($N({}^{31}\text{P}{-}^{1}\text{H}) = 9.5$ Hz, PMe₂), $\delta({}^{1}\text{H}) + 7.1{-}7.7$ (PPh); $\delta({}^{31}\text{P}) + 1.3$ (${}^{1}J({}^{195}\text{Pt}{-}^{31}\text{P}) = 2535$ Hz). ^bConditions: 233 K/CD₂Cl₂/ excess PMe₂Ph. ^c $\delta({}^{31}\text{P})$ (CD₂Cl₂/233 K) -31.8 (2P, ${}^{1}J({}^{195}\text{Pt}{-}^{31}\text{P}) = 2291$ Hz) and -31.4 (1P, ${}^{1}J({}^{195}\text{Pt}{-}^{31}\text{P}) = 1684$ Hz). At lower temperatures the 2P resonance broadens and splits into two: $\delta({}^{31}\text{P})$ (CD₂Cl₂/168 K) -23.3 (1P), -31.4 (1P) and -38.2 (1P) (${}^{195}\text{Pt}$ satellites not apparent). ${}^{d}\delta({}^{1}\text{H})$ (CD₂Cl₂/233 K) +1.47 ($N({}^{31}\text{P}{-}^{1}\text{H}) = ca. 8$ Hz, PMe₂), +1.69 ($N({}^{31}\text{P}{-}^{1}\text{H}) = ca. 9$ Hz, PMe₂), +2.07 (${}^{3}J({}^{31}\text{P}{-}^{1}\text{H}) = ca. 8$ Hz, PMe₂), $+7.1{-}7.7$ (PPh).

two separate sets of resonances, indicating a dynamic exchange process. NMR spectroscopy on a solution of 2 containing excess PMe_2Ph gave the NMR parameters for fully associated 2 (Table 1).

$$[(PMe_2Ph)_2PtB_{10}H_{12}] + PMe_2Ph$$

$$i$$

$$\Rightarrow [(PMe_2Ph)_3PtB_{10}H_{12}]$$

$$(1)$$

The equilibration was best monitored by measurement of the bridging hydrogen atom ¹H resonance position (Figure 2), which changed by some 2.5 ppm between extremes. Here it can be seen from Figure 1 that, in contrast to the nonshielded positioning in compound 1, the bridging hydrogen atom position is in the shielding cone of the phenyl group on P(3) in compound 2, hence accounting for the large shielding change. For ca. 1 M solutions, the equilibrium of eq 1 was entirely to the left-hand side at +70 °C (CDCl₃ solution) and entirely over to the right-hand side at -50 °C (CDCl₃ and CD₂Cl₂ solutions).

An analysis of the curve of Figure 2 gives values for ΔH of 104 ± 8 kJ mol⁻¹ and for ΔS of 335 ± 24 J mol⁻¹ deg⁻¹ for the equilibrium (see the Supporting Information for details of the calculations). The somewhat high ΔS value reflects the specific relative and internal orientations of both the receiving {Pt(PMe₂Ph)₂} ligand-sphere rotamers and of the attacking PMe₂Ph molecule that are required for a close mutual binding approach. The equilibrium is dynamic: the activation energy ΔG^{\ddagger} for the exchange process is best estimated by ³¹P NMR spectroscopy, in which the frequency differences of relevant resonances are far greater than any differences in the ¹H spectra. In the 162 MHz ³¹P{¹H} spectrum, uncomplexed 1 shows a single ³¹P chemical shift with associated ¹⁹⁵Pt satellites, whereas completely complexed 2 (low temperature) exhibits two chemical shifts, as expected from the two types of chemical environments apparent from Figure 2, viz. equatorial (2P) and endo (1P), each also with ¹⁹⁵Pt satellites (Table 1). At intermediate equilibrium, ca. -10 °C, the resonances from both compounds are apparent, as is a resonance from excess

phosphine (eq 1). At higher temperatures broadening and coalescence occurs, with a coalescence temperature of ca. +17 °C, giving a value for ΔG^{\ddagger} of ca. 63 kJ mol⁻¹ for the exchange process at that temperature.

A further interesting dynamic phenomenon in 2 is apparent from the 400 MHz ¹H and 128 MHz ³¹P NMR spectra at the lowest temperatures at which we were able to conduct NMR experiments. Whereas the shift of the phosphorus resonance of intensity 1P remains essentially unchanged at these lowest temperatures, the resonance of intensity 2P broadens and ultimately splits into two resonances, at $\delta(^{31}P)$ -23.3 and -31.4 ppm at -105 °C; this was the lowest temperature available before solvent solidification, and the ¹⁹⁵Pt satellites were not quite apparent. It may be that CSA relaxation of ¹⁹⁵Pt is becoming significant at these lowest temperatures. Nevertheless, a coalescence temperature for the main signals was apparent, at ca. -105 °C, which, together with their frequency separation of 2440 Hz at the particular polarizing field used, gives a value for ΔG^{\ddagger} of ca. 28 kJ mol⁻¹ for the process at that temperature. At the same time one of the two PMe₂Ph ¹H resonances arising from the prochiral nature of the two equatorial phosphines severely starts to broaden, but the relevant frequency separations in the ¹H spectrum are less, and so separation into two resonances and assessment of a coalescence in the ¹H spectrum was not feasible. There also appears to be incipient differentiation into two components of each of the cluster ¹H resonances of relative intensity 2H at these extreme lowest temperatures, but these could not be definitively delineated before solidification ensued. Any corresponding differentiation in the ¹¹B spectra would not be apparent because of the high ¹¹B line widths arising from relaxation broadening at these lowest temperatures. The chemical shift difference between the two new resonances in the ³¹P spectrum is nontrivial, implying two reasonably different environments. This, coupled with the perturbation at the same time of mainly just one of the two signals from the prochiral methyl protons of the equatorial PMe₂Ph ligands, implies a rocking-twisting reciprocating motion of the $\{Pt(PMe_2Ph)_3\}$ unit relative to the $\{\eta^4$ -B₁₀H₁₂ $\}$ cluster unit about an axis through the platinum atom (structures I, Scheme 1). Inspection of Figure 1 suggests that this involves ligand rotamers such that just one of the two PMe₂ methyl groups on both P(1) and P(2) experiences large ¹H shielding changes. It can be seen that the hydrogen atoms on the P(2) methyl carbon atom C(23)are within the shielding cone of the phenyl group on P(1), with one of the methyl hydrogen atoms on C(23) directed toward the centroid of the phenyl ring on P(1) at a distance of 2.58 Å. In the fluxional process, these methyl-group hydrogen atoms will exchange to a less shielded position equivalent to the C(12) methyl group on P(1), which in turn will become more shielded by the phenyl group on P(2) as it adopts a position equivalent to that of C(23). The other methyl group on P(2)does not experience a similar large change in shielding environment as it changes its position. This rocking fluxionality of compound 2 is in contrast with the fluxionality of the bis(phosphine) species $\mathbf{1}$,¹² in which there is a complete contrarotation of the $\{Pt(PMe_2Ph)_2\}$ assembly relative to the ${PtB_{10}H_{12}}$ cluster assembly, though again about an axis through the platinum atom (structures II, Scheme 1).

In terms of the overall molecular structure (Figure 1), there is an obvious change in the $\{(PMe_2Ph)_2\}$ ligand disposition exhibited by 1 as the third PMe_2Ph ligand comes in to occupy the endo position it displays in 2 (structures III and IV). The Scheme 1. Representation of the Proposed Rocking Fluxionality of the $\{Pt(PMe_2Ph)_3\}$ Moiety Observed in Compound 2 (IA/IB) Compared to the Complete Rotation of the $\{Pt(PMe_2Ph)_2\}$ Unit Seen in Compound 1 (IIA/IIB)^{*a*}



"For clarity the Me_2 and Ph designators are omitted from each phosphorus ligand. In all the cluster schematics in this paper, unlabeled cluster vertices are $\{BH(exo)\}$ units.

P(1)–Pt(7)–P(2) plane bends away from its position in 1, which is essentially transoid to the midpoints of the B(2)–B(11) and B(3)–B(8) cluster vectors, and in 2 it becomes essentially coplanar with the five-membered nido 11-vertex open face, albeit with a slight tilt that corresponds to one extreme of the rocking fluxionality discussed in the previous paragraph. The essentially orthogonal angle between the Pt(7)–P(1) and Pt(7)–P(2) vectors remains essentially unchanged at ca. 94.5°, with the new ligand positioned in turn approximately orthogonal to those, with P(3)–Pt(7)–P(1) and P(3)–Pt(7)–P(2) angles of 96.767(13) and 96.296(12)°, respectively.



In comparison to 1, the distances in 2 from Pt(7) to P(1)and P(2) increase by ca. 0.06–0.1 Å, with all three platinum– phosphorus distances now being very similar, although it is not clear whether the increases arise from electronic effects or from steric crowding. Within the cluster, there is a slight increase in the distances from Pt(7) to B(2) and B(3) that are transoid to the new PMe_2Ph ligand and a concomitant reduction of similar magnitude in the distances from Pt(7) to B(8) and B(11) on the nido 11-vertex five-membered open face. These intracluster changes are relatively small, implying no large changes within the cluster bonding, including the metal-to-boron interactions, when compounds 1 and 2 are compared. This conclusion is supported by the cluster ¹¹B NMR shielding considerations discussed below.

The measured ³¹P and ¹H NMR properties of the phosphine ligand sphere are summarized in Table 1. As discussed above, at intermediate temperatures there is a 2:1 relative intensity pattern in the ³¹P spectrum, as expected from the unique position of P(3), and what is at intermediate temperatures a time-averaged equivalency of P(1) and P(2). The coupling constant ${}^{1}J({}^{195}Pt-{}^{31}P)$ for the time-averaged P(1)P(2) pair at ca. 2290 Hz is significantly larger than that for P(3) at ca. 1685 Hz, perhaps implying more s character in the equatorial bonding to P(1) and P(2), and correspondingly less in the endo bonding to P(3). In borane chemistry in general, differences in couplings ${}^{1}I({}^{11}B-{}^{1}H)$ for axial and endo B-H linkages differ for similar reasons. The corresponding coupling constant to P(1) and P(2) in the bis(phosphine) compound 1 is 2534 Hz. At extremely low temperatures P(1) and P(2)become chemically inequivalent; in the crystallographically determined molecular structure (Figure 1) they are different, both in terms of the Pt-P and the other bond rotamers and also in terms of their relative tilt with respect to the open face of the cluster. There are corresponding features in the ¹H NMR spectrum. The phosphorus atoms P(1) and P(2) are prochiral centers, and so on each of these the methyl groups are inequivalent. Each of the overall ¹H resonance patterns for these two different environments shows a pattern that approximates to that of an $[AX_3]_2$ spin system, where A is ³¹P and X is ¹H; there is associated satellite structure arising from ${}^{3}J({}^{195}\text{Pt}-{}^{1}\text{H})$. At the lowest temperatures, the inequivalence of all six methyl groups is expected as the molecular structure settles into that of Figure 1 and its enantiomer. At the lowest temperatures attainable, these differences were not definitively resolvable because of interference by the exchange process which was not sufficiently slowed. Nevertheless, it was apparent that two pairs of these do not differ significantly in their chemical environments, as there is little apparent broadening at the lowest temperatures. In contrast, the other pair broadened significantly, implying incipient de-coalescence into significantly differently shielded resonances. As discussed above, these must correspond to the C(13)/C(23) pair, one of which will be in the anisotropic shielding cone of the phenyl unit on the other phosphine ligand.

The cluster ¹¹B and ¹H NMR chemical shifts for the tris-(phosphine) compound 2 are given in Table 1, together with those of the bis(phosphine) species 1. The ¹¹B shielding patterns are represented schematically in Figure 3, together with those of comparison compounds. Nuclear magnetic shielding depends intimately on the ground- and excited-state molecular orbital structure. Significant changes in cluster bonding will therefore be reflected in significant changes in cluster nuclear shieldings, and it is useful to view the ¹¹B NMR chemical shifts represented in Figure 3 from this perspective. Relative to nido-B₁₀H₁₄, visualizing a simple replacement of two 2-electron bonds to two bridging hydrogen atoms with two 2-electron bonding vectors to the metal (see cluster structures **VI** and **VII**), the effect of platinum in the $[Pt(B_{10}H_{12})_2]^{2-1}$ anion is similar to effect of the main-group metal thallium in the $[Me_2TlB_{10}H_{12}]^-$ anion, and the similarities in overall cluster shielding to nido-B10H14 itself are clear. Progression down the sequence of spectra represented in Figure 3 shows that the shielding pattern of 1 deviates somewhat further from that of nido-B₁₀H₁₄ and that of 2 somewhat more so, but nevertheless the shielding pattern is still directly traceable to that of nido-B₁₀H₁₄, and a crossover to arachno 10-vertex character, typified here by the $[B_{10}H_{14}]^{2-}$ anion, which might be expected for a more oxidative further insertion by the Pt center, to give



Figure 3. Representation of the chemical shifts and relative intensities in the ¹¹B NMR spectra of (from top to bottom) *nido*-B₁₀H₁₄ (data from ref 24), the $[Me_2TlB_{10}H_{12}]^-$ anion (data from ref 25), the $[Pt(B_{10}H_{12})_2]^{2-}$ anion (data from ref 26), $[(PMe_2Ph)_2PtB_{10}H_{12}]$ 1 (data from ref 12a), $[(PMe_2Ph)_3PtB_{10}H_{12}]$ 2 (this work), and the $[arachno-B_{10}H_{14}]^{2-}$ anion (data from ref 27). Hatched lines connect equivalent sites. Note that 10-vertex *nido*-B₁₀H₁₄ and $[arachno-B_{10}H_{14}]^{2-}$ have a numbering convention different from that of the 11-vertex nido-type clusters of the other compounds.

an overall four-electron contribution to the cluster bonding proper, is not apparent. This argues for an effective 18-electron platinum(II) transition-element center for **2**, as compared to 16-electron platinum(II) for **1**. Thus, it can be argued, although the third phosphine ligand ostensibly increases the formal cluster count by two electrons, as required for the Wadian²⁸ nido electron count, nevertheless, the intracluster bonding retains a character very similar to that of the bis(phosphine) compound **1**, which has a closo formal electron count; in these terms, the cluster proper of the tris(phosphine) species **2** also has essentially an unchanged cluster-electron count.

In the more general case, this electron-undercounting syndrome applies also to 11-vertex metallaheteroboranes such as $[8,8-(PPh_3)_2$ -*nido*-8,7-RhSB₉H₁₀], which have attracted much recent interest because of their particular catalytic properties which involve the redox properties of the metallaheteroborane cluster as a unit, as distinct from those of the metal center alone.^{22,23} A view has been proposed, for this type of compound, in which the nido electron count that is axiomatically assumed to be required to provide the observed nido structure is attained via two *ortho*-CH···Rh quasi-agostic interactions from the adjacent phosphine-bound phenyl rings.²⁹ However, DFT calculations on models of $[8,8-(PPh_3)_2$ -*nido*-8,7-RhSB₉H₁₀] and $[8,8-(PPh_3)_2$ -*nido*-8,7-RhNB₉H₁₀] have indicated that the (stable) nido cluster structure does not require



extra electrons donated from agostic interactions.³⁰ The crystallographic and comparative nuclear shielding evidence reported here provides further evidence in this area of *nido*-metallaundecaborane species and directly shows that the extra electron pair from a third phosphine does not substantially alter the structure or the electronic character of the 11-vertex cluster—the effect of the incoming ligand remains localized on the metal. Thus, even allowing for supposed electron-pair "agostic" donations²⁹ in [(PPh₃)₂-*nido*-RhSB₉H₁₀], it may not be assumed that these would be required to account for its observed structure.

Finally, it is pertinent to note that the behavior of $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (1) may be taken as a complementary probe in the assessment of the properties of its diplatinum derivative $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ (3), which readily adds small molecules such as O₂, CO, and SO₂ across the Pt–Pt vector.¹⁸ The last compound features a 12-vertex $\{Pt_2B_{10}\}$ cluster core that has two adjacent $\{Pt(PMe_2Ph)_2\}$ moieties separated by an essentially nonbonding distance of ca. 3 Å (structure V). Similarly to 2, the ¹¹B NMR shielding characteristics of the cluster in 3 are readily traceable to the $[(PMe_2Ph)_2PtB_{10}H_{12}]$ and $B_{10}H_{14}$ precursors. 18a The $\{Pt(PMe_2Ph)_2\}$ moiety in 1 can be regarded as replacing a pair of B₁₀H₁₄ cluster bridging hydrogen atoms (structures VI and VII). Correspondingly, in 3, each of the two {Pt(PMe₂Ph)₂} moieties replaces a pair of $B_{10}H_{14}$ cluster bridging hydrogen atoms (structure VIII); there is a weak-to-nonbonding link between the metal atoms, and the metal moieties thereby retain the essentially empty coordination sites on the platinum to the extent that they are able to accept the incoming small molecules such as O_2 and CO. The incoming molecule effectively occupies the vacant coordination

site that is filled by the PMe₂Ph ligand in the monometallic compound **2** (structures IX and X; note, for ease of comparison, X repeats IV above). However, on dioxygen uptake, for example, there is a reordering of the bonding within the cluster bonding associated with the two metal atoms: the two platinum centers share a pair of electrons from the incoming O₂ moiety to generate a peroxy linkage, and the Pt–Pt distance decreases to a normal metal–metal cluster bonding distance of ca. 2.7 Å. The bimetallic motif in **3** thus affords a combined stronger affinity toward the bound molecules than in its monometallic precursor **1**, permitting an effective oxidative addition of the O₂ molecule to the Pt–Pt linkage in the cluster. In contrast, for the monometallic compound **1**, the ¹¹B NMR spectrum does not show any change up to a pressure of ca. 4 bar, even with CO, which binds to **3** more strongly than O₂.

CONCLUSION

The evidence presented here shows that the take-up of PMe₂Ph, and therefore the acquisition of its associated electron pair, by the metal vertex in the nido cluster compound $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (1) to give $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (2) does not significantly alter the overall electronic character of the metallaborane cluster. This is revealed by the nuclear shielding characteristics in its ¹¹B NMR spectrum of 2, which retain the basic pattern of 1 that is characteristic of nido 11-vertex metallaborane clusters (Figure 3). These results are of significance in countering suppositions that, because nido compounds such as 1 formally have Wadian closo clusterelectron counts, then their structures are "anomalous", rather than expected, and/or that additional interactions involving the metal atom must therefore be invoked to bring the formal cluster electron count up from closo to nido; Wade's rules, although very useful, do not constitute an inviolable scientific law. The behavior of $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (1) with PMe₂Ph to give 2 is also a useful model for the assessment of the approach of small molecules such as O₂, CO, and SO₂ to the metal centers of the diplatinum derivative $[(PMe_2Ph)_4Pt_2B_{10}H_{10}]$ (3), to which they readily add across the Pt-Pt vector.

EXPERIMENTAL SECTION

General Procedures. [(PMe₂Ph)₂PtB₁₀H₁₂] (1) was prepared as described previously.^{18b} Solvents were stored over calcium hydride in evacuated glass bulbs. PMe₂Ph was used as received. Manipulations were in vacuo or under dry dinitrogen; compound 1 and the final product 2 are air-stable in the solid state. NMR spectroscopy was performed at ca. 5.9 and 9.4 T (fields corresponding to 250 and 400 MHz ¹H frequencies, respectively) using commercially available instrumentation and using techniques and procedures as adequately described and enunciated elsewhere.^{8b,24,27,31} Chemical shifts δ are given in ppm relative to $\Xi = 100$ MHz for $\delta(^{1}\text{H})$ (±0.5 ppm) (nominally TMS), $\Xi = 32.083\,972$ MHz for $\delta(^{11}\text{B})$ (±0.5 ppm) (nominally [BF₃(OEt₂)] in CDCl₃),²⁴ and $\Xi = 40.480730$ MHz for $\delta(^{31}\text{P})$ (±0.5 ppm) (nominally 85% aqueous H₃PO₄). Ξ is as defined by McFarlane.³²

Preparation of [(PMe₂Ph)₃PtB₁₀H₁₂] (2). Dichloromethane (ca. 10 mL) was condensed into a Schlenk tube containing [(PMe₂Ph)₂PtB₁₀H₁₂] (1; 147 mg, 248 μ mol) and a magnetic follower. The tube was closed and warmed to ambient temperature with stirring. One equivalent of PMe₂Ph (35 μ L) was added by syringe against a flow of nitrogen, the Schlenk tube closed, and the stirring continued. After 5 min the stirring was halted and the (now paler yellow) solution allowed to stand for 2 h, during which time fine crystals formed. The vessel was then stored at ca. -20 °C overnight. The next day, filtration and washing with 50/50 CH₂Cl₂/hexane afforded 0.11 g (151 μ mol, 61%) of crystalline product identified as $[(PMe_2Ph)_3PtB_{10}H_{12}]$ (2). Anal. Found (calcd): C, 39.34 (39.50); H, 6.23 (6.22). Crystals suitable for single-crystal X-ray diffraction analysis were obtained from saturated CH_2Cl_2 /hexane solution.

Single-Crystal X-ray Diffraction Analysis. Crystal data for 2: $C_{24}H_{45}B_{10}P_3Pt$, M = 729.70, yellow prism, $0.38 \times 0.26 \times 0.13 \text{ mm}^3$, triclinic, space group PI (No. 2), a = 9.5125(2) Å, b = 10.2874(3) Å, c = 16.9338(5) Å, $\alpha = 87.8030(10)^\circ$, $\beta = 85.9790(10)^\circ$, $\gamma = 76.2210(10)^\circ$, V = 1605.07(7) Å³, Z = 2, $D_c = 1.510 \text{ g/cm}^3$, $F_{000} = 724$, Bruker APEX-II CCD, Mo K α radiation, $\lambda = 0.710$ 73 Å, T = 150(2)K, $2\theta_{\text{max}} = 55.0^\circ$, 54 835 reflections collected, 7369 unique reflections ($R_{\text{int}} = 0.0187$), final GOF = 1.107, R1 = 0.0103, wR2 = 0.0237, R indices based on 7083 reflections with I > 2(I) (refinement on F^2), 350 parameters, 0 restraints, Lp and absorption corrections applied, $\mu = 4.536 \text{ mm}^{-1}$. The structure was solved by direct methods and was refined by full-matrix least squares (against all the unique F^2 data) using SHELXL-97.³³ All non-hydrogen atoms were refined with anisotropic displacement parameters. The drawings of the molecular structure in Figure 1 were made using the ORTEP-3 program.³⁴

CCDC 846176 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www. ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

ASSOCIATED CONTENT

Supporting Information

Tables, figures, and a CIF file giving variable-temperature NMR data, details of the calculation of the thermodynamic parameters, and crystal data and selected geometrical dimensions for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

Dedicated to the memory of Gordon Stone; a good man and a good chemist.

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