

A Unique *Nido-Exo-Arachno* Equilibrium Involving [(PPh₃)₂(CO)OsB₅H₉] and Its Base Adducts: Crystal and Molecular Structure of [(PPh₃)₂(CO)OsB₄H₇](BH₂·PPh₂Me)[†]

Lawrence Barton,* Jonathan Bould, Hong Fang, Kevin Hupp, Nigam P. Rath, and Charles Gloeckner¹

Department of Chemistry, University of Missouri—St. Louis
St. Louis, Missouri 63121

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Electron-counting rules for clusters allow predictions to be made about structural changes that result from the addition of electron pairs to cluster molecules.² The anticipated effect is that addition of electron pairs to a cluster results in the opening up of the structure in the sequence *closo*, *nido*, *arachno*, *hypho*.³ There are some simple examples in the literature of systems in which addition of an electron pair to a small *nido*-borane, in the form of an equivalent of Lewis base, forms a conventional *arachno*-cluster. This results when CN⁻ is added to B₅H₉.⁴ In most of the known cases, however, two electron pairs are added to the *nido*-borane to afford a *hypho*-cluster⁵ or the added base cleaves the borane.⁶ The structurally characterized adduct species include B₅H₉·2PMe₃,^{5a} B₄H₈·(Me₂NCH₂)₂,^{5b,c} B₅H₉·(Ph₂P)₂CH₂,^{5c,d} B₅H₉·(Ph₂PCH₂)₂,^{5c,d} B₅H₉·(Me₂NCH₂)₂,^{5c,d} and B₆H₁₀·2PMe₃.⁷ In addition, B₆H₁₀·PMe₃⁸ has also been identified from spectroscopic data. In this paper we describe the formation of a unique *exo-arachno* cluster, from the addition of phosphine bases to [(PPh₃)₂(CO)OsB₅H₉] (**1**),^{9a} in a process which is reversible.

If a mixture of [(PPh₃)₂(CO)OsB₅H₉] (**1**) (0.26 mmol) and PPh₃ (0.35 mmol) in CH₂Cl₂ is refluxed for 14 h under N₂, a pale-yellow, air stable crystalline solid of formulation [(PPh₃)₂(CO)OsB₅H₉·(PPh₃)] (**2**) is obtained in 57% yield. The same species had previously been isolated as a minor product in the preparation of **1**.^{9b} Mass spectral data¹⁰ provided the formulation but identification of **2** eluded us for some time because precedence suggested an *arachno*-type structure^{1,2} and satisfactory elemental analysis data were precluded by the presence of

[†] Suggested name: [2-Carbonyl-2,2-bis(triphenylphosphine)-3-[(diphenylmethylphosphine)boryl]-*nido*-2-osmapentaborane].

(1) Analytical Sciences Center, Monsanto Company, 800 N. Lindbergh Boulevard, St. Louis, MO 63167.

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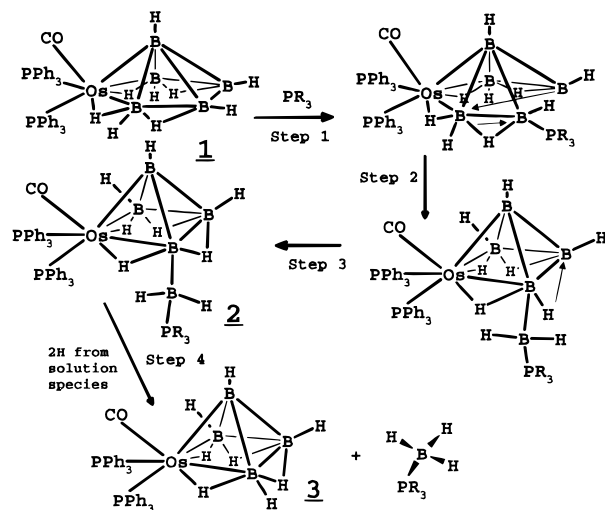
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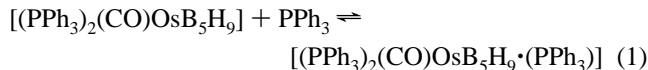
(10) HRMS (Finnigan MAT 95/FAB/positive ion electrospray using electric sector scanning and standardized with PEG1000 in MeOH/CHCl₃ (1:1) with 10 mmol NH₄OH) gave *m/q* for **2** (M - H₂) of ¹²C₅₅¹H₅₂³¹P₃¹¹B₅¹⁹². Os₁¹⁶⁰, 1066.3370 (obsd) and 1066.3346 (calcd).

Scheme 1



solvent in the lattice.¹¹ The ¹¹B NMR spectrum for **2**¹² gave four signals in 2:1:1:1 ratio, and the ¹H{¹¹B} spectra suggested the presence of five terminal and four bridging H atoms, two of them bridging to the metal atom. Selective decoupling experiments indicated that only one terminal H resonance was associated with the boron resonance of intensity 2, suggesting that one boron atom must have a substituent. The low-temperature ³¹P NMR spectrum showed three inequivalent P atoms, one of which was broad suggesting coupling to boron.

The ¹¹B NMR spectrum of **2** is quite similar to that of the osmapentaborane [(PPh₃)₂(CO)OsB₄H₈] (**3**),^{9a} except that one the resonances has been shifted downfield by about 16 ppm and there is an additional resonance B(6) whose chemical shift of -34.4 ppm is close to that for BH₃·PR₃ compounds (ca. -37 ppm).¹³ It is similarly comparable to the ¹¹B spectrum of the substituted derivative [(PPh₃)₂(CO)OsB₄H₇(C₄H₉)].¹⁴ These observations suggested that we had an osmapentaborane with a pendent BH₂·PPh₃ group bonded to one of the basal boron atoms. Selective decoupling experiments indicated that the pendent boron was bonded to a boron adjacent to the Os atom, therefore we presume that the reaction described in eq 1 and illustrated in steps 1–3 of Scheme 1 had taken place. Although



the NMR spectra for [(PPh₃)₂(CO)OsB₅H₉] leave some doubt about its structure, we have recently determined the structure by X-ray analysis and confirmed that the bridging H atoms are symmetrically disposed, as seen in Scheme 1.¹⁵ The reversibility of the reaction was established by heating a purified sample of **2** in CDCl₃ at 40 °C for 17 h, which resulted in recovery of 53% of **1**. Heating **2** for extended periods at 50 °C results in the formation of [(PPh₃)₂(CO)OsB₄H₈] and BH₃·PPh₃. This suggests that the process shown in step 4 of Scheme 1 also occurs.

(11) Anal. Found for C₅₅H₅₂P₃B₅O: C, 59.03; H, 5.06. Calcd: C, 61.84; H, 5.10.

(12) Boron (160.5 MHz), proton (500.1 MHz), and phosphorus (202.5 MHz) NMR data in ppm (CDCl₃ solution, 298 K) for **2** (assignment [δ (¹¹B) (¹H in parentheses)]: δ (¹¹B) B(4) [+9.3 (+5.3)], B(3) [+9.3 (*no H*)], B(5) [-16.4 (+1.3)], B(1) [-28.9 (+0.26)], B(6) [-34.4 (+1.95, +2.05)]; δ (¹H) μ H_{3,4} [-1.4], μ H_{4,5} [-2.3], μ H_{2,5} [-9.2, ²J(³¹P-¹H)*trans* = 42 Hz], μ H_{2,3} [-10.4]; δ (³¹P) P(1) [+14.9, *t*, *J* = 9.3 Hz], P(2) [+9.9, *d*, *J* = 9.3 Hz], P(3) [+24.5, *br s*].

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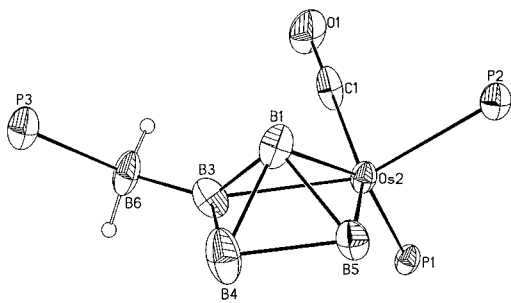


Figure 1. Molecular structure of *nido*-[(PPh₃)₂(CO)OsB₄H₇](BH₂PPh₂Me) (**4**) with 30% probability thermal ellipsoids and the R groups on P and the cage H atoms omitted. Selected interatomic distances (Å) are from Os (B(5) 2.36(2), B(3) 2.40(2), B(1) 2.23(2)), from B(3) (B(4) 1.85(4), B(1) 1.75(3), B(6) 1.69(3)), and B(4)–B(5) 1.79(3) and B(6)–P(3) 1.92(2). Angles (deg) include B(3)–B(6)–P(3) 110.8(13), B(4)–B(3)–B(6) 134(2), and Os–B(3)–B(6) 130.7(12).

Attempts to obtain crystals of **2** suitable for X-ray analysis were unsuccessful. However, we were able to demonstrate similar chemistry with the bases PMe₃ and PPh₂Me, and the adduct (PPh₃)₂(CO)OsB₅H₉·(PPh₂Me) (**4**) provided crystals suitable for a good quality X-ray analysis.¹⁶ The structure of **4**, represented in Figure 1, confirms that the species is an osmapentaborane skeleton with a pendent BH₂·PR₃ group. As expected, the structure differs little from that of B₅H₉ except for features influenced by the presence of the Os atom. Thus, the angle B(5)–Os–B(3) is 69.3(6)° as opposed to 90° in B₅H₉, and the apex–base and the base–base interboron distances are slightly longer in **4** than in the latter.¹⁷ The angle B(1)–B(3)–B(6) of 139(2)°, is similar to the B(1)–B(2)–H(2) angle in B₅H₉ of 130(2)°, indicating that the BH₂·PR₃ moiety occupies a very similar location to the terminal H atom it supplants in B₅H₉. Selected structural parameters are given in Figure 1.

The position of the equilibrium and the tendency to degrade to the osmapentaborane **3** is dependent on the donor strength of the phosphine base. Thus, PMe₃ reacts with **1** to give an analogue of the adduct **2** which on heating does not regenerate **1** but degrades to **3** with the elimination of BH₃·PMe₃. The PPh₂Me adduct **4** is more stable than the PPh adduct **2**, and an equilibrium between **4** and **1** exists in which the former predominates. Thermolysis of **1** under the same conditions (18 h at 50 °C) affords **3**. This was observed previously, although

(16) Crystallographic data for **4**: C₅₁H₅₃B₅Cl₃O₃P₃, monoclinic, *P*2₁, *a* = 10.8064(1), *b* = 12.0477(2), and *c* = 19.9238(4) Å, β = 98.258(1)°, *V* = 2567.03(7) Å³, *Z* = 2, *D*_c = 1.456 Mg m⁻³. Of the 12398 reflections collected (Siemens SMART CCD diffractometer, Mo Kα 293 K), 9312 were independent and 9306 were observed (4σ(*F*_o)). All the cage hydrogens except μH_{2,3} were located from difference Fourier maps but could not be refined; thus, no cage H atoms were included in the final refinement. The other H atoms were treated using appropriate riding models: *S* = 1.014, *R*₁ = 0.074, w*R*₂ = 0.187. Complete NMR data are available for **4**, and they will be included in the full report of this work.

(17) Onak, T. P.; Shore, S. G.; Yamauchi, M. *Gmelin Handbook of Inorganic Chemistry*; Boron Compounds 20; Springer-Verlag: Berlin, 1979; New Supplement Series Vol. 54, pp 14–15.

the earlier study used much higher temperatures (100 °C) to obtain comparable yields of **3**.^{9a} We propose that the formation of the phosphine adducts **2** (or **4**), and the ultimate degradation to the osmapentaborane **3**, proceeds as illustrated in Scheme 1. Coordination of PPh₃ results in the opening of the cage to afford an unstable intermediate *arachno* system that rearranges, as indicated in Scheme 1, to afford (PPh₃)₂(CO)OsB₄H₇(BH₂PPh₃). Loss of phosphine·borane affords the osmapentaborane (PPh₃)₂(CO)OsB₄H₈ (**3**). Obviously this latter step must involve the incorporation of two additional H atoms from solution species since (PPh₃)₂(CO)OsB₄H₇(BH₂PPh₃) (**2**) contains two fewer H atoms than the combination of **3** and BH₃·PPh₃. The observed structure of **4** may be compared to the proposed structure for B₆H₁₀·PMe₃, which, on the basis of NMR evidence, is postulated to be a pentaborane cage with the BH₂L group bridging adjacent basal boron atoms rather than σ-bonded to a single basal B atom as we observed for **4**.⁸ The degradation of metallahexaboranes to clusters containing pendent boron atoms is a process which has only been suggested from *ab initio* calculations,¹⁸ but our results suggest that it may be an important new reaction mode for clusters.

The results suggest a possible mechanism for the formation of 1-[Fe(CO)₃]B₄H₈¹⁹ and 4-[Fe(CO)₃]B₅H₉²⁰ from Fe(CO)₅ and B₅H₉. The former is prepared from the thermolysis of B₅H₉/Fe(CO)₅ mixtures. If the reaction is carried out with frequent removal of excess CO, which is formed in the reaction, then the principal product is [Fe(CO)₃]B₅H₉,²⁰ presumably because CO serves the same role in the latter reaction as does the addition of excess phosphine in the reactions of (PPh₃)₂(CO)OsB₅H₉ described herein. Our results also emphasize the importance of not disregarding trace products in reactions. The initial observation of **2** was as one of several trace byproducts which also included (PPh₃)₂(CO)(H)OsB₃H₈, (PPh₃)₂(CO)OsB₄H₈, Li[(PPh₃)₂(H)OsB₉H₁₃], etc., formed in the preparation of (PPh₃)₂(CO)OsB₅H₉.^{9b}

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Supporting Information Available: Crystallographic data, positional parameters, anisotropic displacement parameters, and bond lengths and angles for **4** (8 pages). See any current masthead page for ordering and Internet access instructions.

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