

# Degradation and modification of metallaboranes

## Part 3. Reactions of the hexaborane(10) analogue *nido*-(PPh<sub>3</sub>)<sub>2</sub>(CO)OsB<sub>5</sub>H<sub>9</sub> with bidentate phosphines containing a rigid backbone: formation of linked cluster systems

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### Abstract

In the reaction between the osmahexaborane *nido*-(PPh<sub>3</sub>)<sub>2</sub>(CO)OsB<sub>5</sub>H<sub>9</sub> (**1**) and the bidentate phosphines, [1,2-(PPh<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>] and [1,3-(PPh<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>] (abbreviated as dppe and dppp, respectively), two products are observed in each case. The major product, (**4a**), [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppe)] (or **4b** –BH<sub>2</sub>·dppp) is an osmapentaborane cluster with a BH<sub>2</sub>·dppp group attached to the cage at a basal B(3) position and the distal end of the pendent bidentate phosphine donor is uncoordinated. In the other (**5a**), [2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-η<sup>2</sup>-3,2-(BH<sub>2</sub>·dppe)] (or **5b** –BH<sub>2</sub>·dppp) the uncoordinated phosphine present in **4a** (or **4b**) has replaced a PPh<sub>3</sub> group on the osmium center. In an effort to avoid intramolecular substitution, bidentate phosphines of the type PPh<sub>2</sub>XPPH<sub>2</sub> {X = 1,4-C<sub>6</sub>H<sub>4</sub>, (arphos), 1,4-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> (dppx), and Fe(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub> (dppf)} were used to preclude the formation of species **5**. However three products were obtained instead of just one. These were [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>·PPh<sub>2</sub>XPPH<sub>2</sub>] (**6**), a linked metallaborane system of the type [{2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>·PPh<sub>2</sub>XPPH<sub>2</sub>}<sub>2</sub>X] (**7**) and a bis-borane adduct of the type [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>·PPh<sub>2</sub>XPPH<sub>2</sub>·BH<sub>3</sub>] (**8**). This chemistry, which is seen for all the rigid backbone bases studied, is similar to that observed in reactions of phosphine bases with **1** which were described previously and is explained in terms of chemistry previously observed in studies of **1**.

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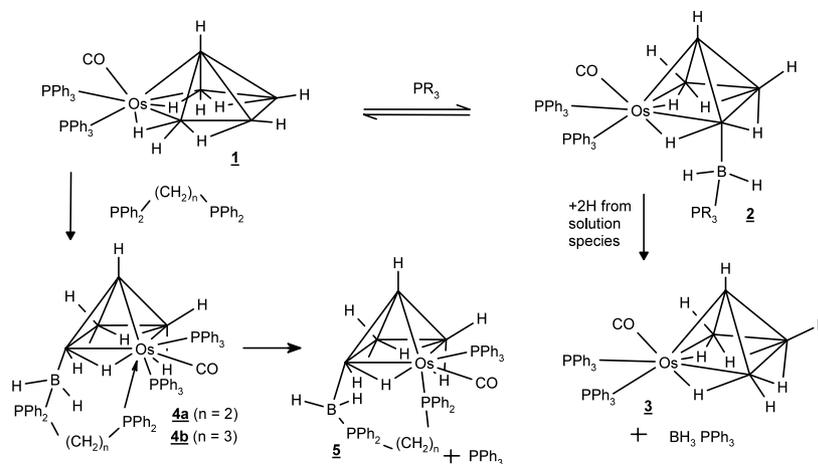
### 1. Introduction

The reactions between small metallaboranes and bases have attracted some interest in recent years [1]. They tend to proceed either by degradation of the cluster framework or by initial rearrangement of the cluster followed by degradation. We previously described the reactions of phosphines with the osmahexaborane [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-OsB<sub>5</sub>H<sub>9</sub> (**1**); the products of which revealed a new type of degradation process for metallaboranes [1a,b]. A phosphine ligand attaches to one of the basal boron atoms in the cage and

after rearrangement, the phosphine moiety remains attached to an exopolyhedral BH<sub>2</sub> group bonded to a basal boron atom in an osmapentaborane cage. This process, which is reversible, is shown in Scheme 1 as the formation of [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·PR<sub>3</sub>)] (**2**) from **1**. In the presence of stronger σ-donor phosphines, phosphine–borane is lost to afford the lower homologue species [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>8</sub>] (**3**). In the case of the bidentate phosphines, [1,2-(PPh<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>] and [1,3-(PPh<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>] (abbreviated as dppe and dppp respectively), species containing a pendant PPh<sub>2</sub> group illustrated as **4a** and **4b** for dppe and dppp ([1,2-(PPh<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>] and [1,3-(PPh<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>]), respectively, in Scheme 1, are observed. In this case the pendant PPh<sub>2</sub> group in species of the type **4** is attached to a flexible hydrocarbon chain and can easily undergo intramolecular substitution to form

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Scheme 1.

products of type **5**. This latter species is formed by replacement of a  $\text{PPh}_3$  group on Os by the pendant  $\text{PPh}_2$  group on the cage. The formation of species **5** is also illustrated in Scheme 1. In order to study reactions of species of type **4**, we considered it necessary to inhibit this intramolecular substitution, otherwise **4** and **5** are formed containing traces of impurity of **5** and **4**, respectively. Thus we decided to prepare analogues of **4** containing bidentate phosphines with less flexible backbones. The idea was that with more rigid backbones, the pendant  $\text{PPh}_2$  group could not attack the Os to replace a  $\text{PPh}_3$  ligand. Thus such species could be studied to probe potential routes to linked cluster systems. This paper describes reactions of **1** with a series of bidentate phosphines containing a rigid backbone.

## 2. Experimental

### 2.1. General procedures

Manipulation of volatile materials was achieved by the use of a standard high vacuum line, and dry box techniques were used for nonvolatile air sensitive materials [2]. Solvents used were distilled and stored as follows: THF and  $\text{Et}_2\text{O}$  were dried over Na metal, distilled from a Na/benzophenone ketyl and stored over Na/benzophenone.  $\text{CH}_2\text{Cl}_2$  was dried and distilled over  $\text{CaH}_2$  and also stored over  $\text{P}_2\text{O}_5$ . MeCN was distilled over  $\text{CaH}_2$  and then stored over 3 Å molecular sieves, which were activated by drying at 120 °C. Pentanes and hexanes were distilled over  $\text{CaH}_2$  and then stored over Na–benzophenone. All distillations were carried out under  $\text{N}_2$  dried by passing it through Drierite and  $\text{P}_4\text{O}_{10}$  columns prior to use. The purified solvents were stored in pyrex vessels with Teflon stopcocks under vacuum. Products were isolated by radial chromatography under a dry nitrogen atmosphere (the Chromatotron was obtained from Harrison Research, Palo Alto, CA) using

a 25 cm diameter circular plate coated with 0.1 cm of silica gel (EM Science), made from aqueous slurries followed by drying at 70 °C. NMR spectroscopy was carried out on a Bruker ARX 500 spectrometer operating at 500.1 MHz for proton, 160.5 MHz for boron-11, and at 202.5 MHz for phosphorus-31 and on a Varian Unity Plus 300 spectrometer operating at 96.2 MHz for  $^{11}\text{B}$ , 299.9 MHz for  $^1\text{H}$  and 121.4 MHz for  $^{31}\text{P}$  nuclei. Chemical shifts are reported in ppm for  $\text{CDCl}_3$  solutions, unless otherwise stated, to low field (high frequency) of  $\text{Et}_2\text{O}\cdot\text{BF}_3$  for  $^{11}\text{B}$ , of  $\text{SiMe}_4$  for  $^1\text{H}$  and of 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$ . Mass spectra were measured on a JEOL MStation JMS700. Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA.  $\text{B}_5\text{H}_9$  was obtained from laboratory stock, and distilled on a high vacuum line before use, and  $[2,2,2\text{-}(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_5\text{H}_9]$  was prepared according to the literature method [3].  $\text{BH}_3\cdot\text{thf}$  was used as received and the bidentate phosphines  $[\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2)_2]$  (dppf) [4],  $[\text{PPh}_2\text{C}_6\text{H}_4\text{PPh}_2]$  (1,4 arphos) [5], and  $[\text{PPh}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{PPh}_2]$  (dppx) [6] were prepared according to literature methods.

### 2.2. Synthesis of 1,4-arphos adducts of $(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9$ : $[2,2,2\text{-}(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_4\text{H}_7\text{-3-(BH}_2\cdot 1,4\text{-arphos)}]$ (**6a**) and $[(2,2,2\text{-}(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_4\text{H}_7\text{-3-BH}_2)_2(1,4\text{-arphos})]$ (**7a**)

A one-necked 50 ml round-bottom flask containing a stir-bar was charged with 130 mg (0.16 mmol) of  $(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9$  and 170 mg (0.38 mmol) of 1,4-arphos.  $\text{CH}_2\text{Cl}_2$  (25 ml) was added and the resulting solution refluxed under a  $\text{N}_2$  atmosphere for 15 h. The solution was then exposed to air and evacuated to dryness. The reaction mixture was then redissolved in 1 ml  $\text{CH}_2\text{Cl}_2$  and applied to a radial chromatograph using 60/40  $\text{C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$  mixture as eluent.  $[2,2,2\text{-}(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_4\text{H}_7\text{-3-(BH}_2\cdot 1,4\text{-arphos)}]$  (**6a**)

mg) (**6a**) [31.9% yield based on  $(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9$ ] and 26 mg of  $[(2,2,2-(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_4\text{H}_7\text{-3-BH}_2)_2(1,4\text{-arphos})]$  (**7a**) [15.4% yield based on  $(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9$ ] were obtained from the reaction mixture. NMR data for **6a** and **7a** can be found in Table 1 [7]. Elemental analysis: **6a** for  $\text{C}_{71}\text{H}_{74.33}\text{B}_5\text{P}_4\text{O}_1\text{Os}_1$ , (i.e. **6a** containing 2/3 mole of  $\text{C}_6\text{H}_{14}$ ) Calc. C, 65.01; H, 5.71. Found: C, 65.13; H, 5.68%. **7a**, for  $\text{C}_{110}\text{H}_{116}\text{B}_{10}\text{P}_6\text{O}_2\text{Os}_2$ , (i.e. **7a** containing 1 mole of  $\text{C}_6\text{H}_{14}$ ) Calc. C, 61.64; H, 5.45. Found: C, 61.78; H, 5.50%. HRMS: FAB (3-NBA and CsI) [8]. **6a**. Calc. For  $^{12}\text{C}_{67}\text{H}_{63}\text{B}_4\text{B}_1^{10}\text{B}_1^{31}\text{P}_4\text{O}_2^{192}\text{Os}_1^{133}\text{Cs}_1$   $[\text{M}+\text{Cs}+\text{O}]^+$  1402.2949, Obs. 1402.3016, ( $\Delta$  6.7ppm). LRMS: FAB (3-NBA). **7a**, Calc. for  $\text{C}_{104}\text{H}_{102}\text{B}_{10}\text{P}_6\text{Os}_2\text{O}_2$   $[\text{M}+\text{O}]^+$ , the base peak, 2058.65, obs. 2058.46. The isotopic pattern for the observed spectrum for **7a** matches that calculated from known isotopic abundances of the constituent elements.

### 2.3. Synthesis of $[2,2,2-(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_4\text{H}_7\text{-3-(BH}_2\cdot 1,4\text{-arphos}\cdot \text{BH}_3)]$ (**8a**)

A one-necked 50 ml round-bottom flask was charged with 80 mg (0.16 mmol) of  $(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9$  and 180 mg (0.40 mmol) of 1,4-arphos. To this 15 ml  $\text{CH}_2\text{Cl}_2$

was added along with a stir bar and the solution refluxed under a  $\text{N}_2$  atmosphere for 20 h. The solution was then evacuated to dryness and the NMR spectrum of a sample of the reaction mixture recorded. The  $^{31}\text{P}$ -NMR spectrum indicated that there had essentially been quantitative conversion of the  $(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9$  starting material to **6a**. The reaction mixture was then redissolved in 15 ml  $\text{CH}_2\text{Cl}_2$ , transferred to a two-necked 50 ml round-bottom flask and evacuated to dryness. The vessel was then attached to the high vacuum line and evacuated.  $\text{CH}_2\text{Cl}_2$  (20 ml) was condensed in at  $-196^\circ\text{C}$  and the system was then allowed to warm to  $-78^\circ\text{C}$ . Under a dynamic flow of  $\text{N}_2$ , 1.0 ml of a 1 M solution of  $\text{BH}_3\cdot\text{thf}$  (1.0 mmol) was added. The solution was allowed to warm to room temperature (r.t.) and stirred for 30 min. Workup of the product mixture proceeded as for **6a** and **7a** and afforded 47 mg (37.4% yield based on  $(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9$ ) of  $[2,2,2-(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_4\text{H}_7\text{-3-(BH}_2\cdot 1,4\text{-arphos}\cdot \text{BH}_3)]$  (**8a**). NMR data for **8a** can be found in Table 1 [7]. Elemental analysis: **8a** for  $\text{C}_{67}\text{H}_{66}\text{B}_6\text{P}_4\text{O}_1\text{Os}_1$ , Calc. C, 63.55; H, 5.25. Found: C, 62.92; H, 5.53%. HRMS: FAB (3-NBA and CsI). **8a**. Calc. for  $^{12}\text{C}_{67}\text{H}_{66}\text{B}_4\text{B}_2^{31}\text{P}_4\text{O}_1^{192}\text{Os}_1^{133}\text{Cs}_1$   $[\text{M}+\text{Cs}]^+$  1399.3364, obs. 1399.3356, ( $\Delta$  0.8 ppm).

Table 1

$^{11}\text{B}$ -,  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR ( $\delta$  in ppm) data for  $[2,2,2-(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_4\text{H}_7\text{-3-(BH}_2\cdot 1,4\text{-arphos})]$  (**6a**),  $[(2,2,2-(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_4\text{H}_7\text{-3-BH}_2)_2(1,4\text{-arphos})]$  (**7a**) and  $[2,2,2-(\text{PPh}_3)_2(\text{CO})\text{-nido-2-OsB}_4\text{H}_7\text{-3-(BH}_2\cdot 1,4\text{-arphos}\cdot \text{BH}_3)]$  (**8a**)

Species	$(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9(1,4\text{-arphos})^a$ ( <b>6a</b> )		$(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9(1,4\text{-arphos})^a$ ( <b>7a</b> )		$(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9(1,4\text{-arphos})\text{BH}_3^a$ ( <b>8a</b> )	
Mode/atom	$^{31}\text{P}\{^1\text{H}\}$		$^{31}\text{P}\{^1\text{H}\}$		$^{31}\text{P}\{^1\text{H}\}$	
P(2) <sup>b</sup>	+14.00t $J = 8.77$		+14.09m		+13.93	
P(1) <sup>b</sup>	+9.35d $J = 9.15$		+9.20d $J = 9.54$		+9.20d $J = 9.15$	
P(3)	+24.34br		+24.67br		+24.95br	
P(4)	-5.19d $J = 1.05$		-		+21.11br	
Mode/atom	$^{11}\text{B}$	$^1\text{H}\{^{11}\text{B}\}$	$^{11}\text{B}$	$^1\text{H}\{^{11}\text{B}\}$	$^{11}\text{B}$	$^1\text{H}\{^{11}\text{B}\}$
4	+8.97	5.24	+8.55	+5.21	+8.58	+5.16
3	+8.97	- <sup>c</sup>	+8.55	- <sup>c</sup>	+8.58	- <sup>c</sup>
5	-16.16	+1.18	-15.57	+1.16	-15.81	+1.19
1 <sup>d</sup>	-29.08d $J =$ 120.51	+0.26	-29.04	+0.24	-29.20d $J = 115.54$	+0.19
6, 6'	-34.25	+2.01, +1.57	-33.86, -37.63	+1.98, +1.80	-34.63	+1.99, +1.79
7 <sup>e</sup>	-	-	-	-	-37.58	+1.26d $J = 16.05$
H(3,4)	-	-1.46	-	-1.51	-	-1.53
H(4,5)	-	-2.33	-	-2.35	-	-2.35
H(2,5)	-	-10.39	-	-10.41	-	-10.40
H(2,3) <sup>f</sup>	-	-9.14d $J =$ 42.51	-	-9.16d $J = 43.01$	-	-9.16d $J = 42.51$
Ph <sup>g</sup>	-	7.01-7.85m	-	6.94-7.79m	-	6.95-7.78m

<sup>a</sup>  $\text{CDCl}_3$ , 298 K. Coupling constants giving in Hz.

<sup>b</sup> P(2) is coupling with both P(1) and P(3). P(1) is only coupling with P(2).

<sup>c</sup> Site of  $\text{BH}_2(\text{PPh}_2)$  substituent.

<sup>d</sup>  $J(^{11}\text{B}-^1\text{H})$ .

<sup>e</sup>  $^2J(^{31}\text{P}-^1\text{H})$ .

<sup>f</sup> Doublets due to  $^2J(^{31}\text{P}-^1\text{H})\text{trans}$  coupling.

<sup>g</sup> Includes phenyl protons of 1,4-arphos and  $\text{PPh}_3$  coordinated to Os center.

2.4. *Synthesis of dppf adducts of  $(PPh_3)_2(CO)OsB_5H_9$ :  $[2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-(BH_2 \cdot dppf)]$  (**6b**),  $[(2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-BH_2)_2(dppf)]$  (**7b**) and  $[2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-(BH_2 \cdot dppf \cdot BH_3)]$  (**8b**)*

A one-necked round-bottom flask was charged with 250 mg (0.31 mmol) of  $(PPh_3)_2(CO)OsB_5H_9$  and 260 mg (0.47 mmol) of dppf. This was then dissolved in 25 ml  $CH_2Cl_2$  and allowed to stir at 5 °C for 24 h. The solution was then evacuated to dryness and a NMR sample of the reaction mixture recorded.  $^{31}P$ -NMR spectrometry showed that all of the  $(PPh_3)_2(CO)OsB_5H_9$  [7] starting material had reacted, generating a mixture of three dppf complexes of  $(PPh_3)_2(CO)OsB_5H_9$ . The reaction mixture was then redissolved in 1 ml  $CH_2Cl_2$  and applied to a radial chromatograph using 60/40  $C_5H_{12}-CH_2Cl_2$  mixture as eluent. A total of 154 mg of  $[2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-(BH_2 \cdot dppf)]$  (**6b**) [36.5% yield based on  $(PPh_3)_2(CO)OsB_5H_9$ ] was isolated, and  $[(2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-BH_2)_2(dppf)]$  (**7b**) with  $[2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-(BH_2 \cdot dppf \cdot BH_3)]$  (**8b**) were obtained in a single fraction. This band containing **7b** and **8b** was redissolved in 1 ml  $CH_2Cl_2$  and subjected to a second separation using a 70/30  $C_5H_{12}-CH_2Cl_2$  eluent. From this separation 42 mg of **7b** [12.6% yield based on  $(PPh_3)_2(CO)OsB_5H_9$ ] and 15 mg of **8b** [3.5% yield based on  $(PPh_3)_2(CO)OsB_5H_9$ ] were obtained from the reaction mixture.

In a separate experiment **8b** was prepared independently. Compound **6b** (40 mg, 0.029 mmol) was placed in a 50 ml two-necked round-bottom flask, which was then connected to a high vacuum line and evacuated. It was then cooled to -196 °C and 20 ml thf condensed in. The system was then allowed to warm to -78 °C and under a dynamic flow of  $N_2$ , 0.5 ml of a 1 M solution of  $BH_3 \cdot thf$  (0.5 mmol) was added. The solution was allowed to warm to r.t., stirred for 30 min, exposed to air and filtered through a 1-cm silica plug. The resulting solution was then condensed to 1 ml in volume and then applied to the radial chromatograph using 50/50  $CH_2Cl_2-C_5H_{12}$  as eluent. Using this method 28 mg (69% yield based on **6b**) of **8b** was obtained. Analysis and spectral data for **8b** obtained both ways were identical.

The NMR data for **6b**, **7b** and **8b** can be found in Table 2 [7]. Elemental analysis: **6b** for  $C_{71}H_{67}B_5P_4Fe_1O_1Os_1$  Calc: C, 62.69; H, 4.96. Found: C, 62.45; H, 5.08%. Compound **7b** for  $C_{108}H_{106}B_{10}P_6Fe_1O_2Os_2$  Calc: C, 59.88; H, 4.93. Found: C, 59.45; H, 4.93%. Compound **8b** for  $C_{71}H_{70}B_6P_4Fe_1O_1Os_1$  Calc: C, 62.06; H, 5.13. Found: C, 62.21; H, 5.26%. HRMS: FAB (3-NBA). Compound **6b**: Calc. For  $^{12}C_{71}H_{66}B_{11}B_4^{31}P_4^{56}Fe_1^{16}O_1^{192}Os_1 [(M+H)-H_2]^+$  1360.3530, obs. 1360.3567, ( $\Delta$  2.7 ppm). Compound **7b**: the parent ion was not observed,

however clusters centered around 1340 and 1080 were observed, but as yet these remain unidentified. Compound **8b**: Calc. for  $^{12}C_{71}H_{69}B_{11}B_5^{31}P_4^{56}Fe_1^{16}O_1^{192}Os_1 [(M+H)-H_2]^+$  1374.3857, obs. 1374.3885, ( $\Delta$  2.0 ppm).

2.5. *Synthesis of dppx adducts of  $(PPh_3)_2(CO)OsB_5H_9$ :  $[2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-(BH_2 \cdot dppx)]$  (**6c**) and  $[(2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-BH_2)_2(dppx)]$  (**7c**)*

A one-necked 50 ml round-bottom flask containing a stir-bar was charged with 200 mg (0.25 mmol) of  $(PPh_3)_2(CO)OsB_5H_9$ . The vessel was then placed in the dry box and 295 mg (0.62 mmol) of dppx was added. After it was removed from the dry box it was connected to high vacuum line and evacuated.  $CH_2Cl_2$  (25 ml) was condensed in at -196 °C and the resulting solution stirred at r.t. for 16 h. The solution was then exposed to air and evacuated to dryness on a rotary evaporator.  $^{31}P$ -NMR spectra indicated the absence of  $(PPh_3)_2(CO)OsB_5H_9$ , but that new dppx complexes of  $(PPh_3)_2(CO)OsB_5H_9$  had formed. The reaction mixture was then redissolved in 1 ml  $CH_2Cl_2$  and applied to a radial chromatograph using 50/50  $C_6H_{14}-CH_2Cl_2$  mixture as eluent. A total of 100 mg of  $[2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-(BH_2 \cdot dppx)]$  (**6c**) [31.2% yield based on  $(PPh_3)_2(CO)OsB_5H_9$ ] and 26 mg of  $[(2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-BH_2)_2(dppx)]$  (**7c**) [10.0% yield based on  $(PPh_3)_2(CO)OsB_5H_9$ ] were obtained from the reaction mixture. NMR data for **6c** and **7c** can be found in Table 3 [7]. Elemental analysis: **6c** for  $C_{73.5}H_{77.5}B_5P_4O_2Os_1$ , i.e. **6c** containing 3/4 mole of  $C_6H_{14}$  and the uncoordinated phosphine as  $Ph_2PO$ , Calc. C, 64.86; H, 5.74. Found: C, 65.02; H, 5.73%. Compound **7c** for  $C_{112}H_{120}B_{10}P_6O_2Os_2$ , (i.e. **7c** containing 1 mol  $C_6H_{14}$ ) Calc. C, 61.92; H, 5.57. Found: C, 62.59; H, 5.45%. LRMS: FAB (3-NBA). Compound **6c**. Calc. For  $C_{69}H_{66}B_5P_4O_2Os_1 [(M+O+H)-H_2]^+$  1295.41, obs. 1295.42. The isotope pattern for the observed spectrum for **6c** matches that calculated from known isotopic abundances of the constituent elements. LRMS: FAB (3-NBA). Compound **7c** Calc. for  $C_{106}H_{106}B_{10}P_6Os_2O_2 [(M+O+H)]^+$  2087.69, obs. 2087.30. The isotope pattern for the observed spectrum for **7c** matches that calculated from known isotopic abundances of the constituent elements.

2.6. *Synthesis of  $[2,2,2-(PPh_3)_2(CO)-nido-2-OsB_4H_7-3-(BH_2 \cdot dppx \cdot BH_3)]$  (**8c**)*

A two-necked 50 ml round-bottom flask containing a stir-bar was charged with 152 mg (0.19 mmol) of  $(PPh_3)_2(CO)OsB_5H_9$ . The vessel was then placed in the dry box where 135 mg (0.28 mmol) of dppx was added. After it was removed from dry box it was connected to a

Table 2

<sup>11</sup>B-, <sup>1</sup>H- and <sup>31</sup>P-NMR ( $\delta$  in ppm) data for [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppf)] (**6b**), [(2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>)<sub>2</sub>(dppf)] (**7b**) and [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppf·BH<sub>3</sub>)] (**8b**)

Species	(PPh <sub>3</sub> ) <sub>2</sub> (CO)OsB <sub>5</sub> H <sub>9</sub> (dppf) <sup>a</sup> ( <b>6b</b> )		((PPh <sub>3</sub> ) <sub>2</sub> (CO)OsB <sub>5</sub> H <sub>9</sub> ) <sub>2</sub> (dppf) <sup>a</sup> ( <b>7b</b> )		(PPh <sub>3</sub> ) <sub>2</sub> (CO)OsB <sub>5</sub> H <sub>9</sub> (dppf)BH <sub>3</sub> <sup>a</sup> ( <b>8b</b> )	
Mode/atom	<sup>31</sup> P{ <sup>1</sup> H}		<sup>31</sup> P{ <sup>1</sup> H}		<sup>31</sup> P{ <sup>1</sup> H}	
P(2) <sup>b</sup>	+14.35t <i>J</i> = 8.71		+14.35m		+13.90t <i>J</i> = 9.53	
P(1) <sup>b</sup>	+9.27d <i>J</i> = 8.71		+9.05d <i>J</i> = 8.46		+9.36d <i>J</i> = 9.27	
P(3)	+18.61br		+18.53br, +18.23br		+19.01br	
P(4)	−18.06s		−		+15.80br	
Mode/atom	<sup>11</sup> B	<sup>1</sup> H{ <sup>11</sup> B}	<sup>11</sup> B	<sup>1</sup> H{ <sup>11</sup> B}	<sup>11</sup> B	<sup>1</sup> H{ <sup>11</sup> B}
4	+8.88	5.23	+8.53	+5.21	+8.77	+5.21
3	+8.88	− <sup>c</sup>	+8.53	− <sup>c</sup>	+8.77	− <sup>c</sup>
5	−16.79	+0.95	−16.69	+1.16	−16.32	+1.18
1	−29.05	+0.35	−29.14	+0.24	−29.01	+0.21
6, 6'	−34.22	+2.01, +1.72	−33.61	+1.98, +1.80	−35.21	+2.04, +1.75
7 <sup>d</sup>	−	−	−	−	−37.93	+1.15d <i>J</i> = 16.02
H(3,4)	−	−1.56	−	−1.60, −1.63	−	−1.58
H(4,5)	−	−2.40	−	−2.40	−	−2.39
H(2,5)	−	−10.47	−	−10.47	−	−10.50
H(2,3) <sup>e</sup>	−	−9.16d <i>J</i> = 42.51	−	−9.21m	−	−9.21d <i>J</i> = 41.76
Cp <sup>f</sup>	−	+3.85, +3.92, +4.11, +4.18, +4.29, 4.53, +4.56, +4.71	−	+3.87, +4.00, +4.45, +4.53, +4.59, +4.62, +4.64, +4.68	−	+4.07, +4.14, +4.21, + 4.40, +4.44, +4.70, + 4.74, +4.80
Ph <sup>g</sup>	−	6.91–7.43m	−	6.93–7.50m	−	6.94–7.53m

<sup>a</sup> CDCl<sub>3</sub>, 298 K. Coupling constants giving in Hz.

<sup>b</sup> P(2) is coupling with both P(1) and P(3). P(1) is only coupling with P(2).

<sup>c</sup> Site of BH<sub>2</sub>(PPh<sub>2</sub>) substituent.

<sup>d</sup> <sup>2</sup>*J*(<sup>31</sup>P–<sup>1</sup>H).

<sup>e</sup> Doublets due to <sup>2</sup>*J*(<sup>31</sup>P–<sup>1</sup>H)*trans* coupling.

<sup>f</sup> Protons on Cp rings of dppf ligand.

<sup>g</sup> Includes phenyl protons of 1,4-arphos and PPh<sub>3</sub> coordinated to Os center.

high vacuum line and evacuated. CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was condensed in at −196 °C and the resulting solution stirred at r.t. for 17 h. The solution was then cooled to −78 °C and under a dynamic flow of N<sub>2</sub>, 0.7 ml of 1 M BH<sub>3</sub>·thf (0.7 mmol) was added. It was then allowed to warm to r.t. and stirred for 30 min. The solution was then exposed to air and evacuated to dryness on a rotary evaporator. <sup>31</sup>P-NMR spectrometry showed that 10% of the (PPh<sub>3</sub>)<sub>2</sub>(CO)OsB<sub>5</sub>H<sub>9</sub> [7] starting material remained, while all uncoordinated phosphines had been converted to the analogous phosphine–borane moieties. The reaction mixture was then redissolved in 1 ml CH<sub>2</sub>Cl<sub>2</sub> and applied to a radial chromatograph using a 60/40 C<sub>6</sub>H<sub>14</sub>–CH<sub>2</sub>Cl<sub>2</sub> mixture as eluent. [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppx·BH<sub>3</sub>)] (**8c**) was isolated, however, it contained a large amount of the bis-borane adduct of dppx. This sample was then evacuated, redissolved in 1 ml CH<sub>2</sub>Cl<sub>2</sub> and applied to a radial chromatograph using 50/50 C<sub>6</sub>H<sub>14</sub>–CH<sub>2</sub>Cl<sub>2</sub> mixture as eluent. From this separation a single fraction was obtained which contained **8c** and 20% of the bis-borane adduct of dppx. The sample was then evacuated to remove solvent and re-dissolved in 15 ml of a 9:1 mixture of Et<sub>2</sub>O–CH<sub>2</sub>Cl<sub>2</sub> to give a cloudy solution which was then filtered through a 1 cm plug of Celite.

Compound **8c** (70 mg) [28.4% yield based on (PPh<sub>3</sub>)<sub>2</sub>(CO)OsB<sub>5</sub>H<sub>9</sub>] were isolated. NMR data for **8c** can be found in Table 3 [7]. Elemental analysis: **8c** for C<sub>72</sub>H<sub>77</sub>B<sub>6</sub>P<sub>4</sub>O<sub>1</sub>Os<sub>1</sub>, (i.e. **8c** containing 0.5 moles of C<sub>6</sub>H<sub>14</sub>) Calc. C, 64.66; H, 5.80. Found: C, 64.93; H, 5.82%. LRMS: FAB (3-NBA and CsI). Compound **8c** Calc. for C<sub>69</sub>H<sub>70</sub>B<sub>6</sub>P<sub>4</sub>Os<sub>1</sub>O<sub>1</sub> [M+Cs]<sup>+</sup> 1427.37, obs. 1427.36. The isotope pattern for the observed spectrum for **8c** matches that calculated from known isotopic abundances of the constituent elements.

### 3. Results and discussion

The reaction between **1** and bidentate phosphines of the type PPh<sub>2</sub>XPPH<sub>2</sub> (X = Fe(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>, 1,4-C<sub>6</sub>H<sub>4</sub> and 1,4-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>) initially produces a species in which a BH<sub>2</sub>·PPh<sub>2</sub>XPPH<sub>2</sub> moiety is appended to a basal boron atom adjacent to the Os atom in the newly formed *nido*-osmapentaborane cluster. This initially formed product is similar to that observed in the reaction of **1** and bidentate phosphines containing an aliphatic hydrocarbon chain backbone, e.g. PPh<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>; that is they contain a pendent PPh<sub>2</sub> group. The chemistries of these analogous species in solution however, are remarkably

Table 3

<sup>11</sup>B-, <sup>1</sup>H- and <sup>31</sup>P-NMR ( $\delta$  in ppm) data for [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppx)] (**6c**), [(2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>)<sub>2</sub>(dppx)] (**7c**) and [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppx·BH<sub>3</sub>)] (**8c**)

Species Mode/atom	(PPh <sub>3</sub> ) <sub>2</sub> (CO)OsB <sub>5</sub> H <sub>9</sub> (dppx) <sup>a</sup> ( <b>6c</b> ) <sup>31</sup> P{ <sup>1</sup> H}		((PPh <sub>3</sub> ) <sub>2</sub> (CO)OsB <sub>5</sub> H <sub>9</sub> ) <sub>2</sub> (dppx) <sup>a</sup> ( <b>7c</b> ) <sup>31</sup> P{ <sup>1</sup> H}		(PPh <sub>3</sub> ) <sub>2</sub> (CO)OsB <sub>5</sub> H <sub>9</sub> (dppx)BH <sub>3</sub> <sup>a</sup> ( <b>8c</b> ) <sup>31</sup> P{ <sup>1</sup> H}	
Mode/atom	<sup>11</sup> B	<sup>1</sup> H{ <sup>11</sup> B}	<sup>11</sup> B	<sup>1</sup> H{ <sup>11</sup> B}	<sup>11</sup> B	<sup>1</sup> H{ <sup>11</sup> B}
P(2) <sup>b</sup>	+13.72m		+13.79m		+13.66m	
P(1) <sup>b</sup>	+9.45d <i>J</i> = 9.90		+9.37m		+9.36d <i>J</i> = 7.84	
P(3)	+22.54br		+22.56m		+22.55br	
P(4)	-9.91d <i>J</i> = 4.25		-		+17.93br	
Mode/atom	<sup>11</sup> B	<sup>1</sup> H{ <sup>11</sup> B}	<sup>11</sup> B	<sup>1</sup> H{ <sup>11</sup> B}	<sup>11</sup> B	<sup>1</sup> H{ <sup>11</sup> B}
4	+8.52	5.37	+8.67	+5.39	+8.32	+5.34
3	+8.52	- <sup>c</sup>	+8.67	- <sup>c</sup>	+8.32	- <sup>c</sup>
5	-15.78	+1.28	-15.20	+1.27	-15.27	+1.30
1 <sup>d</sup>	-29.49d <i>J</i> = 109.27	0.23	-29.42	+0.18	-29.55d <i>J</i> = 104.61	+0.19
6, 6'	-36.45	+1.66, +1.44	-36.26	+1.65, +1.44	-38.58	+1.59, +1.40
7	-	-	-	-	-38.58	+0.94d <i>J</i> = 15.92
H(3,4)	-	-1.47	-	-1.46	-	-1.51
H(4,5)	-	-2.30	-	-2.30	-	-2.31
H(2,5)	-	-10.36	-	-10.38	-	-10.37
H(2,3) <sup>e</sup>	-	-9.17d <i>J</i> = 43.51	-	-9.19d <i>J</i> = 40.51	-	-9.21d <i>J</i> = 41.51
CH <sub>2</sub> <sup>f</sup>	-	+3.86m, +3.61m, + 3.31s	-	+3.74m, + 3.60m	-	+3.86m, +3.57m, +3.48d <i>J</i> = 11.45
Ph <sup>g</sup>	-	6.78–7.70m	-	6.51–7.69m	-	6.61–7.72m

<sup>a</sup> CDCl<sub>3</sub>, 298 K. Coupling constants giving in Hz.

<sup>b</sup> P(2) is coupling with both P(1) and P(3). P(1) is only coupling with P(2).

<sup>c</sup> Site of BH<sub>2</sub>(PPh<sub>2</sub>) substituent.

<sup>d</sup> *J*(<sup>11</sup>B–<sup>1</sup>H).

<sup>e</sup> Doublets due to <sup>2</sup>*J*(<sup>31</sup>P–<sup>1</sup>H)*trans* coupling.

<sup>f</sup> Methylene protons on dppx backbone.

<sup>g</sup> Includes phenyl protons of dppx and PPh<sub>3</sub> coordinated to Os center.

different. When the more flexible alkyl-bridged bidentate phosphines are used, the resulting species can undergo intramolecular substitution to generate a species in which a BH<sub>2</sub>·PPh<sub>2</sub>(CH<sub>2</sub>)<sub>*n*</sub>·PPh<sub>2</sub> moiety bridges between a basal boron atom and the osmium center. The details of such reactions have been reported earlier [1b]. With rigid backbone bidentate phosphines this intramolecular substitution is not possible and is thus not observed. Indeed rigid backbone bidentate phosphines have been employed in efforts to preclude chelation to metal centers [9]. We did not observe any reaction between **1** and 1,2-(PPh<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and presume that the latter is too sterically hindered to approach a basal boron atom in **1**. With the other rigid backbone bidentate phosphines, the initial species formed [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>·PPh<sub>2</sub>XPPH<sub>2</sub>] where X = 1,4-C<sub>6</sub>H<sub>4</sub>, (**6a**), Fe(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>, (**6b**) or 1,4-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>, (**6c**), reacts further with a second molecule of **1** to produce a system in which two *nido*-osmapentaborane clusters are linked. We did not observe this reaction mode for alkyl bridged bidentate phosphines, presumably because the intramolecular chelation is favored entropically over intermolecular reactions.

We noted previously that, when simple tertiary phosphines react with **1**, the complex formed [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·PR<sub>3</sub>)] either reverts to the osmahexaborane or degrades to an osmapentaborane **3** and BH<sub>3</sub>·PR<sub>3</sub> [1a,b]. It appears that such chemistry takes place in the case of all the bases we have studied herein, although in the case of 1,4-arphos, only traces of the ultimate phosphine–borane [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·1,4-arphos·BH<sub>3</sub>)] (**8a**) were observed in NMR spectra of the crude product mixture and these were only identifiable after the species had been prepared independently [7].

Thus, for example, in the reactions of **1** with dpff, the reaction mixture initially contains three products, all of which are dpff complexes of **1** and were identified as [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dpff)] (**6b**), [(2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>·PPh<sub>2</sub>)<sub>2</sub>(dpff)] (**7b**) and [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>·dpff·BH<sub>3</sub>] (**8b**), illustrated as Fig. 1a, b and c, respectively. Presumably **6b** forms initially and then reacts with a second mole of **1** to afford **7b**. Degradation of **7b** to phosphine–borane and osmapentaborane, in this case, **8b** and **3**, or to form **6b** and **1**, follows. This is illustrated in Scheme B. The species **6b**, **7b** and **8b** were all identified as components of the product mixture,

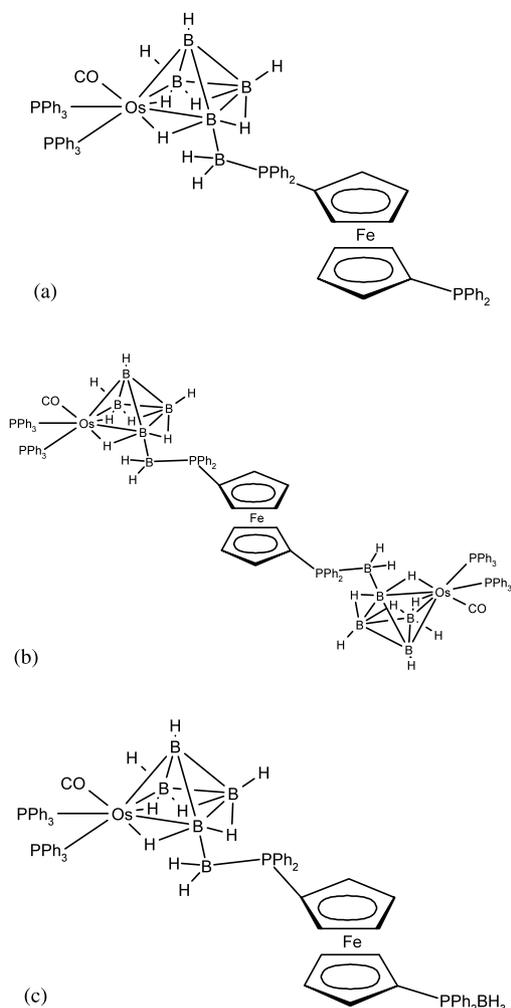


Fig. 1. Schematic representations of the proposed structures for (a) [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppf)] (**6b**), (b) [(2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>)<sub>2</sub>(dppf)] (**7b**) and (c) [2,2,2-(PPh<sub>3</sub>)<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppf·BH<sub>3</sub>)] (**8b**).

from their NMR spectra [7] and by elemental analysis and high-resolution mass spectrometry. In the latter measurement we found that CsI may be added to the sample in FAB experiments to avoid problems of overlap from fragment ions involving H atoms loss [7]. Unfortunately, none of the species we identified in this study proved to be amenable to study by X-ray diffraction. There are two possible explanations for this and they both relate to the problem stability of samples in solution during attempts at crystal growth. One is the fact that the species with pendent PPh<sub>2</sub> groups can degrade or revert to the free base and osmhexaborane. Also the pendent phosphines can oxidize easily to form the phosphine oxide. This latter we observed in the mass spectral analysis of species involving the phosphines arphos and dppx.

In the case of the formation of **6b**, **7b** and **8b**, the species were obtained in 36.5, 12.6 and 3.5% yields, respectively, based on [(PPh<sub>3</sub>)<sub>2</sub>(CO)OsB<sub>5</sub>H<sub>5</sub>]. Species **8b**

was prepared independently, in 69% yield from the reaction between **6b** and excess BH<sub>3</sub>·thf to afford product with identical spectral and analytical properties to the other samples of **8b**.

Although more rigid than the alkyl-bridged diphosphines, dppf is quite flexible in some respects and can adopt several different conformations. These conformations are available through rotation of the two Cp rings, relative to each other. For example, in the solid state, free dppf has a *trans* arrangement of PPh<sub>2</sub>C<sub>5</sub>H<sub>4</sub> rings [10]. This *trans* or staggered arrangement is also observed for the bis-borane adduct of dppf and in systems where dppf is seen as a bridging ligand [11]. This versatile ligand however, can also act as a monodentate ligand and examples of this have been reported [11a,12]. Here the C<sub>5</sub>H<sub>4</sub> moieties have moved away from a completely staggered conformation and are approaching that of an eclipsed conformation. Finally dppf can also act as a chelating ligand and this bonding motif can be seen in numerous systems [10,11b]. When dppf adopts this binding mode the two C<sub>5</sub>H<sub>4</sub> units are in an eclipsed or nearly eclipsed conformation. Although X-ray crystallographically determined structures for the dppf containing species were not obtained, we were able to utilize the different chemical shifts of the Cp protons in the predicted staggered conformation of the dppf adducts to follow the reactions. The patterns resulting from the 8 aromatic protons differ, so transformations of **7b** could be monitored by <sup>1</sup>H-NMR spectroscopy. In this experiment 25 mg of **7b** was dissolved in 0.7 ml of CDCl<sub>3</sub>, and the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H}-NMR spectra were monitored over the period of a week. The initial <sup>1</sup>H- and <sup>31</sup>P{<sup>1</sup>H}-NMR spectra showed the presence of only a single species, namely **7b**. After a period of 24 h the NMR sample was re-examined and the Cp region of the <sup>1</sup>H spectrum showed the presence of several more signals. Over a period of a few days these peaks grew in intensity and were assigned to the species **6b** and **8b**. This was also confirmed by <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum which additionally showed the presence of **1** and the *nido*-osmapentaborane cluster, (PPh<sub>3</sub>)<sub>2</sub>(CO)OsB<sub>4</sub>H<sub>8</sub> (**3**). The presence of these products was expected, since the equilibration of **7b** to **6b** would release **1**, and **3** would be formed when **7b** degraded to **8b**. The resonances due to **6b** and **8b** grew in intensity and after a period of seven days no **7b** could be detected by NMR spectroscopy. The major species remaining in solution was **6b**, suggesting that the major mode of decomposition of **7b** favored the production of **6b**. The relative ratio of **6b** and **8b** present was determined by integration of the peaks in the Cp region in the <sup>1</sup>H-NMR spectrum. This indicated that the decomposition of **7b** gave approximately 60% of **6b** and 40% of **8b**. <sup>31</sup>P{<sup>1</sup>H}-NMR spectra provided support for the ratio of **1** and **3** present in solution, although the value can only be approximate since both **6b** and **8b** also degrade slowly in solution.

The decomposition of **6b** and **8b** could generate a number of products, including dppf,  $\text{BH}_3 \cdot \text{dppf} \cdot \text{BH}_3$ ,  $\text{O} \cdot \text{dppf} \cdot \text{O}$ ,  $\text{BH}_3 \cdot \text{dppf}$ ,  $\text{O} \cdot \text{dppf}$ ,  $\text{BH}_3 \cdot \text{dppf} \cdot \text{O}$  and the metallaboranes **1** and **3**. Thus, determination of accurate values for the amounts of **6b** and **8b**, from longer term monitoring of NMR spectra became quite difficult but our assumptions illustrated in Scheme B were certainly given credence by these results.

The reaction between **1** and dppx afforded all three products [2,2,2-( $\text{PPh}_3$ )<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppx)] (**6c**), [(2,2,2-( $\text{PPh}_3$ )<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-BH<sub>2</sub>)<sub>2</sub>(dppx)] (**7c**) and [2,2,2-( $\text{PPh}_3$ )<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppx·BH<sub>3</sub>)] (**8c**) but the bis-borane adduct for dppx, **8c**, was isolated only in very small amounts from the reaction of **1** and dppx only after extended reaction times. The traces of **8c** formed were identified by comparison with samples prepared independently from the reaction between **6c** and  $\text{BH}_3 \cdot \text{thf}$ . This suggests that the same reaction pathway as that indicated in Scheme 2 for the dppf ligand is applicable herein. It also suggests that the linked cluster system, **7c**, is thermodynamically more stable in solution than the dppf analogue, therefore less **8c** was formed.

In the complexes of the dppx ligand with the osmaboranes, the coordination mode of the phosphorus atom has a profound effect on the methylene protons on the dppx backbone. An expansion of the proton-NMR spectra of **6c**, **7c** and **8c** showing the methylene regions are given in Fig. 2. From Fig. 2 it is clear that the change in coordination mode of both phosphorus atoms can have a dramatic influence on the multiplicity observed

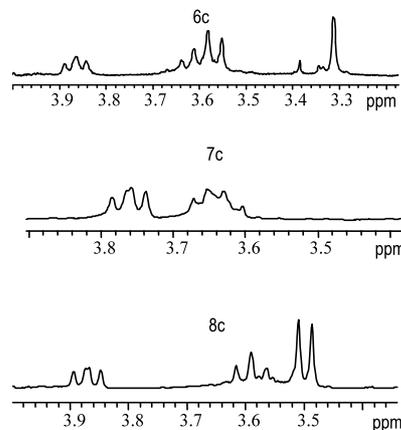
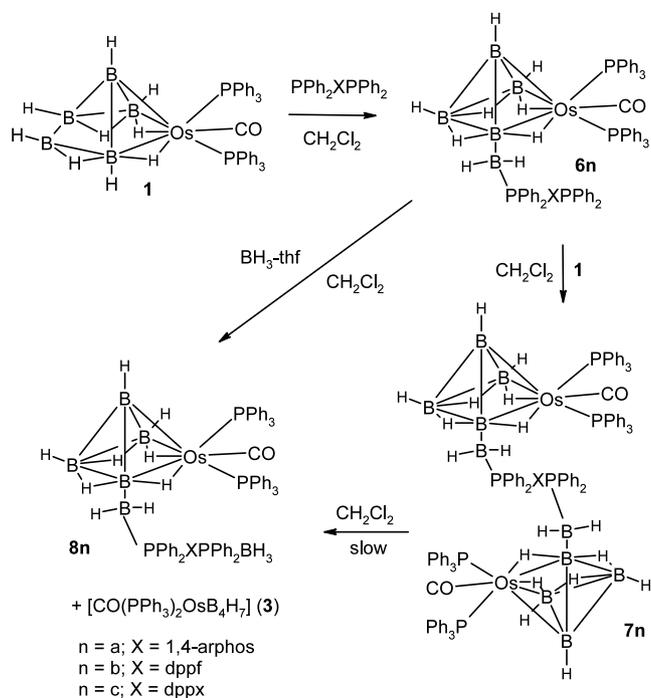


Fig. 2. An expansion of the  $^1\text{H}$ -NMR spectra of **6c**, **7c** and **8c** showing the methylene proton regions.

for the methylene protons. For **6c** there are three resonances in an approximate 1:1:2 ratio. The two resonances of area one arise from the methylene protons adjacent to the  $\text{PPh}_2 \cdot \text{BH}_2$  moiety. Two resonances are observed due to the effect of the chiral *nido*-osmapentaborane cluster, which renders these protons diastereotopic. The signals are observed as two pseudo-triplets due to overlapping  $^2J_{\text{H-H}}$  and  $^2J_{\text{H-P}}$  couplings. The disparity in the signal centered at 3.6 ppm is due by the presence of traces of [2,2,2-( $\text{PPh}_3$ )<sub>2</sub>(CO)-*nido*-2-OsB<sub>4</sub>H<sub>7</sub>-3-(BH<sub>2</sub>·dppx·O)], arising from the air oxidation of **6c**. The remaining resonance arises from the methylene protons adjacent to the uncoordinated phosphine. This appears as a singlet (3.31 ppm) and no coupling is observed between these protons and the adjacent phosphine. For **7c** two resonances are observed both of area one. Similar to **6c**, this is due to the chirality of the *nido*-osmapentaborane cluster, which renders these methylene protons diastereotopic. Only two signals are observed due to overlap between the methylene protons at both ends of the ligand. For **8c** three resonances are observed for the methylene protons, in a 1:1:2 area ratio. The resonances of area ratio one arise from the methylene protons adjacent to  $\text{PPh}_2 \cdot \text{BH}_2$  moiety. Two resonances are observed for a similar reason to that explained for **6c** and **7c**. The remaining resonance appears as a doublet and arises from the methylene protons adjacent to the *nido*-osmapentaborane cluster in all 3 species gave two give two resonances in a 1:1 area ratio. For **6c** and **8c** a third resonance is observed. It is this third resonance of area two, which differs in multiplicity in the two cases. This change in multiplicity arises from the differing coordination at the phosphine center, which apparently modifies the hybridization of the phosphorus atom. When the phosphorus is trivalent or uncoordinated, the hybridization of the phosphorus atom is essentially  $\text{p}^3$ , with the lone pair primarily located in the s-orbital. However, when the



phosphorus becomes four coordinate (i.e. pseudo-tetrahedral) the hybridization changes to approximately  $sp^3$ . Thus, since coupling information is communicated primarily via the s electrons, the more s character a bond has the higher the coupling between the atoms, and this series of compounds demonstrates this. Similar observations of very low or effectively zero  $^1H-^{31}P$  coupling have been made previously and accounted for in the terms of the hybridization of the phosphorus atom [13].

#### 4. Summary

The reaction between rigid bidentate phosphines of the type  $PPh_2XPPH_2$  [ $X = Fe(C_5H_4PPh_2)_2$ , 1,4- $C_6H_4$  and 1,4- $CH_2C_6H_4CH_2$ ] and **1** affords three products. The initial species produced is one in which a  $BH_2 \cdot PPh_2XPPH_2$  moiety is appended to a basal boron atom in a *nido*-osmapentaborane cluster. This does not result in intramolecular substitution reactions, as seen for systems involving simple tertiary bidentate phosphines with alkyl group backbones, but it also does not allow convenient study of reactions at the pendent  $PPh_2$  group. This latter reacts further with a second molecule of **1** to afford a system in which two *nido*-osmapentaborane clusters are linked through a  $BH_2 \cdot PPh_2XPPH_2 \cdot BH_2$  moiety. This linked cluster system can then degrade to generate a species in which there is a  $BH_2 \cdot PPh_2XPPH_2 \cdot BH_3$  moiety appended to a *nido*-osmapentaborane cluster. As discussed earlier the rate of this decomposition is dependent on the phosphine utilized. Linked borane cluster systems have been reported before, and can be linked by a vertex [14], a single atom [15], or by a bidentate ligand as seen here [6,13c,16].

Although we were unable to obtain crystals suitable for X-ray analysis on any of the species described here, NMR and mass spectral data along with elemental analysis were consistent with the formation of the nine species described. Clearly in order to study species with tailored groups coordinated to the pendent  $PPh_2$  group in species of type 6, approaches such as reaction of functionalized bidentate phosphines with the osmahexaborane **1** will be required and we are currently exploring this chemistry.

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