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Degradation and Modification of Metallaboranes: Reactions of the Hexaborane(10) Analogue *nido*-$(PPh_3)_2(CO)OsB_5H_9$ with Phosphines and the Crystal and Molecular Structure of [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-$BH_2\cdot PPh_2Me$]

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The reaction between the osmahexaborane [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_5H_9] (**1**) and bases such as PPh_3, PPh_2Me, and PMe_3 in refluxing CH_2Cl_2 affords unique adducts of the type [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-$BH_2\cdot PR_3$] (**2**) for which spectroscopic data suggest the presence of a pendent boryl group. This was confirmed by a crystal structure determination for the PPh_2Me adduct which shows that **2** is a *nido*-osmapentaborane with a terminal $BH_2\cdot PPh_2Me$ moiety on a basal boron atom adjacent to the metal. The reaction is reversible in the case of PPh_3 and to a lesser extent PPh_2Me, but not for PMe_3. Heating the PPh_3 adduct affords the osmahexaborane **1**, liberating PPh_3, but degradation to the osmapentaborane [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_8] (**6**) and $BH_3\cdot PPh_3$ competes. The tendency to degrade to phosphine·borane increases markedly down the series R_3 = Ph_3, Ph_2Me, and Me_3. When the bidentate bases [1,2-$(PPh_2)_2(CH_2)_2$] and [1,3-$(PPh_2)_2(CH_2)_3$] (abbreviated as dppe and dppp, respectively) are used, two major products are observed in each case. One (**3a**) [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-(BH_2·dppe)] (or **3b**, BH_2·dppp) is analogous to **2** with one end of the bidentate phosphine donor uncoordinated. In the other (**4a**) [2,2-(PPh_3)(CO)-*nido*-2-OsB_4H_7-η^2-3,2-(BH_2·dppe)] (or **4b**, BH_2·dppp), the free end of the bidentate ligand has replaced a PPh_3 group on Os. In the reaction of [$(PPh_2)_2(CH_2)$] (abbreviated as dppm) with **1**, only a species analogous to **3** is observed. The species **3b**, the one involving dppp, has been further modified at the free phosphine end of the ligand, to form [2,2,2-(PPh_3)(CO)-*nido*-2-OsB_4H_7-3-(BH_2·dppp·BH_3)] (**5**).

Introduction

The interaction of boron hydrides with bases represents a major feature in the classical chemistry of these interesting species.[1] The boron hydrides are acidic, from both the perspectives of the Lewis and Brønsted definitions of acidity. Thus, they form simple adducts, are cleaved by bases in well-understood processes, and, in some cases, undergo substantial degradation. The relatively recent development of electron counting rules for clusters allows predictions to be made about structural changes that result from the addition of electron pairs to boranes and indeed to all nonclassical cluster molecules.[2] Electron counting rules predict that addition of electron pairs to a cluster results in the opening up of the polyhedron in the sequence *closo*, *nido*, and *arachno*.[3] There are some simple examples in the literature of systems in which addition of a single electron pair to a small *nido*-borane, in the form of 1 equiv of Lewis base, forms a conventional *arachno*-cluster. This results when CN^- is added directly to B_5H_9[4a] and also from indirect reactions involving PMe_3.[4b] In most of the known cases, however, two electron pairs are added to the *nido*-borane to afford a *hypho*-cluster,[5] or the added base cleaves the borane.[6] There are some examples in which partial degradation of the cage has taken place.[5] The structurally characterized adduct species include $B_5H_9\cdot 2PMe_3$,[5a] $B_4H_8\cdot(Me_2NCH_2)_2$,[5b,c] $B_5H_9\cdot(Ph_2P)_2CH_2$,[5c,d] $B_5H_9\cdot(Ph_2PCH_2)_2$,[5c,d] $B_5H_9\cdot(Me_2NCH_2)_2$,[5c,d] and $B_6H_{10}\cdot 2PMe_3$.[7] Some of these species, for example, $B_5H_9\cdot(Me_2NCH_2)_2$[5c,d] and an unpublished form of $B_5H_9\cdot 2PMe_3$,[8] contain pendent B atoms and can be considered as examples of partial borane cage degradation. In addition, $B_6H_{10}\cdot PMe_3$[9] has also been

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identified from spectroscopic data. Cleavage of boranes by bases played an important role in the early systematization of the boranes. Boranes, generally, are cleaved by bases in processes described as symmetrical and nonsymmetrical cleavage.[6] Parry and Edwards used the results to systematize boranes in terms of reactivity and geometry.[6] There is much less information about degradation mechanisms for boranes, probably due to the inherent fragility of the borane cluster. However, metallaboranes tend to be more robust than the parent borane and are thus more amenable to the study of their reaction chemistry. This is particularly true in the case of hexaborane(10) and its metallahexaborane analogues[10] $[(PPh_3)_2(CO)OsB_5H_9]$ (**1**)[11a] and $[(PPh_3)_2(CO)IrB_5H_8]$.[11b] Hexaborane(10) is quite difficult to handle, readily decomposing at temperatures above about −20 °C in vacuo or inert atmospheres,[12] whereas the metallahexaboranes can be handled in air with relative ease.[10,11] Herein we describe the reactions of phosphine bases with the metallahexaborane $[(PPh_3)_2(CO)OsB_5H_9]$ (**1**).[11a] We describe the formation of a unique species which represents an intermediate in the base-promoted degradation of $[(PPh_3)_2(CO)OsB_5H_9]$ to $[2,2,2\text{-}(PPh_3)_2(CO)\text{-}\textit{nido}\text{-}2\text{-}OsB_4H_8]$ (**6**), and we extend this chemistry to bidentate phosphines and demonstrate a method for the further modification of the metallahexaborane via tethered base reactions. We also suggest that the extrusion/inclusion of a boron vertex may be one of the important processes involved in isomerization processes in boranes and metallaboranes. Some of these results have been described recently in a preliminary communication.[13]

Experimental Section

General Procedures. Solvents used were reagent grade and were dried before use. Some reactions were carried out using a standard vacuum line, a glovebox, and standard techniques for handling air-sensitive compounds.[14] Products were isolated in air using thin layer chromatography (TLC) on 20 × 20 cm glass plates coated with 0.1 cm of silica gel (Aldrich standard grade with gypsum binder and fluorescent indicator), made from aqueous slurries followed by drying in air at 80 °C. Some species were purified using a chromatotron (a radial chromatograph obtained from Harrison Research, Palo Alto, CA) using a 25 cm diameter circular plate coated with 0.1 cm of silica gel (EM Science). $[(PPh_3)_2(CO)OsB_5H_9]$ (compound **1**) was prepared according to the literature method.[11a] The phosphines were obtained as follows. PMe_3 was prepared from PCl_3 and LiMe as described in the literature,[15] PPh_3 and $[(PPh_2)_2(CH_2)_2]$ (abbreviated as dppe) were obtained from Aldrich, PPh_2Me, $[(PPh_2)_2(CH_2)]$ (dppm), and $[(PPh_2)_2(CH_2)_3]$ (dppp) were obtained from Strem, and $THF{\cdot}BH_3$ was obtained from Aldrich. Solvents used were reagent grade and were dried before use. 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 202.5 MHz for phosphorus-31 and on a Varian Unity Plus 300 spectrometer operating at 96.2 MHz for ^{11}B, 299.9 MHz for ^{1}H, and 121.4 MHz for ^{31}P. Chemical shifts are reported in parts per million for $CDCl_3$ solutions, unless otherwise stated, to low field (high frequency) of $Et_2O{\cdot}BF_3$ for ^{11}B, of $SiMe_4$ for ^{1}H, and of 85% H_3PO_4 for ^{31}P. IR spectra were run on 3M sample cards with a Teflon window and also as KBr pellets on a Perkin-Elmer 1600 FT-IR spectrometer and on a Mattson Galaxy 6000 FT-IR spectrometer. Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA. Low-resolution mass spectra were recorded at Monsanto Co., St. Louis, on a Finnegan MAT 95 mass spectrometer in the FAB mode using a 3-nitrobenzyl alcohol matrix (NBA). High resolution mass spectra were obtained by positive ion electrospray using electric sector scanning and standardized with PEG1000. Samples were run in $MeOH/CHCl_3$ (1:1) with 10 mmol of NH_4OH. The masses reported are for the most abundant peak (100%) in the molecular ion envelope, except where indicated otherwise. Mass spectra were also measured on a VG ZAB-E in the FAB mode using 3-NBA at the Washington University Mass Spectrometry Resource.

Synthesis of $[2,2,2\text{-}(PPh_3)_2(CO)\text{-}\textit{nido}\text{-}2\text{-}OsB_4H_7\text{-}3\text{-}BH_2{\cdot}PPh_3]$ (2a). Prior to use, $[(PPh_3)_2(CO)OsB_5H_9]$ (**1**) was dissolved in CH_2Cl_2, filtered through silica gel, washed with CH_2Cl_2, and dried on a rotary evaporator. NMR spectra were run in $CDCl_3$ on **1** to ensure the stability of the compound after storage at 5 °C for several days. Once satisfactory NMR spectra were obtained, **1** was then washed with anhydrous pentane, and the solvent was removed on a rotary evaporator. $[(PPh_3)_2(CO)OsB_5H_9]$ (**1**; 0.204 g, 0.26 mmol) and 0.091 g (0.35 mmol) of PPh_3 were refluxed in 15 mL of dry CH_2Cl_2 for 14 h under an atmosphere of N_2 and then slowly cooled to room temperature. Exploratory paper chromatography using 30:70 CH_2Cl_2/C_5H_{12} on the product mixture and **1** identified the presence of a new compound, **2a**. NMR measurements on the crude sample identified the major impurities as $(PPh_3)_2(CO)OsB_4H_8$[11a] and $BH_3{\cdot}PPh_3$.[16] The product mixture was vacuum-filtered through silica gel; the silica gel was washed with CH_2Cl_2, and solvent was removed from the resulting solution on a rotary evaporator. Purification was effected by TLC using 45:55 $(C_2H_5)_2O/C_5H_{12}$. Bands appeared at R_f 0.1 and R_f 0.8 under UV light. The R_f 0.1 band, after further purification by repeated TLC, gave the title compound **2a** (0.1076 g, 0.1148 mmol) in 44% yield. In an experiment performed using a chromatotron to isolate the product with 70:30 C_5H_{12}/CH_2Cl_2 as eluent and increasing the CH_2Cl_2 composition until the major band separated well, reaction between 0.056 g (0.070 mmol) of **1** and 0.98 g (0.374 mmol) of PPh_3 afforded 0.059 g (0.0553 mmol) of **2a** corresponding to a 79.4% yield. Experiments in an NMR tube indicated that the actual reaction is essentially quantitative, suggesting that some loss of product occurs during chromatographic separation, probably due to reverse equilibration on removal of the excess phosphine. NMR spectra for **2a** are summarized in Table 1 along with those for $(PPh_3)_2(CO)OsB_4H_8$[17] and $(PPh_3)_3(CO)OsB_4H_7(C_4H_9)$[18] for comparison. The IR spectrum of **2a** showed ν_{BH} at 2526 and ν_{CO} at 1941 cm^{-1}. Elemental analysis for $C_{56}H_{56}B_5Cl_2OOsP_3$ {i.e., containing 1.0 mol of CH_2Cl_2 solvent as $\{(PPh_3)_2(CO)OsB_4H_7\}(BH_2{\cdot}PPh_3){\cdot}CH_2Cl_2$} gave C, 59.03; H, 5.06; calcd C, 58.33; H, 4.90. HRMS for **2a** (Finnegan MAT, FAB with 3-NBA) gave m/z (for $M - H_2$)$^+$, $^{12}C_{55}{}^{1}H_{52}{}^{31}P_3{}^{11}B_5{}^{192}Os_1{}^{16}O_1$, 1066.3370 (obsd) 1066.3346 (calcd). Attempts to grow crystals of **2a** for X-ray diffraction study, employing various techniques using combinations involving benzene, chloroform, dichloromethane, pentane, and cyclohexane, were unsuccessful since, in solution during the recrystallization period, **2a** forms an equilibrium mixture (vide infra) from which only $[(PPh_3)_2(CO)OsB_5H_9]$ (**1**) preferentially crystallizes.

Reversibility of the Formation of 2a. Compound **2a** reverted to $[(PPh_3)_2(CO)OsB_5H_9]$ (**1**) when left in solution at room temperature for any length of time. To confirm this, a sample of **2a** in $CDCl_3$ was placed in a 40 °C water bath and monitored periodically. ^{1}H and ^{11}B NMR spectra, obtained after 7 h, showed the presence of compound **2a** and $[(PPh_3)_2(CO)OsB_5H_9]$ (**1**) as the only boron-containing constituents. The bridging proton resonances were sufficiently well

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Table 1. ^{11}B, ^{1}H, and ^{31}P NMR (δ, ppm) for [2,2,2-$(PPh_3)_2(CO)$-2-$OsB_5H_9(Me_3P)$] (**2c**), [2,2,2-$(PPh_3)_2(CO)$-2-$OsB_5H_9(MePh_2P)$] (**2b**), and [2,2,2-$(PPh_3)_2(CO)$-2-$OsB_5H_9(PPh_3)$] (**2a**), with Data for *nido*-[2,2,2-$(PPh_3)_2(CO)$-2-OsB_4H_8][17] and *nido*-[2,2,2-$(PPh_3)_2(CO)$-2-OsB_4H_7(4-*n*Bu)][18] for Comparison

mode/nucleus	$(PPh_3)_2(CO)OsB_5H_9(Me_3P)$[a] (**2c**) $^{31}P\{^1H\}$	$(PPh_3)_2(CO)OsB_5H_9(MePh_2P)$[a] (**2b**) $^{31}P\{^1H\}$	$(PPh_3)_2(CO)OsB_5H_9(Ph_3P)$[a] (**2a**) $^{31}P\{^1H\}$	$(PPh_3)_2(CO)OsB_4H_8$[b] $^{31}P\{^1H\}$	$(PPh_3)_2(CO)OsB_4H_7(n\mathrm{Bu})$ $^{31}P\{^1H\}$
P(2)[d]	+14.5, *t*, $J = 10.4$	+14.6, *t*, $J = 12.1$	+14.9, *t*, $J = 9.3$	+14.1, *d*, $J = 12.2$	+14.4, *d*, $J = 8.6$
P(1)[d]	+9.5 *d*, $J = 9.7$	+9.5, *d*, $J = 9.7$	+9.9, *d*, $J = 9.3$	+7.0, *d*, $J = 12.2$	+6.9, *d*, $J = 8.6$
P(3)	+1.6 (br)	+13.9 (br)	+24.5		

mode/nucleus	$(PPh_3)_2(CO)OsB_5H_9(Me_3P)$[a] (**2c**)		$(PPh_3)_2(CO)OsB_5H_9(MePh_2P)$[a] (**2b**)		$(PPh_3)_2(CO)OsB_5H_9(Ph_3P)$[a] (**2a**)		$(PPh_3)_2(CO)OsB_4H_8$		$(PPh_3)(CO)OsB_4H_7(n\mathrm{Bu})$	
	^{11}B	$^{1}H\{^{11}B\}$	^{11}B	$^{1}H\{^{11}B\}$	^{11}B	$^{1}H\{^{11}B\}$	^{11}B	$^{1}H\{^{11}B\}$	^{11}B	$^{1}H\{^{11}B\}$
4	+8.6	+5.9	+8.6	+5.8	+9.3	+5.3	+8.9	+6.04	+23.2	*c*
3	+8.6	*e*	+8.6	*e*	+9.3	*e*	−7.5	+3.32	−8.9	+3.1
5	−15.1	+0.49, $J = 16$[f]	−16.3	+1.2, $J = 16$[f]	−16.4	+1.3, $J = 16$[f]	−14.2	+1.41	−15.3	+0.92
1[g]	−29.6, $J = 150$	+0.07	−29.5, $J = 122$	+0.06	−28.9, $J = 137$	+0.26	−34.4	+0.25	−29.9	+0.41
6′, 6	−34.4	+0.87,[i] +1.05[i]	−35.5	+1.52, +1.65	−34.4	+1.89, +2.09				
H(3,4)		−1.3		−1.4		−1.4		−1.68		−1.6
H(4,5)		−2.1		−2.3		−2.3		−2.03		−1.9
H(2,5)		−10.3		−10.4		−10.4		−10.34		−10.5
H(2,3)[h]		−9.3, $J = 43$		−9.2, $J = 42$		−9.1, $J = 42$		−9.75, $J = 37$		−10.1, $J = 42$
Me[f]		+1.34, $J = 10$		+1.89, $J = 10$						

[a] $CDCl_3$, 298 K. [b] $CDCl_3$, 294 K for ^1H and ^{11}B and 223 K for ^{31}P NMR. [c] Site of the *n*Bu substituent. [d] P(2) couples with both P(1) and P(3). P(1) couples only with P(2). [e] Site of the $BH_2(L')$ substituent. See assignment B(5) below. [f] Doublets due to $J(^{31}P-^{1}H)$ coupling. [g] Doublets due to $J(^{11}B-^{1}H)$ coupling. [h] Doublets due to $^2J(^{31}P-^{1}H)$ *trans* coupling. [i] Resonances exhibit additional unresolved fine structure due probably to long-range ^1H and ^{31}P coupling.

separated to allow a determination, by peak integration, that they were present as a 50:50 mixture. After an additional 31 h at 50 °C small amounts of [$(PPh_3)_2(CO)OsB_4H_8$] and $BH_3{\cdot}PPh_3$ were observed. Addition of excess PPh_3 to a sample of the 50:50 mixture of **2a** and [$(PPh_3)_2(CO)OsB_5H_9$] followed by warming to 40 °C for a day resulted in the complete disappearance of compound **1**, leaving an essentially pure solution of **2a**.

Synthesis of [{$(PPh_3)_2(CO)OsB_4H_7$}($BH_2{\cdot}PPh_2Me$)] (2b). A 0.252 g (0.321 mmol) sample of **1** was added to a 50 mL two-neck round-bottom flask attached to a small condenser on the vacuum line. Into the flask was transferred 20 mL of dry distilled CH_2Cl_2 on the vacuum line, and under N_2 flow, 0.072 mL (0.383 mmol) of PPh_2Me was introduced via syringe. The mixture was stirred and allowed to reflux for 16 h. The solvent was removed on a rotary evaporator and the product recrystallized by dissolving it in CH_2Cl_2 and adding C_5H_{12} to afford 261 mg of product corresponding to an 82% yield. The purity of the species was confirmed by NMR spectral data, which are found in Table 1. The IR spectrum of **2b** showed ν_{BH} at 2522 and ν_{CO} at 1941 cm^{-1}. Elemental analysis for $C_{50}H_{52}ClP_3B_5OsO$ {i.e., containing 0.5 mol of solvent as {$(PPh_3)_2(CO)OsB_4H_7$}($BH_2{\cdot}PPh_2Me$)$\cdot 0.5CH_2Cl_2$} gave C, 57.45; H, 5.04; calcd C, 57.66; H, 5.03. Crystals suitable for X-ray diffraction were grown as thin colorless plates from $CDCl_3/Et_2O$.

Synthesis of [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_7-3-$BH_2{\cdot}PMe_3$] (2c). A 0.206 g (0.256 mmol) sample of **1** was added to a 50 mL two-neck round-bottom flask attached to a small condenser. Under N_2 flow, 20 mL of dry distilled benzene was introduced using a syringe. The flask was attached to a vacuum line, via the condenser, and evacuated, and 0.247 mmol of PMe_3 was condensed in at −196 °C from a calibrated flask. The mixture was stirred for 22 h at 50 °C and then slowly cooled to room temperature. Solvent was removed on a rotary evaporator, and the product was identified, in quantitative yield, as **2c** by its NMR spectral data, which are given in Table 1. The IR spectrum of **2c** showed ν_{BH} at 2517 and ν_{CO} at 1940 cm^{-1}. Elemental analysis for $C_{41}H_{48}P_3B_5OsO$ gave unsatisfactory results.

Thermolysis of 2a, 2b, and 2c. NMR samples consisting of 20 mg of sample dissolved in 1 mL of $CDCl_3$ were heated at 40 °C for 17 h, examined using proton NMR spectrometry, then heated at 50 °C for an additional 18 h, and examined again spectrometrically. The results are summarized in Table 2.

Synthesis of dppe Adducts of $OsB_5H_9(PPh_3)_2(CO)$: [{$(PPh_3)_2(CO)OsB_4H_7$}($BH_2{\cdot}$dppe)] (3a) and [2,2-$(PPh_3)(CO)$-*nido*-2-OsB_4H_7-η^2-3,2-($BH_2{\cdot}$dppe)] (4a). A 135 mg (0.168 mmol) sample of $OsB_5H_9(PPh_3)_2(CO)$ and 68 mg (0.171 mmol) of dppe were placed in a one-neck 50 mL round-bottom flask, and 10 mL of CH_2Cl_2 was condensed into the flask at −198 °C. The mixture was allowed to warm to room temperature and stirred for 4 days. After being concentrated to about 0.5 mL, by rotary evaporation, the solution was applied to a TLC plate (with silica gel to a thickness of 0.1 cm) and separated using 70:30 CH_2Cl_2/C_5H_{12} as the mobile phase. A large band at R_f 0.5 was shown, by ^{31}P NMR spectrometry, to consist of a mixture of two dppe complexes of **1**, about 96 mg, *ca*. 50% yield. The mixture of complexes was redissolved in 0.5 mL of CH_2Cl_2 and subjected to a second TLC separation using 60:40 CH_2Cl_2/C_5H_{12}. [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_7-3-($BH_2{\cdot}$dppe)] (**3a**) was isolated at R_f 0.4 in 9.3% yield (63 mg) and [2,2-$(PPh_3)(CO)$-*nido*-2-OsB_4H_7-η^2-3,2-($BH_2{\cdot}$dppe)] (**4a**) at R_f 0.3 in 9.7% yield (14 mg). These yields were not optimized. Using a chromatotron, starting with 50 mg (0.062 mmol) of **1**, yields of 66% **3a** (49 mg, 0.041 mmol) and 19% **4a** (11 mg, 0.012 mmol) were obtained. Attempts to grow crystals suitable for X-ray diffraction were unsuccessful. NMR data for **3a** and **4a** are found in Tables 3 and 4, respectively, along with data for **2b** for comparison. Elemental analysis: **3a** for $C_{63}H_{63}B_5OOsP_4$ gave C, 61.79; H5.30; calcd C, 62.83; H, 5.27. Compound **4a** gave unsatisfactory results. Mass spectrometric data: (**3a**) LRMS, VG ZAB with 3-NBA, calcd for $C_{63}H_{63}B_5OOsP_4$ $[M]^+$ 1205.2, obsd 1204.39; (**4a**) HRMS, VG ZAB with 3-NBA, calcd for $C_{45}H_{48}B_5OOsP_3$ $[M + Li - H]^+$ 948.312, obsd 948.309. The mass envelopes for the measured masses for both **3a** and **4a** match those calculated from the known isotopic abundances of the constituent elements. The data are available as Supporting Information.

Reaction of 1 with dppe Monitored over Time in an NMR Tube. 1:1 Mole Ratio. A 25 mg sample of $OsB_5H_9(PPh_3)_2(CO)$ and 13 mg

Table 2. Results of the Thermolysis of [$(PPh_3)_2(CO)OsB_4H_7{\cdot}BH_2{\cdot}PPh_3$] (**2a**), [$(PPh_3)_2(CO)OsB_4H_7\text{-}BH_2{\cdot}PPh_2Me$] (**2b**) and [$(PPh_3)_2(CO)OsB_4H_7\text{-}BH_2{\cdot}PMe_3$] (**2c**), in $CHCl_3$ Solution Followed by ^1H NMR Spectroscopic Examination[a]

temp (°C), time (h)	thermolysis products	**2a**, L′ = PPh_3	**2b**, L′ = PPh_2Me	**2c**, L′ = PMe_3	**1**
40, 17 h	$L_3OsB_5H_9{\cdot}L'$	53	85	66	0
	$L_3OsB_5H_9$	47	15	0	89
	$L_3OsB_4H_8$	0	0	34	11
40, 35 h	$L_3OsB_5H_9{\cdot}L'$	37	80	51	0
	$L_3OsB_5H_9$	63	20	0	85
	$L_3OsB_4H_8$	0	0	49	15
40, 35 h; 50, 18 h	$L_3OsB_5H_9{\cdot}L'$	18	51	0	
	$L_3OsB_5H_9$	60	35	0	46
	$L_3OsB_4H_8$	22	14	100	54

[a] Also included are data for thermolysis of [$(PPh_3)_2(CO)OsB_5H_9$] (**1**). $(PPh_3)_2(CO)$ is abbreviated as L_3. Values in percent normalized to 100%. Obtained by relative peak area measurement for the bridging proton resonances.

Table 3. ^{11}B, ^1H, and ^{31}P NMR (δ, ppm) Data for [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}PPh_2Me)$] (**2b**), [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppe)$] (**3a**), with Data for [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppp)$] (**3b**) and [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppm)$] (**3c**)

mode/nucleus	$(PPh_3)_2(CO)OsB_5H_9(MePh_2P)$[a] (**2b**) $^{31}P\{^1H\}$	$(PPh_3)_2(CO)OsB_5H_9(dppe)$[a] (**3a**) $^{31}P\{^1H\}$	$(PPh_3)_2(CO)OsB_5H_9(dppp)$[a] (**3b**) $^{31}P\{^1H\}$	$(PPh_3)_2(CO)OsB_5H_9(dppm)$[a] (**3c**) $^{31}P\{^1H\}$
P(2)[b]	+14.6, *t*, $J = 12.1$	+13.9, *t*, $J = 11$	+14.3, *t*, $J = 11.0$	+13.4, *t*, $J = 10.6$
P(1)[b]	+9.5, *d*, $J = 9.7$	+9.8, *d*, $J = 10$	+9.2, *d*, $J = 10.3$	+9.6, *d*, $J = 10.6$
P(3)	+13.9 (br)	+22.1, *d*, $J = 42$	+19 (br)	+19.9, *d*, $J = 36.6$
P(4)		−11.4, *d*, $J = 42$	−18.3	−25.8, *d*, $J = 36.6$

	$(PPh_3)_2(CO)OsB_5H_9(MePh_2P)$[a] (**2b**)		$(PPh_3)_2(CO)OsB_5H_9(dppe)$[a] (**3a**)		$(PPh_3)_2(CO)OsB_5H_9(dppp)$[a] (**3b**)		$(PPh_3)_2(CO)OsB_5H_9(dppm)$[a] (**3c**)	
mode/nucleus	^{11}B	$^1H\{^{11}B\}$	^{11}B	$^1H\{^{11}B\}$	^{11}B	$^1H\{^{11}B\}$	^{11}B	$^1H\{^{11}B\}$
4	+8.6	+5.8	+8.8	+5.45	+8.53	+5.44	+8.3	5.47
3	+8.6	*c*	+8.8	*c*	+8.53	*c*	+8.3	*c*
5[d]	−16.3	+1.2, *d*, $J = 16$	−14.9	+1.34	−15.34	+1.31	−15.7	+1.37
1[e]	−29.5, *d*, $J = 122$	+0.06	−29.4, *d*, $J = 119$	+0.17	−29.62	+0.08	−29.6, *d*, $J = 117$	0.09
6, 6′	−35.5	+1.65, +1.52	−37.9	+1.74, +1.52	−37.36	+1.66, +1.48	−34.4	+1.87, +1.64
H(3,4)		−1.4		−1.54		−1.55		−1.38
H(4,5)		−2.3		−2.26		−2.26		−2.25
H(2,5)		−10.4		−10.31		−10.33		−10.31
H(2,3)[f]		−9.2, $J = 42$		−9.28, $J = 42$		−9.11, $J = 33$		−9.22, $J = 41$
CH_2[g]				+2.15, *m*, 2H +2.30, *m*, 1H +2.58, *d*, 1H[h]		+2.51, *m*, 2H +1.7, m, 4H		+3.27, *dd*, 2H $J_{H-P} = 9.5$ $J_{H-H} = 2.8$
Me[d]		+1.89, *d*, $J = 10$						

[a] $CDCl_3$, 298 K. [b] P(2) couples with both P(1) and P(3). P(1) couples only with P(2). [c] Site of the $BH_2(L')$ substituent. [d] $J(^{31}P-^1H)$. [e] $J(^{11}B-^1H)$. [f] Doublets due to $^2J(^{31}P-^1H)$*trans* coupling. [g] Methylene protons on bidentate phosphine backbone. [h] $^1H\{^{31}P\}$spectrum: δ +2.15 resonance, $P(4)Ph_2CH_2$, δ +2.30 and +2.58 resonances are dt, $H_2BPPh_2CH_2$, $J(^1H-^1H') = 4.0$, $J(^1H-^1H) = 13.5$ Hz.

of dppe were dissolved in 0.7 mL of $CDCl_3$ in an NMR tube. After 1 day at room temperature, the ^{31}P NMR spectrum indicated that complexes **3a** and **4a** were present in a 2:1 ratio. If the mixture is allowed to stand for 4 days at room temperature, the ratio of two complexes falls to 1:1.

1:2 Mole Ratio. A 30 mg sample of $OsB_5H_9(PPh_3)_2(CO)$ and 31 mg of dppe were dissolved in 0.7 mL of $CDCl_3$ in an NMR tube. After 3 h at room temperature, 90% of complex **3a** and only 10% of **4a** were observed by ^{31}P NMR. After 4 days at room temperature, 75% of complex **3a** and 25% of complex **4a** remained.

Synthesis of dppp Adducts of $OsB_5H_9(PPh_3)_2(CO)$: [2,2,2-$(PPh_3)_2$-(CO)-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppp)$] (3b) and [2,2-$(PPh_3)(CO)$-*nido*-2-OsB_4H_7-η^2-3,2-$(BH_2{\cdot}dppp)$] (4b). A 100 mg (0.124 mmol) sample of $(PPh_3)_2(CO)OsB_5H_9$ and 55 mg (0.133 mmol) of dppp were placed in a one-necked 50-mL round-bottom flask. To this was added 25 mL of freshly distilled CH_2Cl_2, and the mixture was then allowed to stir at room temperature for 6 h. Solvent was completely removed on a rotary evaporator, and NMR studies were carried out on the crude product. The ^{31}P NMR spectrum suggested that there had been quantitative conversion of $(PPh_3)_2(CO)OsB_5H_9$ to compounds **3b** and **4b**, in a ratio of 2:1. The mixture of complexes was then redissolved in 0.5 mL of CH_2Cl_2 and applied to a TLC plate. A 60:40 mixture of CH_2Cl_2/C_5H_{12} was used as eluent. [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppp)$] (**3b**) was isolated at R_f 0.35 in 18.6% yield (30 mg), and [2,2-(PPh_3)-(CO)-*nido*-2-OsB_4H_7-η^2-3,2-$(BH_2{\cdot}dppp)$] (**4b**) was isolated at R_f 0.45 in 12.7% yield (16 mg); both yields were not optimized. Using a chromatotron, starting with 50 mg of **1** (0.062 mmol), yields of 60% **3b** (45 mg, 0.037 mmol) and 22.6% **4b** (13 mg, 0.014 mmol) were obtained. Elemental analysis: **3b** for $C_{64}H_{65}B_5O_1Os_1P_4$ gave C, 62.41; H, 5.68; calcd C, 63.09; H, 5.38. Compound **4b** gave unsatisfactory results. Mass spectrometric data: (**3b**) HRMS, VG ZAB-E, FAB with 3-NBA, calcd for $^{12}C_{64}{}^1H_{64}{}^{11}B_4{}^{10}B_1{}^{16}O_1{}^{192}Os_1{}^{31}P_4$ $[M + H - H_2]^+$ 1218.4034, obsd 1218.3878; (**4b**) LRMS, VG ZAB-SET in FAB mode with 3-NBALi, calcd for $(M + Li - H)^+$ $^{12}C_{46}{}^1H_{49}{}^{11}B_5{}^{192}Os_1{}^{31}P_3{}^7Li$ 964.32, obsd 964.33. The mass envelope for the observed spectrum for **4b** matches that calculated from the known isotopic abundances of the constituent elements. A major envelope is also centered at 946.32 corresponding to [2,2,2-$(PPh_3)(dppp)(CO)OsB_4H_8$], one of the expected degradation products of **4b**. The data are available as Supporting Information. NMR data for **3b** and **4b** are found in Tables 3 and 4, respectively, along with data for **2b** for comparison.

Reaction of 1 with dppp Monitored over Time in an NMR Tube. A 20 mg (0.025 mmol) sample of [2,2,2-$(PPh_3)_2(CO)$-*nido*-2-OsB_5H_9] (**1**) and 21 mg (0.051 mmol) of dppp were placed in an NMR tube and

Table 4. ^{11}B, ^{1}H, and ^{31}P NMR (δ, ppm) Data for [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-(BH_2·PPh_2Me)] (**2b**), [2,2-(PPh_3)(CO)-*nido*-2-OsB_4H_7-η^2-3,2-(BH_2·dppe)] (**4a**), [2,2-(PPh_3)(CO)-*nido*-2-OsB_4H_7-η^2-3,2-(BH_2·dppp)] (**4b**), and [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-(BH_2·dppp.BH_3)] **5**

mode/nucleus	$(PPh_3)_2(CO)OsB_5H_9(PPh_2Me)$[a] (**2b**)^{31}P{^{1}H}	$(PPh_3)(CO)OsB_5H_9$(dppe)[a] (**4a**) ^{31}P{^{1}H}	$(PPh_3)(CO)OsB_5H_9$(dppp)[a] (**4b**) ^{31}P{^{1}H}	$(PPh_3)_2(CO)OsB_5H_9(dppp)BH_3$[a] (**5**) ^{31}P{^{1}H}
P(2)[b]	+14.6, *t*, $J = 9.7$	+14.3[c]	+13.64[c]	+13.60[c]
P(1)[b]	+9.5, *d*, $J = 12.1$	+10.0, *d*, $J = 10.0$	+9.29, *d*, $J = 10.1$	+9.13, *d*, $J = 11.9$
P(3)	+13.9 (br)	+23 (br)	+19.4 (br)	+18.8 (br)
P(4)				+16 (br)

	$(PPh_3)_2(CO)OsB_5H_9(PPh_2Me)$[a] (**2b**)		$(PPh_3)(CO)OsB_5H_9$(dppe)[a] (**4a**)		$(PPh_3)(CO)OsB_5H_9$(dppp)[a] (**4b**)		$(PPh_3)_2(CO)OsB_5H_9(dppp)BH_3$[a] (**5**)	
mode/nucleus	^{11}B	^{1}H{^{11}B}	^{11}B	^{1}H{^{11}B}	^{11}B	^{1}H{^{11}B}	^{11}B	^{1}H{^{11}B}
4	+8.6	+5.8	+9.3	+5.36	+8.97	+5.38	+8.3	+5.38
3	+8.6	*d*	+9.3	*d*	+8.97	*d*	+8.3	*d*
5[e]	−16.3	+1.2, *d*, $J = 16$	−16.6	+1.01	−15.40	+1.25	−15.2	+1.48
1[f]	−29.5, *d*, $J = 122$	+.06	−29.1	+0.18	−29.68	−0.01	−29.7	−0.01
6, 6′	−35.5	+1.65, +1.52	−37.4	+1.71, +1.57	−38.57	+1.60, +1.44	−38.9	+1.62, +1.46
7							−38.9	+0.91, *d*, $J = 16.1$
H(3,4)		−1.4		−1.63		−1.61		−1.61
H(4,5)		−2.3		−2.34		−2.30		−2.26
H(2,5)		−10.4		−10.42		−10.35		−10.28
H(2,3)[g]		−9.2, $J = 42$		−9.23, $J = 41$		−9.35, $J = 33.1$		−9.32, *d*, $J = 39.5$
CH_2[h]				+2.5, *m*, 4H	+2.36, *m*, 4H	+1.77, *m*, 2H		2.47, 2.25, 1.81, each *m*, 2H
Me[e]		+1.89, *d*, $J = 10$						

[a] $CDCl_3$, 298 K. [b] P(2) couples with both P(1) and P(3). P(1) couples only with P(2). [c] Unresolved triplet. [d] Site of $BH_2(L')$ substituent. [e] $J(^{31}P-^{1}H)$. [f] $J(^{11}B-^{1}H)$. [g] Doublets due to $^{2}J(^{31}P-^{1}H)$ *trans* coupling. [h] Methylene protons on the bidentate phosphine backbone.

dissolved in 1 mL of $CDCl_3$. The ^{31}P NMR spectrum was monitored periodically at room temperature. After 1 h, 92% **3b** and 8% **4b** were present in the sample, along with traces of PPh_3. After approximately 2 h, 87% **3b** and 13% **4b** were present, and after 6 h, 84% **3b** and 16% **4b** were present in the solution along with ca. 2.4% PPh_3.

Synthesis of [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-(BH_2·dppm)] (3c). A 100 mg (0.124 mmol) sample of $(PPh_3)_2(CO)OsB_5H_9$ and 53 mg (0.138 mmol) of dppm were placed in a one-neck 50 mL round-bottom flask. To this was added 25 mL of freshly distilled CH_2Cl_2. The mixture was then allowed to stir at room temperature for 6 h. The mixture was pumped dry on a rotary evaporator, and NMR studies were carried out on the crude product. The ^{31}P NMR spectrum showed that there had been quantitative conversion of $(PPh_3)_2(CO)OsB_5H_9$ to compound **3c**. In an attempt to purify the product it was redissolved in 0.5 mL of CH_2Cl_2 and applied to a TLC plate. A 50:50 mixture of CH_2Cl_2/C_5H_{12} was used as eluent. [{$(PPh_3)_2(CO)OsB_5H_7$}(BH_2·dppm)] (**3c**) was isolated at R_f 0.5 in 35% yield (51 mg); the yield was not optimized. However, using the chromatotron, yields of up to 83%, based on **1**, were obtained. Elemental analysis: **3c** for $C_{62}H_{61}B_5OOsP_4$ gave C, 60.26; H, 5.22; calcd for $C_{62.5}H_{62}B_5OOsP_4Cl$, i.e., containing 0.5 mol of CH_2Cl_2, C, 60.76; H, 5.06. Mass spectrometric data: LRMS, VG ZAB-E in FAB mode with 3-NBA, calcd for $(M - CO)^+$ $^{12}C_{61}{}^{1}H_{62}{}^{11}B_5{}^{192}Os_1{}^{31}P_4$ 1165.4, obsd 1165.4. The mass envelope for the observed spectrum for **3c** matches that calculated from the known isotopic abundances of the constituent elements. The data are available as Supporting Information. NMR data for **3c** are found in Table 2, along with data for **2b** for comparison.

Synthesis of [2,2,2-(PPh_3)(CO)-*nido*-2-OsB_4H_7-3-(BH_2·dppp·BH_3)] (5). In a two-neck 50 mL round-bottom flask was placed 50 mg (0.041 mmol) of **3b**, and the flask was then connected to a high-vacuum line and evacuated. The flask was cooled to −196 °C, and 20 mL of CH_2Cl_2 was condensed in. The mixture was allowed to warm to −78 °C, where, under a dynamic flow of dry nitrogen gas, 0.4 mL of 1.0 M BH_3·THF (0.4 mmol) was added. The solution was allowed to warm to room temperature slowly and maintained at that temperature for 30 min. Then the mixture was evacuated to complete dryness and then exposed to the air. A ^{31}P NMR spectrum of the crude product showed that no **3b** remained but a new species (**5**) was detected. This crude product was then applied to a TLC plate and separated using a 50:50 CH_2Cl_2/C_5H_{12} mobile phase. [2,2,2-(PPh_3)(CO)-*nido*-2-OsB_4H_7-3-(BH_2·dppp·BH_3)] (**5**) was isolated as a broad band at R_f 0.3 in 55% yield (28 mg based on **3b**). Experiments using a chromatotron, in which the intermediate compound **3b** was not isolated, afforded yields of 42.5%, based on 50 mg (0.062 mmol) of **1**. NMR data for **5** are found in Table 4, along with data for **2b** for comparison. Elemental analysis for $C_{64}H_{68}B_6O_1Os_1P_4$ gave C, 60.61; H, 6.06; calcd C 62.38; H, 5.56. Mass spectral data: HRMS VG ZAB, FAB with 3-NBA, calcd for $^{12}C_{64}{}^{1}H_{67}{}^{11}B_6{}^{16}O_1{}^{192}Os_1{}^{31}P_4$, $(M + H - H_2)^+$ 1234.4393, obsd 1234.4356.

X-ray Diffraction Analysis. A thin colorless plate crystal of compound **2b** was mounted onto glass fibers in a random orientation. Preliminary examination and data collection were performed using a Siemens SMART charge-coupled device (CCD) detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Preliminary unit cell constants were determined with a set of 45 narrow-frame scans (0.3° in ω). A total of 4026 frames of intensity data were collected with a frame width of 0.3° in ω at a crystal-to-detector distance of 4.91 cm. The double-pass method of scanning was used to reduce noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT[19a] was used for frame integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by a global refinement of the *x, y, z* centroids of 8192 reflections ($\theta < 26.0°$). Absorption corrections were applied to the data using equivalent reflections (SADABS).[19b] Crystal data and parameters for intensity data collection are listed in Table 5.

The SHELXTL-PLUS software package[19c] was used for structure solutions (by direct methods) and refinement. Full-matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)_2$. The non-hydrogen atoms were refined anisotropically to convergence. All the hydrogen atoms, except the cage H atoms, were included in their calculated positions. Some cage hydrogens were located from the difference Fourier map but were not included in the final refinement as they could not be refined to confirm their positions. The structure refinement parameters are given in Table 5, and selected bond angles and distances are given in Table 6. A complete list of positional and isotropic displacement coefficients for the hydrogen atoms, anisotropic displacement coefficients for the non-hydrogen atoms, and bond distances and angles are available as Supporting Information.

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(19) (a) Siemens Analytical X-Ray, Madison, WI, 1995. (b) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−38. (c) Sheldrick, G. M. Bruker Analytical X-Ray Division, Madison, WI, 1999.

Table 5. Crystal Data and Structure Refinement for **2b**

identification code	b9895ns
empirical formula	$C_{51}H_{53}B_5Cl_3OOsP_3$
fw	1125.44
temp, K	293(2)
wavelength, Å	0.710 73
cryst syst	monoclinic
space group	P2(1)
unit cell dimensions	$a = 10.806\,40(10)$ Å, $\alpha = 90°$ $b = 12.0477(2)$ Å, $\beta = 98.2580(10)°$ $c = 19.9238(4)$ Å, $\gamma = 90°$
vol, Å^3	2567.03(7)
Z	2
D_{calcd}, Mg/m^3	1.456
abs coeff, mm^{-1}	2.770
F(000)	1128
cryst size, mm^3	0.1 × 0.1 × 0.05
θ range for data collectn, deg	1.90−26.00
index ranges	$-13 \leq h \leq 10, -14 \leq k \leq 14, -24 \leq l \leq 21$
no. of reflns collected	12 397
independent reflns	9311 [R(int) = 0.0702]
completeness to $\theta = 26.00°$, %	99.9
abs correctn	semiempirical, sadabs
max and min transm	0.93 and 0.55
refinement method	full-matrix least-squares on F^2
no. of data/restraints/ param	9311/1/577
goodness-of-fit on F^2	1.015
final R indices [$I > 2\sigma(I)$]	R1 = 0.0738, wR2 = 0.1660
R indices (all data)	R1 = 0.1103, wR2 = 0.1837
absolute structure parameter	−0.061(16)
largest diff peak and hole, e·Å^{-3}	1.874 and −1.865

Table 6. Bond Lengths (Å) and Angles (deg) for **2b**

Os(2)−C(1)	1.881(17)	Os(2)−B(1)	2.226(18)
Os(2)−P(2)	2.333(4)	Os(2)−B(5)	2.353(17)
Os(2)−P(1)	2.356(4)	Os(2)−B(3)	2.40(2)
P(3)−B(6)	1.92(2)	O(1)−C(1)	1.14(2)
B(1)−B(5)	1.70(3)	B(1)−B(4)	1.72(3)
B(1)−B(3)	1.76(3)	B(3)−B(6)	1.70(3)
B(3)−B(4)	1.85(3)	B(4)−B(5)	1.78(3)
C(1)−Os(2)−B(1)	98.9(7)	C(1)−Os(2)−P(2)	92.6(5)
B(1)−Os(2)−P(2)	97.3(5)	O(1)−C(1)−Os(2)	170.6(17)
B(1)−Os(2)−B(5)	43.5(7)	P(2)−Os(2)−B(5)	87.3(5)
C(1)−Os(2)−P(1)	96.0(6)	B(1)−Os(2)−P(1)	153.6(5)
P(2)−Os(2)−P(1)	103.67(14)	B(5)−Os(2)−P(1)	121.1(6)
C(1)−Os(2)−B(3)	88.5(7)	B(1)−Os(2)−B(3)	44.5(6)
P(2)−Os(2)−B(3)	141.3(5)	B(5)−Os(2)−B(3)	69.1(6)
P(1)−Os(2)−B(3)	114.7(5)	B(5)−B(1)−B(4)	62.5(14)
B(5)−B(1)−B(3)	102.3(15)	B(4)−B(1)−B(3)	64.2(13)
B(5)−B(1)−Os(2)	72.2(9)	B(4)−B(1)−Os(2)	105.8(12)
B(3)−B(1)−Os(2)	73.0(9)	B(6)−B(3)−B(1)	138.5(17)
B(6)−B(3)−B(4)	133.9(16)	B(1)−B(3)−B(4)	56.9(11)
B(6)−B(3)−Os(2)	130.7(12)	B(1)−B(3)−Os(2)	62.5(8)
B(4)−B(3)−Os(2)	95.4(12)	B(1)−B(4)−B(5)	58.2(11)
B(1)−B(4)−B(3)	58.8(12)	B(5)−B(4)−B(3)	96.0(12)
B(1)−B(5)−B(4)	59.3(13)	B(1)−B(5)−Os(2)	64.2(8)
B(4)−B(5)−Os(2)	99.1(12)	B(3)−B(6)−P(3)	110.7(13)

Results and Discussion

Reactions of Simple Organophosphines with [2,2,2-$(PPh_3)_2$-(CO)-*nido*-2-OsB_5H_9] (1). Refluxing [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_5H_9] (**1**) with a slight excess of PPh_3 in CH_2Cl_2 under N_2 affords a pale-yellow, air-stable crystalline solid [2,2,2-$(PPh_3)_2$-(CO)-*nido*-2-OsB_4H_7-3-BH_2·PPh_3] (**2a**) in essentially quantitative yield. The species **2a** was first observed in our laboratory as a minor impurity in the preparation of **1**,[11a] along with traces of $(PPh_3)_2(CO)(H)OsB_3H_8$,[20] $(PPh_3)_2(CO)OsB_4H_8$,[11a,17,21] and [$(PPh_3)_2(CO)OsB_9H_{13}$].[21] Mass spectrometric data for the trace quantities obtained suggested the formulation, but identification of **2a** initially eluded us because precedence based on electron counting rules suggested an *arachno*-type structure[2] and satisfactory elemental analysis data were obtainable only after we discovered how to prepare the species in reasonable quantities. NMR data for **2a** are given in Table 1. The ^{11}B NMR spectrum exhibits four signals in a 2:1:1:1 area ratio at +9.3, −16.4, −28.9, and −34.4 ppm, respectively, and the ^{1}H{^{11}B} spectra suggested the presence of five terminal and four bridging H atoms, affording resonances at +5.32, +2.09, +1.89, +1.3, +0.26, −1.4, −2.3, −9.1, and −10.4 ppm. Two of the resonances assigned to bridging hydrogens were at high field, a doublet at −9.1 and a singlet at −10.4 ppm, suggesting that they were bridging to the metal atom. Selective decoupling experiments indicated that single terminal H resonances were associated with each of three of the boron resonances, including the one of intensity 2, and the high-field boron resonance was associated with two terminal H atoms. This suggested that one boron atom had a substituent and that the substituent probably contained a BH_2 group. In accord with this, the two inequivalent terminal proton resonances at +0.87 and +1.05 ppm feature symmetrical, mirror-image fine structure which we attribute to long-range ^{1}H and ^{31}P coupling and which results in an apparent doublet structure. This is consistent with the proposed structure because the two hydrogens are on a prochiral center and are, therefore, diastereotopic, thus exhibiting different chemical shifts. Irradiation at +9.3 ppm, the boron-11 resonance of area 2, led to decoupling of the proton resonance at +5.32 ppm and the bridging H resonance at −1.4 ppm. Also the doublet resonance at −9.1 ppm showed decoupling as did the B−H−B resonance at −2.3 ppm although the effect for the latter was much weaker. This allowed assignments of the resonances for **2a** given in Table 1 which were confirmed by 2-D COSY experiments. The low-temperature ^{31}P NMR spectrum indicated the presence of three inequivalent P atoms; a doublet and a triplet at +9.9 and +14.9 ppm, respectively, were assigned to the ligands on Os, and are analogous to those seen for **1** and [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_8] (**6**)[11a,17] and a broad resonance at +24.5 ppm, suggesting that this P atom was bonded directly to boron.

The ^{11}B NMR spectrum of **2a** is similar to that of the osmapentaborane [$(PPh_3)_2(CO)OsB_4H_8$] (**3**)[11a,17] except that one of the resonances is shifted downfield by about +17 ppm and there is an additional resonance, B(6), whose chemical shift of −34.4 ppm is comparable to those for BH_3·PR_3 compounds (ca. −37 ppm).[16,22] The ^{11}B spectrum is similarly comparable to that of the substituted derivative [$(PPh_3)_2(CO)OsB_4H_7(C_4H_9)$],[18] for which the resonance containing the substituent is shifted +18 ppm downfield from that for the unsubstituted species **6**. These observations suggested that **2a** is an osmapentaborane with a pendent BH_2·PPh_3 group bonded to one of the basal boron atoms. Selective decoupling experiments indicated that the pendent boron was bonded to a basal boron atom adjacent to the Os atom, so we presumed that the reaction described in eq i

$$[(PPh_3)_2(CO)OsB_5H_9] + PPh_3 \rightleftharpoons [\{(PPh_3)_2(CO)OsB_4H_7\}(BH_2{\cdot}PPh_3)] \quad \text{(i)}$$

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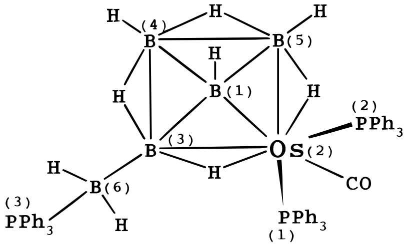

Figure 1. Proposed structure of [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-BH_2•PPh_3] (**2a**).

had taken place and that the structure of **2a** was that represented in the sketch shown in Figure 1. Stick diagrams comparing the ^{11}B NMR spectra of [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_5H_9] (**1**),[11a] [2,2,2-$(PPh_3)_2$(CO)-*nido*-OsB_4H_7-4-(C_4H_9)],[18] [2,2,2-*nido*-$(PPh_3)_2$-(CO)OsB_4H_8] (**6**),[17] and [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-BH_2•PPh_3] (**2a**) are given in Figure 2, and a similar comparison for the ^{1}H NMR spectra is given in the Supporting Information. They nicely illustrate the assignments we make above. Although the NMR spectra for [$(PPh_3)_2$(CO)OsB_5H_9] and [$(PPh_3)_2$(CO)-OsB_4H_8] leave some doubt about their structures, since all the bridging H atoms are inequivalent, we have recently determined their structures by X-ray crystallography and confirmed that the bridging H atoms are symmetrically disposed as shown in Figure 2.[21] Attempts to obtain crystals of **2a** suitable for X-ray analysis were unsuccessful. However, we were able to demonstrate similar chemistry with the bases PMe_3 and PPh_2Me, and the species [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-BH_2•PPh_2Me] (**2b**) provided crystals suitable for a high-quality X-ray analysis.

The structure of **2b**, represented in Figure 3, confirms that the species is an osmapentaborane skeleton with a pendent BH_2•PR_3 group. As expected the structure differs little from that of B_5H_9 except for features influenced by the presence of the Os atom. Thus, the angle B(5)−Os−B(3) is 69.1(6)° as opposed to 90° in B_5H_9, and the apex−base and the base−base interboron distances are slightly longer in **2b** than in the latter.[23] The angle B(1)−B(3)−B(6), 138.5(17)°, is quite close to the B(1)−B(2)−H(2) angle in B_5H_9, 130(2)°, indicating that the BH_2•PR_3 moiety occupies a location very similar to that of the terminal H atom it supplants in B_5H_9. Crystal data are given in Table 5, and selected bond distances and angles are given in Table 6.

The reversibility of the reaction described in eq i was established by heating a purified sample of **2a** in $CDCl_3$ at 40 °C for 17 h, which resulted in recovery of 53% of **1**. Heating **2a** for extended periods at 50 °C results in the formation of [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_8] (**6**) and BH_3•PPh_3. A suggested general reaction pathway is given in Scheme 1. Nucleophilic attack by the phosphine PR_3 would be expected to take place at a basal boron atom.[24] Attachment of the phosphine would supply two electrons, and thus the cluster would open up to form an unstable intermediate *arachno*-species that rearranges, as indicated in Scheme 1, to afford [$(PPh_3)_2$(CO)-OsB_4H_7(BH_2•PR_3)] (**2**). Loss of phosphine•borane affords the osmapentaborane [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_8] (**6**). Obviously this latter step must involve the incorporation of two additional H atoms from solution species since [$(PPh_3)_2$(CO)-OsB_4H_7(BH_2•PR_3)], which is **2**, contains two fewer H atoms than the combination of **6** and BH_3•PR_3.

The position of the equilibrium and the tendency to degrade to the osmapentaborane **6** are dependent on the base strength. The reactions between **1** and PPh_2Me and PMe_3 afford products analogous to **2a**, [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-BH_2•PPh_2-Me] (**2b**), and [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-BH_2•PMe_3] (**2c)**. The details of their formation and characterization are given in the experimental section, and NMR spectral data are given in Table 1. As seen in Table 1, the NMR data for the three species **2a**, **2b**, and **2c** are very similar. Results obtained for the comparative stability of products of reactions of **1** with the bases PPh_3, PPh_2Me, and PMe_3, i.e., **2a**, **2b**, and **2c**, are given in Table 2. Thus, PMe_3 reacts with **1** to afford **2c**, which on heating does not regenerate **1** but degrades to [2,2,2-$(PPh_3)_2$-(CO)-*nido*-2-OsB_4H_8] (**6**), with the elimination of BH_3•PMe_3, which was identified by its ^{31}P NMR spectrum. Our inability to obtain analytical data for **2c**, other than NMR spectra, is presumably a consequence of its much greater tendency to degrade to **6** than **2a** or **2b**. The PPh_2Me derivative, **2b**, is more stable than the PPh_3 derivative **2a**, and an equilibrium between **2b** and **1** exists in which the former predominates. Thermolysis of **1** under the same conditions (18 h at 50 °C) affords a 46:54 mixture of **1** and **6.** Formation of **6** from the thermolysis of **1** was observed previously, although the earlier study reports that much higher temperatures (100 °C) were required to effect complete conversion of **1** to **6**.[9a]

Our results suggest a possible mechanism for the formation of [1-{$Fe(CO)_3$}B_4H_8] (**7**)[25] and [4-{$Fe(CO)_3$}B_5H_9] (**8**)[26] from $Fe(CO)_5$ and B_5H_9. These species are prepared from the thermolysis of B_5H_9/$Fe(CO)_5$ mixtures in a hot−cold reactor.[25,26] If the reaction is carried out with frequent removal of excess CO, which is formed in the reaction, then the principal product is [$Fe(CO)_3$]B_5H_9,[26] presumably because CO serves the same role in the latter reaction as does the addition of excess phosphine in the reactions of $(PPh_3)_2$(CO)OsB_5H_9 described herein. Thus, the reaction pathway illustrated in Scheme 2 is proposed. If 4-[$Fe(CO)_3$]B_5H_9 is the initially formed species in the reaction, then removal of excess CO, a base, should allow isolation of **8**; however, the presence of excess base could result in a reaction shown as step 1 in Scheme 2, followed by steps 2 and 3 which are analogous to the same steps in Scheme 1. The product of this reaction, when excess CO is not removed, is **7**, [1-{$Fe(CO)_3$}B_4H_8] and this may be explained by the action of base, in the form of CO, on **8** to catalyze the isomerization of [2-{$Fe(CO)_3$}B_4H_8] to **7**. Such isomerization reactions have been studied in detail,[27] and the most plausible mechanism involves a diamond−square−diamond rearrangement.[28]

The observed structure of **2b** may be compared to the proposed structure for B_6H_{10}•PMe_3, which is formally isoelectronic with **2a**, **2b**, and **2c**. The hexaborane(10) monoadduct, on the basis of NMR evidence, is postulated to be a pentaborane cage, with the BH_2L group bridging adjacent basal boron atoms rather than ó-bonded to a single basal B atom as we observed

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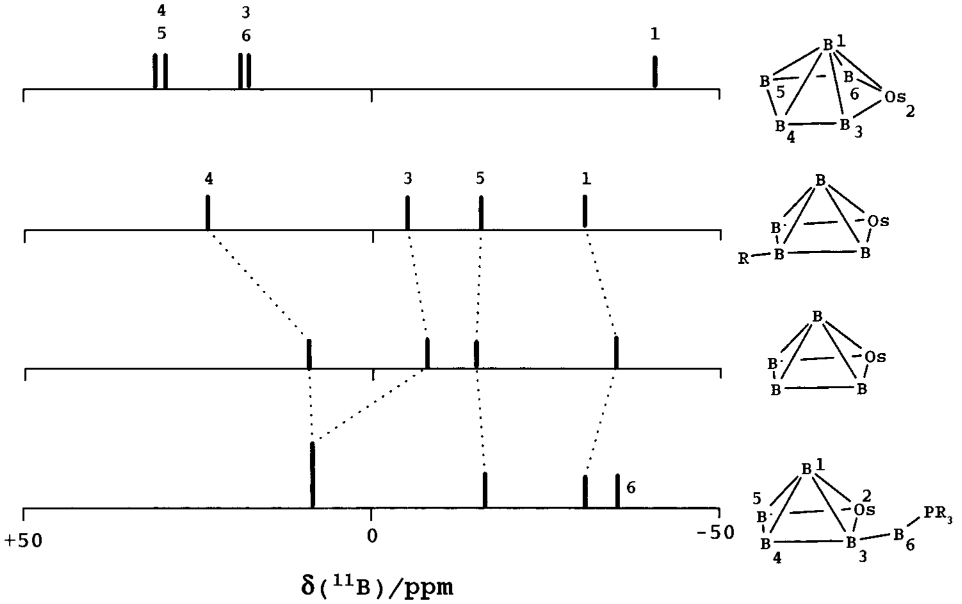


Figure 2. Stick diagrams of the ^{11}B NMR spectra of [(PPh$_3$)$_2$(CO)OsB$_5$H$_9$] (**1**),[11a] [(PPh$_3$)$_2$(CO)OsB$_4$H$_7$(C$_4$H$_9$)],[18] [(PPh$_3$)$_2$(CO)OsB$_4$H$_8$],[17] and [{(PPh$_3$)$_2$(CO)OsB$_4$H$_7$}(BH$_2$·PPh$_3$)] (**2a**) (this work).

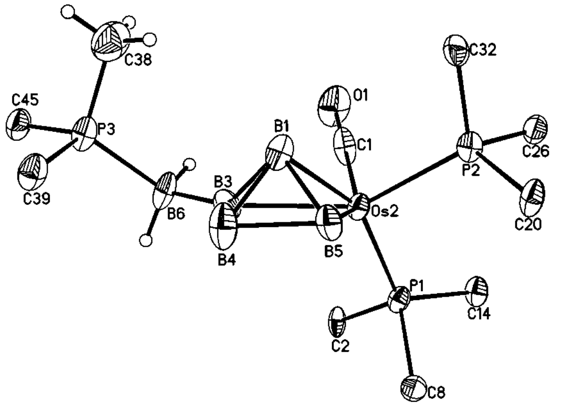
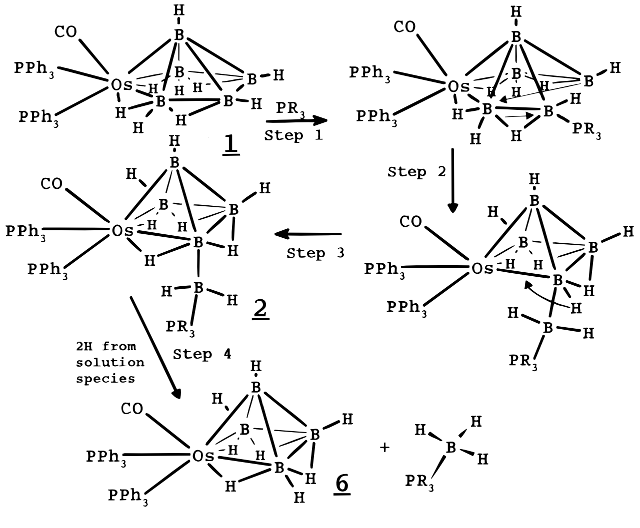


Figure 3. Projection of the crystal structure of **2b** with 30% thermal ellipsoids. Only the *ipso*-carbon atoms of the phenyl groups are shown for simplicity. The H atoms on B(6) are in calculated positions.

Scheme 1



for **2b**.[9] Although we are unaware of other structurally characterized analogues of **2b** in which there is a dangling BH$_2$L group, such species have been suggested in both B$_4$H$_{10}$[29] and B$_5$H$_9$[5,8] chemistry although the published structure for B$_5$H$_9$·(Me$_2$NCH$_2$)$_2$[5c,d] does not contain this moiety but a L$_2$BH moiety. The degradation of metallahexaboranes to clusters containing pendent boron atoms is a process which has only been suggested from *ab initio* calculations,[30] but our results suggest that it may be an important new reaction mode for other borane clusters too, and we discuss this briefly in the summary.

Reactions of Bidentate Phosphines with [(PPh$_3$)$_2$(CO)OsB$_5$H$_9$] (1). The reaction of dppe with **1** forms two products, [2,2,2-(PPh$_3$)$_2$(CO)-*nido*-2-OsB$_4$H$_7$-3-(BH$_2$·dppe)] (**3a**) and [2,2-(PPh$_3$)(CO)-*nido*-2-OsB$_4$H$_7$-η^2-3,2-(BH$_2$·dppe)] (**4a**). The proposed reactions taking place are illustrated in Scheme 3. NMR spectra suggest that species **3a** is similar to **2a** except that **3a** contains the PPh$_2$C$_2$H$_4$PPh$_2$ group instead of the PPh$_3$ group on the BH$_2$ moiety, and there is a pendent PPh$_2$ group which is uncoordinated, indicating the species [2,2,2-(PPh$_3$)$_2$(CO)-*nido*-2-OsB$_4$H$_7$-3-BH$_2$·PPh$_2$(CH$_2$)$_2$PPh$_2$] (**3a**). The NMR spectral data are given in Table 3 and are compared to those for **2b**, [2,2,2-(PPh$_3$)$_2$(CO)-*nido*-2-OsB$_4$H$_7$-3-BH$_2$·PPh$_2$Me]. The ^{11}B and ^{1}H NMR spectra for the species [2,2,2-(PPh$_3$)$_2$(CO)-*nido*-2-OsB$_4$H$_7$-3-(BH$_2$·dppe)] (**3a**) are quite similar to those for compounds **2a**−**c** and were assigned using ^{1}H{^{11}B} experiments. The ^{31}P NMR spectrum exhibits resonances for the PPh$_3$ groups coordinated to Os at +13.9 and +9.5 ppm, a resonance at +22.1 ppm assigned to the BH$_2$PPh$_2$ group, and an additional resonance at −11.4 ppm. This latter is close to the value of −11.9 ppm for free dppe and is assigned to the other uncoordinated end of the ligand. The ^{31}P resonance for the BH$_2$PPh$_2$ group is assigned by comparison with the spectra for **2a**−**c** and on the basis of its broadness, which suggests that it is bonded to a boron atom. Elemental analysis for **3a** and mass spectrometry supported the formulation shown as **3a** in Scheme 3. Many attempts to grow crystals suitable for X-ray analysis were unsuccessful. Perhaps this was because, in solution, **3a** slowly converts to **4a**. Indeed the initially formed solution from the reaction of **1** with dppe contained both **3a** and **4a**, but extended reaction times, for

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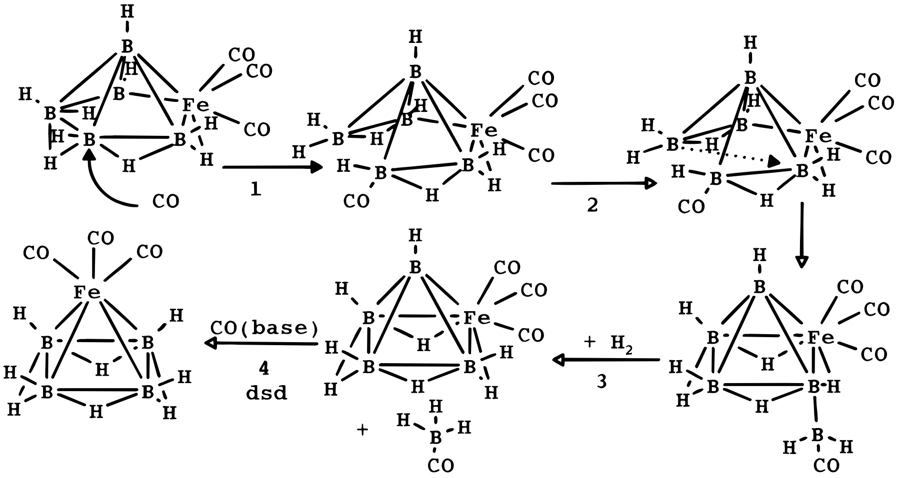
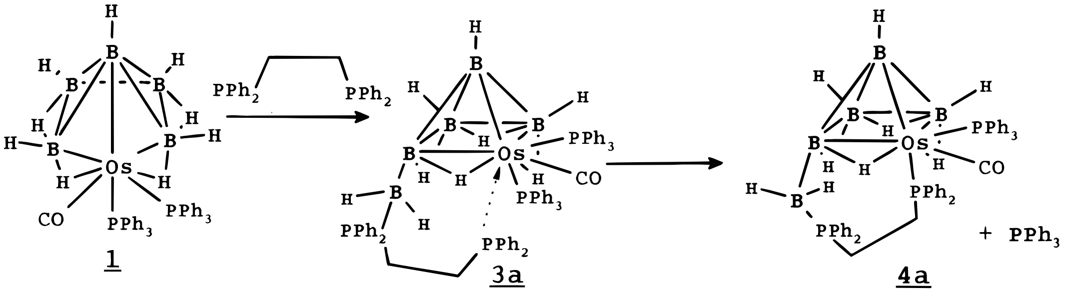
Scheme 2



Scheme 3



reactions conducted and monitored in an NMR tube, showed that **3a** slowly converted to **4a**. The NMR spectra for **4a**, as seen in Table 4, are very similar to those for **2b**, and this initially suggested two possible identities for **4a**. The major difference between **3a** and **4a** is the absence of one of the ^{31}P resonances assigned to the dangling PPh_2 group. This could arise from intramolecular substitution for one of the phosphines on Os, by attack of the dangling PPh_2 group on the Os, releasing PPh_3, which is observed in the ^{31}P NMR spectrum of the product mixture. Alternatively, the dangling PPh_2 group could attack the borane cage of another molecule of **1** in an intermolecular process similar to that illustrated in Scheme 1, but in this case PPh_3 should not be released in the reaction. Although we were unable to obtain good elemental analysis data for **4a**, mass spectrometry confirmed that the formulation of **4a** is [2,2-(PPh_3)-(CO)-*nido*-2-OsB_4H_7-η^2-3,2-$(BH_2{\cdot}dppe)$], and we presume that a process shown in Scheme 3 takes place in solution. Purification of these species was quite difficult due to the transformation from **3a** to **4a** and the relatively long reaction times required for isolation of **4a** free of **3a**. Similar chemistry was observed using the ligand dppp, to give **3b**, [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppp)$], and in this case, although again we were unable to grow crystals suitable for X-ray analysis, we were able to obtain elemental analysis and high-resolution mass spectrometry, which supported the formulation for **3b**. As was the case for **3a**, **3b** also slowly converts to **4b**, [2,2-(PPh_3)-(CO)-*nido*-2-OsB_4H_7-η^2-3,2-$(BH_2{\cdot}dppp)$], the dppp analogue of **4a**. The ^{31}P NMR resonance for the dangling PPh_2 end in **3b** is −18.26 ppm and compares well to the value of −17.3 ppm, which we measured under the same conditions, for pure dppp.

Reactions between **1** and dppm afforded only a single product for which NMR spectra suggested a species analogous to **3a** and **3b** with a monocoordinated bisphosphine. We conclude from this that the free PPh_2 end of the dppm is not long enough to attack the Os atom effectively, and thus only the species [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppm)$] (**3c**) is observed. NMR data, given in Table 3, are very similar to those for **3a**, **3b**, and especially **2b**. The resonance assigned to the dangling PPh_2 moiety, observed at −25.83 ppm, is close to the value for free dppm of −22.26 ppm, measured under the same conditions. These two values differ more than for the analogous ones observed for **3a** and **3b**, but in those cases the spacer groups between the PPh_2 moieties are longer, so the chemical shifts of the pendent PPh_2 groups in **3a** and **3b**, would be expected to resemble those for the free ligands more closely than for dppm, which only has a single CH_2 spacer group. The alternative to the analogues of **4a** and **4b**, i.e., a species in which the ligand bridges two $\{(PPh_3)_2(CO)OsB_4H_7{\cdot}BH_2\}$ clusters was not observed, although one might expect it to be seen in more concentrated solutions.

Reactions of the Uncoordinated PPh_2 Group in [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppp)$] (3b). To see whether we could form derivatives at the free phosphine moiety in **3a** or **3b**, we allowed **3b** to react with a 10-fold excess of $BH_3{\cdot}THF$ in CH_2Cl_2. TLC separation allowed the isolation of the new species [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppp{\cdot}BH_3)$] (**5**) (Figure 4) in 55% yield, and these yields increased to *ca.* 70% when separation was carried out using a chromatotron. Compound **5** was characterized by ^{11}B, ^{1}H, and ^{31}P NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry. The ^{11}B NMR spectrum showed overlapping resonances at −38.9 ppm arising from the BH_2PPh_2 and the BH_3PPh_2 moieties, and the $^{1}H\{^{11}B\}$ spectrum shows an additional resonance at +2.25 ppm assigned to the 3H atoms on B. The ^{31}P NMR spectrum exhibited four resonances, two assigned to the PPh_3 ligands on the Os and two others which were quite broad, both at the low-field end of the spectrum and in the region where phosphine boranes are usually seen.[16] The

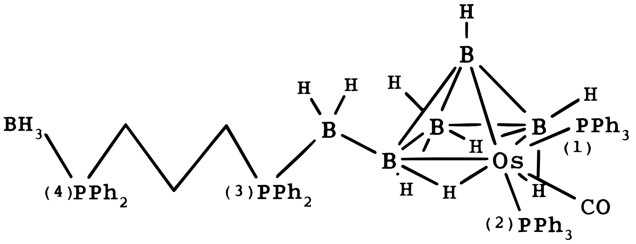


Figure 4. Proposed structure of [2,2-(PPh_3)(CO)-*nido*-2-OsB_4H_7-3-$(BH_2{\cdot}dppp{\cdot}BH_3)$] (**5**).

NMR spectral data, given in Table 4, are quite similar to those for the other compounds reported in this study and are strong evidence of the formation of this novel example of linked borane moieties. Although we were unable to obtain crystals suitable for X-ray analysis and the elemental analysis data are not so good, we were able to obtain high-resolution mass spectra, which gave results comparable to those of the calculated spectrum to within ±3.5 ppm. The formation of compound **5** suggests that perhaps linked metallaborane—borane or metallaborane—metallaborane clusters should be available using this route.

Summary

This study has identified a new base-promoted degradation route for metallaborane and possibly borane clusters, and this route may have applicability to other degradation and possible rearrangement mechanisms in metallaborane chemistry. There are many examples of rearrangement and degradation processes in polyhedral borane chemistry which are not well understood, and perhaps processes similar to those shown in Scheme 1 apply in these cases. Thus, for example, it has been observed that in the presence of base 6-rhenadecaboranes[31] and 6-rhodadecaboranes[32] degrade to the corresponding metallanonaboranes. Such degradation processes can easily be accounted for by a process related to that shown in Scheme 1 as could the well-known so-called decapitation reactions of icosahedral metallaboranes and -carboranes.[33] Analogously, the 5- and 6-positions in *nido*-metalladecaboranes and *nido*-dicarbadecaboranes, in some cases, appear to trade places in rearrangement processes,[32,34] and related 11-vertex metallacarboranes undergo similar rearrangements.[35] In both cases processes in which reaction with base (L) form species with pendent BH_2—L groups which lose borane or in which the BH_2 group reincorporates into the cluster to effect isomerization, in processes analogous to those described herein, could possibly account for these heretofore not well understood processes.

Our results involving bidentate phosphines have shown that species such as compound **5** may be formed. The latter may be considered to be a prototypical linked cluster. Other derivatives with polyborane or single metal or polymetal clusters at the other end of the bidentate phosphine ligand are clearly realistic synthetic targets. Furthermore, the chemistry leading to compounds **4a** and **4b** could result in the formation of linked OsB_5 cluster species if the reactions are carried out in concentrated solutions. Our results also emphasize the importance of not disregarding trace products in reactions. The initial observation of **2a** was as one of several trace byproducts, which also included $(PPh_3)_2(CO)(H)OsB_3H_8$, $(PPh_3)_2(CO)OsB_4H_8$, $[(PPh_3)_2(CO)OsB_9H_{13}]$, etc., formed in the preparation of $(PPh_3)_2(CO)OsB_5H_9$. All aspects of this work continue.

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Supporting Information Available: X-ray structural data for **2a**, including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic displacement parameters and detailed mass spectral data for **3a**, **3c**, **4a**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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