

Chemistry of the Hexaborane(10) Analogue $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$: Formation and Characterization of the Heterobimetallaheptaboranes $1,1,1-(\text{CO})_3-2,2-(\text{CO})_2-2,4-(\text{PPh}_3)_2\text{-}closo\text{-}1,2\text{-FeIrB}_5\text{H}_4$ and $2-(\text{CO})_2-2,2-(\text{PPh}_3)_2\text{-}7\text{-Cl-}7-(\text{PMe}_2\text{Ph})\text{-}nido\text{-}2,7\text{-IrPtB}_5\text{H}_7$

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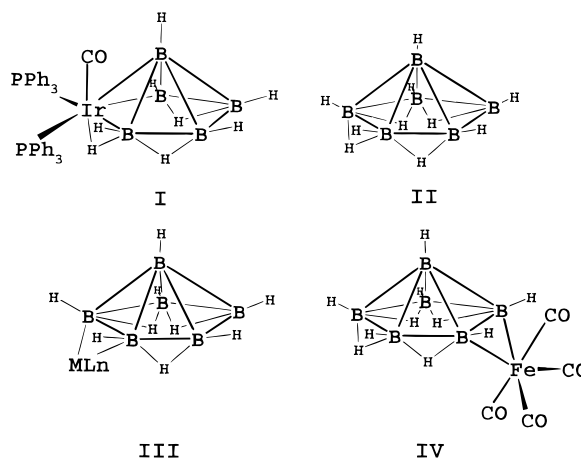
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The chemistry of the hexaborane(10) analogue $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$ (**4**) has been investigated. The two standard reactions in which metal-containing moieties may be incorporated into the B_6H_{10} cage find success when applied to the iridahexaborane (**4**). The reaction of $\text{Fe}_2(\text{CO})_9$ with $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$ in C_6H_6 solution affords $1,1,1-(\text{CO})_3-2,2-(\text{CO})_2-2,4-(\text{PPh}_3)_2\text{-}closo\text{-}1,2\text{-FeIrB}_5\text{H}_4$ (**1**) in moderate (28.5%) yield. Except for carborane derivatives, **1** is the first pentagonal bipyramidal metallaheptaborane to be structurally characterized. Compound **1** was identified by NMR, IR, and high-resolution mass spectroscopy and by a single-crystal X-ray diffraction study. Crystal data: triclinic, space group $P\bar{1}$, $a = 10.675(5)$ Å, $b = 10.736(3)$ Å, $c = 19.221(7)$ Å, $\alpha = 88.90(2)^\circ$, $\beta = 78.26(4)^\circ$, $\gamma = 71.69(3)^\circ$, $Z = 2$, $V = 2045.2(13)$ Å³. Treatment of a THF solution of the sodium anion salt of **4**, $\text{Na}[(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_7]$, with $[\text{Pt}(\text{PMe}_2\text{Ph})\text{Cl}_2]_2$ in CH_2Cl_2 affords yellow solid $2-(\text{CO})_2-2,2-(\text{PPh}_3)_2\text{-}7\text{-Cl-}7-(\text{PMe}_2\text{Ph})\text{-}nido\text{-}2,7\text{-IrPtB}_5\text{H}_7$ (**2**) in 5% yield. **2** is identified similarly. It exists as a *nido* seven-vertex cluster formally derived by removal of a vertex of connectivity 5 from a closed triangulated dodecahedral polyhedron. Crystal data: monoclinic, space group $P2_1/n$, $a = 15.434(2)$ Å, $b = 18.597(1)$ Å, $c = 17.200(1)$ Å, $\beta = 92.73(1)^\circ$, $Z = 4$, $V = 4931.1(7)$ Å³. **2** is two skeletal electrons short of the electron count for a classical *nido* cluster, and it is compared to systems with related structures and also to other systems containing the Pt moiety functioning as a two-orbital two-electron donor.

Introduction

In our efforts to prepare intermediate-sized heterobimetallaheptaboranes containing five or six boron atoms, we chose to use as starting materials the metallaheptaboranes *nido*- $(\text{PPh}_3)_2(\text{CO})\text{OsB}_5\text{H}_9$ (**3**)¹ and $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$ (**4**)² (illustration I) which are reported to be air-stable and much easier to prepare and handle than the parent B_6H_{10} .^{3a} These species are essentially isoelectronic and isostructural with hexaborane (illustration II) and recently attracted the attention of theorists.⁴ A second metal could be incorporated into **3** or **4** by deprotonation followed by addition of a metal-containing electrophile, analogous to the formation of $2,3\text{-}\mu\text{-}nido\text{-}metallaboranes$ ^{3,5} (illustration III) or by addition of a 16-electron metal moiety to a basal B–B or B–M bond, analogous to the formation of $\text{B}_6\text{H}_{10}\text{Fe}(\text{CO})_4$ (illustration IV) and related irida, rhoda, and platina analogues.⁶ The former has been accomplished previously by the incorpora-



tion of a Pt moiety into **3** to form $(\text{PPh}_3)_2(\text{CO})\text{Os}(\text{PhMe}_2\text{P})\text{-ClHPtB}_5\text{H}_7$, (**5**),⁷ and application of the latter is formally equivalent to the formation of $\text{Cu}(\text{PPh}_3)_2\text{B}_6\text{H}_9\text{Fe}(\text{CO})_4$, which we reported earlier.⁸ There are very few other examples of heterobimetallahepta- or octaboranes, especially if carboranyl derivatives are excluded. The species $\text{Cu}(\text{PPh}_3)_2\text{B}_5\text{H}_8\text{Fe}(\text{CO})_3$,

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a bimetalaborane in which the Fe is a true vertex and the Cu group may be considered as a pseudoproton, was prepared from $\text{B}_5\text{H}_9\text{Fe}(\text{CO})_3$,⁹ and the osmaplatinaheptaborane **5** and its thermolysis product $(\text{CO})(\text{PPh}_3)(\text{PPh}_2)\text{Os}(\text{PPh}_3)\text{PtB}_5\text{H}_7\text{Ph}$ were prepared a little later.⁷ $\text{Cu}(\text{PPh}_3)_2\text{B}_6\text{H}_9\text{Fe}(\text{CO})_4$ mentioned above is also a member of this class. It is an *arachno*-bimetallo-octaborane, and both metals may be regarded as pseudoprotons in that they both formally replace bridging H atoms whereas **5** is a true heterobimetalloheptaborane in that both metals may be considered to be true vertices. *closo*-Heterobimetalloboranes containing five or six boron atoms, excluding carborane derivatives, are also very rare. Only recently were the novel species $\{\eta^5\text{-C}_5\text{Me}_5\text{Fe}\}(\text{ML}_3\text{H})\text{B}_5\text{H}_7$ (M = Mo, L = PMe_2Ph ; M = W, L = PMe_3)¹⁰ reported, and we just described the preparation and complete characterization of *pileo*- $\{(\text{PPh}_3)\text{-COIr}\}_\text{B}_5\text{H}_5\{(\text{PPh}_3)_2(\text{CO})\text{Os}\}$.¹¹ This paper describes two routes to the incorporation of a second metal into **4** and describes the complete characterization of 1,1,1-(CO)₃-2,2-(CO)₂-2,4-(PPh₃)₂-*closo*-1,2-FeIrB₅H₄ (**1**) and 2-(CO)-2,2-(PPh₃)₂-7-Cl-7-(PMe₂Ph)-*nido*-2,7-IrPtB₅H₇ (**2**). Preliminary reports of the preparation of **1** and **2** have appeared.^{12,13}

Experimental Section

Where appropriate, reactions were carried out on a vacuum line using standard methods.¹⁴ Thin-layer chromatography (TLC) of the products was performed in air using 20 × 20 cm glass plates coated with 0.1 cm of silica gel (Aldrich standard grade with gypsum binder and fluorescent indicator). Solvents used were reagent grade and were dried before use. $\text{Fe}_2(\text{CO})_9$ was used as purchased, and $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$ was prepared essentially according to the literature method^{1,2} except that NaH was used to deprotonate the B_5H_9 and isolation was effected by precipitation methods rather than chromatography, giving more rapid routine yields of ca. 70%.² NMR spectroscopy was carried out on a Bruker ARX 500 spectrometer operating at 500.1 and 160.5 MHz to observe proton and boron-11 spectra, respectively, and on a Varian XL 300 MHz spectrometer operating at 122 MHz for ³¹P spectra. Chemical shifts are reported in ppm for CDCl_3 solutions unless otherwise stated to low field (high frequency) of $\text{Et}_2\text{O}\cdot\text{BF}_3$ for ¹¹B, of SiMe_4 for ¹H, and of 85% H_3PO_4 for ³¹P. High-resolution mass spectra were recorded at the Monsanto Co., St. Louis, on a Finnigan MAT 95 mass spectrometer by positive ion electrospray using electric sector scanning and standardized with PEG1000. Samples were run in $\text{MeOH}/\text{CHCl}_3$ (1:1) with 10 mmol of NH_4OH . The masses reported are for the most abundant peak (100%) in the molecular ion envelope. Low-resolution mass spectra were obtained using FAB with a nitrobenzyl alcohol matrix. Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA.

Synthesis of 1,1,1-(CO)₃-2,2-(CO)₂-2,4-(PPh₃)₂-*closo*-1,2-FeIrB₅H₄ (1**).** In initial experiments, 200 mg (0.25 mmol) of $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$ and $\text{Fe}_2(\text{CO})_9$ (90 mg, 0.25 mmol) were placed in a 50 mL round-bottom flask containing a stir bar, and the flask was evacuated. Approximately 20 mL of CH_2Cl_2 was condensed in and the mixture stirred overnight, during which a reddish solution formed containing undissolved solid. ¹¹B NMR spectra of the solution showed resonances attributable to new borane-containing species and none of the starting

iridahexaborane. The reaction mixture was filtered through silica gel, and the filtrate was reduced in volume, applied to a preparative TLC plate, and developed with CH_2Cl_2 /pentane as the mobile phase. A number of bands were apparent, only one of which, a yellow band at R_f 0.3, contained boron. The band was identified as described in the text as 1,1,1-(CO)₃-2,2-(CO)₂-2,4-(PPh₃)₂-*closo*-1,2-FeIrB₅H₄ (**1**) and crystallized by diffusion of pentane into a CH_2Cl_2 solution of the compound at -5 °C, giving yellow orange blocks suitable for X-ray diffraction analysis [1.8 mg, 1.9 μmol, 0.75% yield. Anal. Found (calcd): C, 50.35 (50.73); H, 3.36 (3.53). IR data (CHCl_3 solution)/ cm^{-1} : $\nu(\text{BH})$ 2500 (vb), $\nu(\text{CO})$ 2043 (s), 2001 (s), 1953 (m)]. Mass spectra were unobtainable. Boron (160.5 MHz), proton (500.1 MHz), and phosphorus (96 MHz) NMR data (CDCl_3 , 25 °C, intensities in parentheses): $\delta(^{11}\text{B})/\text{ppm}$ (resonances too broad to observe proton coupling), $\delta(^1\text{H})$ shifts, related by $^1\text{H}\{^1\text{B}_{\text{selective}}\}$ experiments, in brackets []: +46.3 {[5.12], B(3 or 6)}; +46.7 {[5.12], B(6 or 3)}; +12, +10.7 {[3.16, 3.09], B(4/7, 7/4)}; -3.1 {[phosphine-substituted B(5)}]; phenyl H resonances +7.0 to +7.5; $\delta(^{31}\text{P})$ +20.7 (1, sh), ca. +20 (1, br). Refluxing 300 mg of $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$ and 135 mg of $\text{Fe}_2(\text{CO})_9$ in dry, degassed CH_2Cl_2 under nitrogen for 2 h and isolation of the products as described above gave **1** (4.0 mg, 1.1% yield).

An alternative, higher yield synthesis was subsequently developed using C_6H_6 as solvent. $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$ (170 mg, 0.21 mmol) and $\text{Fe}_2(\text{CO})_9$ (76 mg, 0.21 mmol) were placed in a two-neck flask with one neck fitted with an extractor and the other neck stoppered. A 15 mL portion of C_6H_6 was syringed into the flask, and the reaction mixture was stirred for 2 h at 25 °C. During that time, the reaction mixture was monitored using TLC periodically until the starting material disappeared. When the reaction was complete, the mixture was filtered and a clear brown solution was obtained. The filtrate volume was reduced in vacuum and the process continued until a dry brown powder was obtained. NMR spectra indicated that this mixture contained **1** in 60% yield. Purification on TLC plates using 40/60 CH_2Cl_2 /pentane as the mobile phase gave three bands; the lowest band at R_f 0.4 was collected. A 58 mg amount of **1** was obtained corresponding to 28.5% yield. The identity of the product was confirmed by ¹H, ¹¹B, and ³¹P NMR spectra. It is very easily recrystallized from CH_2Cl_2 /pentane mixtures.

Synthesis of 2-(CO)-2,2-(PPh₃)₂-7-Cl-7-(PMe₂Ph)-*nido*-2,7-IrPtB₅H₇ (2**).** $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$ (250 mg, 0.31 mmol) and NaH (50% active, 14.5 mg, 0.3 mmol) were placed in a 50 mL round-bottom flask with a side arm holding a tipper tube containing [(PMe₂Ph)PtCl₂]₂ (125 mg, 0.16 mmol), and the vessel was evacuated. A 20 mL quantity of THF was condensed in, and the reactants were left to stir overnight at ambient temperature. Only a small amount of excess pressure, in the resultant yellow solution, presumably due to hydrogen, was evident. The platinum complex was added, and a small amount of effervescence ensued. After 1 h, an orange solution was obtained. The solution was reduced in volume, the reaction vessel opened, CH_2Cl_2 added, and the mixture filtered through silica gel. The filtrate was applied to preparative TLC plates and developed in 100% CH_2Cl_2 , giving an orange band at R_f 0.8 which contained the starting iridahexaborane and a small amount of red material which contained no boron and is probably a mixed-metal complex. A second yellow band at R_f 0.3 was identified as the title complex 2-(CO)-2,2-(PPh₃)₂-7-Cl-7-(PMe₂Ph)-*nido*-2,7-IrPtB₅H₇ (**2**). Repeated TLC of the compound resulted in some decomposition and the re-formation of the band at R_f 0.8. Microcrystals of the complex were obtained by reducing a chloroform solution of **2** with a stream of nitrogen [orange-yellow crystals, 17.0 mg, 14.5 μmol, 4.7% yield]. IR/ cm^{-1} : $\nu(\text{CO})$ 2035 (s), $\nu(\text{BH})$ 2504 (s). Mass spectrum for $\{\text{C}_{45}\text{H}_{48}\text{B}_5\text{ClIrPtOP}_3\}\text{NH}_4$ obs (calcd): 1193.254 (1193.269). Low-resolution mass spectra gave m/z 1174 (1174). Single crystals were difficult to obtain, as slightly impure solutions decomposed before crystals of suitable size could be obtained. However, in one case, diffusion of pentane through a layer of benzene into a dichloromethane solution of the compound at -5 °C gave orange-red blocks suitable for X-ray diffraction analysis. Use of the reagent (PMe₂Ph)₂PtCl₂ for the preparation of **2** gave very similar results.

X-ray Diffraction

Crystals of compounds **1** and **2** were obtained as described above and mounted on a glass fiber in random orientation. Preliminary

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Table 1. Crystal Data and Structure Refinement Details for Compounds **1** and **2**

	1	2
empirical formula	C ₄₁ H ₃₄ B ₅ FeIrO ₅ P ₂	C ₅₁ H ₅₄ B ₅ ClIrOP ₃ Pt
fw	970.72	1252.64
temp/K	298(2)	298(2)
crystal system	triclinic	monoclinic
space group	P1	P2 ₁ /n
a/Å	10.6913(2)	15.434(2)
b/Å	10.7595(1)	18.597(1)
c/Å	19.2528(3)	17.200(1)
α/deg	88.974(1)	90
β/deg	78.312(1)	92.73(1)
γ/deg	71.614(1)	90
V/Å ⁻³	2055.56(5)	4931.2(7)
Z	2	4
D(calcd)/Mg m ⁻³	1.568	1.687
abs coeff/mm ⁻¹	3.707	5.718
cryst size/mm	0.50 × 0.30 × 0.20	0.30 × 0.30 × 0.20
F(000)	956	2440
θ range for data colln/deg	1.08–28.27	1.61–24.99
index ranges	–14 ≤ h ≤ 14, –13 ≤ k ≤ 14, –25 ≤ l ≤ 25	–5 ≤ h ≤ 18, –6 ≤ k ≤ 22, –20 ≤ l ≤ 20
reflens colld	13 403	10 207
independent reflcns	9428 (R _{int} = 0.0327)	8653 (R _{int} = 0.0589)
data/restraints/parameters	9427/4/512	8649/0/583
goodness-of-fit on F ²	1.112	1.033
final R [I > 2σ(I)]:R ₁ (F)	0.0492	0.0611
final R [all data]: R _{2w} (F ²)	0.1141	0.1455
largest diff peak and hole/e Å ⁻³	4.369 and –1.386	0.999 and –0.679

examination and data collection were performed using a Siemens SMART CCD system (**1**) and a Siemens P4 (**2**) automated single-crystal X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å).

A Siemen's SMART Charge Coupled Device (CCD) detector system with a sealed-tube X-ray source (50 kV × 40 mA) was employed for data collection on the same crystal that was used with a sealed-tube point detector system for **1**.¹² Preliminary unit cell constants were determined with a set of 45 narrow-frame (0.3° in $\bar{\omega}$) scans. A total of 1.3 hemispheres (1167 frames) of intensity data were collected with a frame width of 0.3° in $\bar{\omega}$ and counting time of 10 s/frame at a crystal to detector distance of 4.93 cm. The double-pass method of scanning was used to exclude any noise. Data were collected at room temperature for a total time of 5.51 h. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package^{15b} was used for data collection, and SAINT 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 xyz centroids of 8192 reflections. An empirical absorption correction was carried out using an ellipsoidal model based upon the Laue symmetry using equivalent reflections. The integration process yielded 13 403 reflections of which 9428 were independent.

Autoindexing of 10 centered reflections from the rotation photograph indicated a monoclinic lattice for **2**. Equivalent reflections were checked to confirm the Laue symmetry, and a fractional index search was conducted to confirm the cell lengths.^{15a} Final cell constants and orientation matrix for data collection were calculated by least-squares refinement of the setting angles for 24 (12° < 2θ < 35°) reflections. Intensity data were collected using $\bar{\omega}$ scans with variable scan speed. Three representative reflections measured every 97 reflections showed approximately 16.5% variation during data collection. Crystal data and intensity data collection parameters are listed in Table 1. Data reduction was carried out using XSCANS, and structure solution and refinement were carried out using the SHELXTL-PLUS (5.0) software package.¹⁶ An absorption correction was applied to the data using ψ -scan reflections (XEMP, SHELXTL-PLUS).

The structures were solved using the Patterson method and refined successfully in the space groups P1 (**1**) and P2₁/n (**2**). Full-matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$.

For (CO)₅(PPh₃)-*closo*-1,2-FeIrB₅H₄(PPh₃) (**1**) the non-hydrogen atoms were refined anisotropically to convergence. Only three hydrogen atoms out of four connected to boron atoms were located from the difference Fourier synthesis and were refined isotropically. The phenyl hydrogens were refined using a riding model (AFIX 43, SHELXTL-PLUS (5.0)).¹⁶ The final residual values were R(F) = 4.92 for reflections with F > 4σ(F), R_w(F²) = 11.41%, s = 1.112. There was a heavy residual peak, of 4.4 e/Å³ close to the Fe atom, due to unresolved disorder involving B(5), B(4), and the Fe atom. This also has resulted in large anisotropic displacement parameters for B(5). Various disorder models were attempted to model the disorder, but none were successful. In all cases, the model after refinement resulted in a very short B(4)–Fe distance. Previous refinements based on comparable data collected with a point detector system on the same crystal had resulted in isotropic refinement only for B(5) and yielded substantially higher R₁(F) = 0.073 and R_{2w}(F²) = 0.153.¹² Structure refinement parameters are listed in Table 1. The atomic coordinates for the non-hydrogen atoms and selected bond distances and angles are listed in Tables 2 and 3, respectively. A projection view of the molecule with non-hydrogen atoms represented by 50% probability ellipsoids for **1** is shown in Figure 1.

For (CO)(PPh₃)₂Cl(PMe₂Ph)IrPtB₅H₇ (**2**), the non-hydrogen atoms were refined anisotropically to convergence. All hydrogen atoms on the boron cage were located from difference Fourier syntheses and were refined isotropically except H(1) (thermal parameter was held fixed). The methyl group H atoms were refined using the riding model AFIX 133 and phenyl H atoms were refined using AFIX 43.¹⁶ The solvent benzene molecule was refined as a rigid body. The final residual values were R(F) = 6.11% for observed reflections with F > 4σ(F), R_w(F²) = 14.55%, s = 1.033. Structure refinement parameters are listed in Table 1. The atomic coordinates for the non-hydrogen atoms and the geometrical parameters are listed in Tables 4 and 5, respectively. A projection view of the molecule with non-hydrogen atoms represented by 50% probability ellipsoids and showing the atom labeling is presented in Figure 2.

Complete positional parameters and isotropic displacement coefficients for hydrogen atoms and anisotropic displacement coefficients for the non-hydrogen atoms are provided as Supporting Information.

(15) (a) XSCANS; Siemens Analytical X-ray Instruments: Madison, WI, 1994. (b) SMART Siemens Analytical X-Ray Instruments: Madison, WI, 1994.

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **1**^a

atom	x	y	z	U(eq)
Fe(1)	2858(2)	448(1)	3251(1)	34(1)
Ir(2)	1382(1)	1671(1)	2301(1)	32(1)
P(1)	747(3)	3030(3)	1387(1)	37(1)
P(2)	4621(3)	2806(3)	3536(2)	35(1)
O(1)	767(9)	1663(8)	4509(4)	55(2)
O(2)	1903(11)	-1770(9)	3130(6)	79(3)
O(3)	5040(11)	-917(9)	3937(6)	74(3)
O(4)	-1155(9)	3141(9)	3375(5)	57(2)
O(5)	808(13)	-624(10)	1670(6)	89(4)
C(1)	1591(12)	1190(10)	4022(6)	40(3)
C(2)	2288(13)	-908(12)	3162(6)	48(3)
C(3)	4186(12)	-391(12)	3661(6)	45(3)
C(4)	-252(12)	2594(12)	2963(6)	39(3)
C(5)	981(15)	248(13)	1906(6)	54(3)
C(6)	-15(12)	4779(10)	1646(6)	38(2)
C(7)	374(14)	5335(12)	2164(7)	55(3)
C(8)	-123(17)	6645(13)	2319(9)	74(5)
C(9)	-1134(16)	7432(14)	1996(8)	66(4)
C(10)	-1530(14)	6903(13)	1500(8)	61(4)
C(11)	-1029(14)	5587(12)	1325(6)	53(3)
C(12)	2141(13)	2947(13)	639(6)	49(3)
C(13)	2456(14)	4049(14)	394(7)	59(3)
C(14)	3575(19)	3911(18)	-154(9)	86(5)
C(15)	4333(17)	2717(22)	-454(8)	86(6)
C(16)	4011(16)	1608(17)	-229(7)	78(5)
C(17)	2900(15)	1731(16)	326(7)	66(4)
C(18)	-524(13)	2630(12)	1016(6)	47(3)
C(19)	-379(16)	2395(16)	294(8)	74(5)
C(20)	-1404(21)	2085(21)	44(10)	104(7)
C(21)	-2532(21)	2011(20)	507(12)	105(7)
C(22)	-2695(16)	2280(18)	1203(10)	82(5)
C(23)	-1741(15)	2637(16)	1461(8)	69(4)
C(24)	3431(11)	3440(10)	4371(6)	37(2)
C(25)	2666(13)	4735(13)	4457(7)	55(3)
C(26)	1689(16)	5216(15)	5077(8)	73(4)
C(27)	1493(15)	4356(16)	5590(7)	68(4)
C(28)	2224(15)	3082(16)	5518(7)	65(4)
C(29)	3200(13)	2605(12)	4893(6)	49(3)
C(30)	6159(10)	1839(10)	3796(5)	33(2)
C(31)	6436(13)	2057(14)	4450(6)	52(3)
C(32)	7634(14)	1266(14)	4625(7)	57(4)
C(33)	8540(14)	302(13)	4151(8)	57(3)
C(34)	8306(12)	119(12)	3496(8)	54(3)
C(35)	7112(12)	867(12)	3324(7)	47(3)
C(36)	4961(12)	4215(11)	3084(6)	43(3)
C(37)	5767(14)	4821(12)	3311(9)	66(4)
C(38)	5988(16)	5936(13)	3018(9)	73(5)
C(39)	5342(15)	6481(14)	2488(9)	69(4)
C(40)	4600(18)	5871(15)	2229(8)	75(5)
C(41)	4338(15)	4717(13)	2543(7)	63(4)
B(3)	3412(14)	278(13)	2057(7)	43(3)
B(4)	4604(13)	569(12)	2432(7)	42(3)
B(5)	3933(13)	1809(12)	2960(6)	36(3)
B(6)	2292(12)	2559(11)	2970(6)	32(3)
B(7)	3469(15)	1938(13)	2113(7)	43(3)

^a U(eq) is defined as one-third of the orthogonalized U_{ij} tensor.

Results and Discussion

Deprotonation of **4** followed by addition of [Pt(PMe₂Ph)₂Cl]₂ affords the expected species 2-(CO)-2,2-(PPh₃)₂-7-Cl-7-(PMe₂Ph)-*nido*-2,7-IrPtB₅H₇, **2**, a third example of this rare class of metallaborane clusters, but treatment of **4** with Fe₂(CO)₉, effectively addition of Fe(CO)₄ followed by loss of 2 mol of H₂, leads to the formation of the first heterobimetalla-*closo*-heptaborane, 1,1,1-(CO)₃-2,2-(CO)₂-2,4-(PPh₃)₂-*closo*-1,2-FeIrB₅H₄, **1**. Both of these species are characterized by their NMR spectra and X-ray crystallography.

Stirring a 1:1 molar ratio mixture of (CO)(PPh₃)₂-*nido*-IrB₅H₈ with Fe₂(CO)₉ in C₆H₆ for 2 h followed by thin-layer-chromatography of the resultant mixture gave 1,1,1-(CO)₃-2,2-

Table 3. Selected Interatomic Distances (\AA) and Angles (deg) for **1**

Ir(2)-C(5)	1.919(12)	Fe(1)-C(3)	1.752(12)
Ir(2)-C(4)	1.924(12)	Fe(1)-C(2)	1.769(12)
Ir(2)-B(6)	2.155(12)	Fe(1)-C(1)	1.793(12)
Ir(2)-B(3)	2.175(14)	Fe(1)-B(5)	2.127(13)
Ir(2)-B(7)	2.29(2)	Fe(1)-B(4)	2.218(13)
Ir(2)-P(1)	2.332(3)	Fe(1)-B(6)	2.240(11)
P(1)-C(18)	1.817(12)	Fe(1)-B(3)	2.245(14)
P(1)-C(12)	1.828(13)	Fe(1)-Ir(2)	2.706(2)
P(1)-C(6)	1.830(11)	O(1)-C(1)	1.145(13)
P(2)-C(30)	1.807(10)	O(2)-C(2)	1.132(14)
P(2)-C(24)	1.824(11)	O(3)-C(3)	1.138(13)
P(2)-C(36)	1.828(12)	O(4)-C(4)	1.119(13)
P(2)-B(5)	1.944(12)	O(5)-C(5)	1.129(14)
B(3)-B(4)	1.69(2)	B(5)-B(6)	1.68(2)
B(3)-B(7)	1.81(2)	B(5)-B(7)	1.79(2)
B(4)-B(5)	1.57(2)	B(6)-B(7)	1.85(2)
B(4)-B(7)	1.77(2)		
C(3)-Fe(1)-C(2)	96.1(6)	C(5)-Ir(2)-C(4)	104.5(5)
C(3)-Fe(1)-C(1)	99.7(5)	C(5)-Ir(2)-B(6)	155.3(5)
C(2)-Fe(1)-C(1)	95.5(6)	C(4)-Ir(2)-B(6)	82.9(4)
C(3)-Fe(1)-B(5)	86.1(5)	C(5)-Ir(2)-B(3)	81.5(6)
C(2)-Fe(1)-B(5)	158.2(5)	C(4)-Ir(2)-B(3)	151.6(5)
C(1)-Fe(1)-B(5)	105.5(5)	B(6)-Ir(2)-B(3)	81.4(5)
C(3)-Fe(1)-B(4)	79.8(5)	C(5)-Ir(2)-B(7)	125.2(5)
C(2)-Fe(1)-B(4)	116.6(5)	C(4)-Ir(2)-B(7)	129.8(4)
C(1)-Fe(1)-B(4)	147.8(5)	B(6)-Ir(2)-B(7)	49.0(4)
B(5)-Fe(1)-B(4)	42.4(5)	B(3)-Ir(2)-B(7)	47.7(5)
C(3)-Fe(1)-B(6)	126.8(5)	C(5)-Ir(2)-P(1)	92.4(4)
C(2)-Fe(1)-B(6)	137.1(5)	C(4)-Ir(2)-P(1)	92.2(3)
C(1)-Fe(1)-B(6)	79.5(4)	B(6)-Ir(2)-P(1)	111.1(3)
B(5)-Fe(1)-B(6)	45.1(5)	B(3)-Ir(2)-P(1)	115.6(4)
B(4)-Fe(1)-B(6)	75.6(4)	B(7)-Ir(2)-P(1)	92.8(3)
C(3)-Fe(1)-B(3)	113.7(5)	C(5)-Ir(2)-Fe(1)	101.9(4)
C(2)-Fe(1)-B(3)	84.3(5)	C(4)-Ir(2)-Fe(1)	98.3(3)
C(1)-Fe(1)-B(3)	146.4(5)	B(6)-Ir(2)-Fe(1)	53.4(3)
B(5)-Fe(1)-B(3)	75.0(5)	B(3)-Ir(2)-Fe(1)	53.4(4)
B(4)-Fe(1)-B(3)	44.6(5)	B(7)-Ir(2)-Fe(1)	66.9(3)
B(6)-Fe(1)-B(3)	78.1(5)	P(1)-Ir(2)-Fe(1)	159.47(8)
C(3)-Fe(1)-Ir(2)	163.9(4)	B(7)-B(3)-Fe(1)	85.7(7)
C(2)-Fe(1)-Ir(2)	88.1(4)	Ir(2)-B(3)-Fe(1)	75.5(4)
C(1)-Fe(1)-Ir(2)	95.3(3)	B(5)-B(6)-B(7)	60.7(7)
B(5)-Fe(1)-Ir(2)	84.4(3)	B(5)-B(6)-Ir(2)	116.7(7)
B(4)-Fe(1)-Ir(2)	84.4(3)	B(7)-B(6)-Ir(2)	69.3(6)
B(6)-Fe(1)-Ir(2)	50.6(3)	B(5)-B(6)-Fe(1)	63.9(6)
B(3)-Fe(1)-Ir(2)	51.1(4)	B(7)-B(6)-Fe(1)	85.0(6)
B(4)-B(3)-B(7)	60.8(8)	Ir(2)-B(6)-Fe(1)	76.0(4)
B(4)-B(3)-Ir(2)	118.2(8)	B(4)-B(7)-B(5)	52.4(7)
B(7)-B(3)-Ir(2)	69.5(6)	B(4)-B(7)-B(3)	56.4(7)
B(4)-B(3)-Fe(1)	66.9(6)	B(5)-B(7)-B(3)	95.7(9)
B(5)-B(4)-B(3)	109.3(10)	B(4)-B(7)-B(6)	97.9(8)
B(5)-B(4)-B(7)	64.2(7)	B(5)-B(7)-B(6)	55.0(7)
B(3)-B(4)-B(7)	62.8(8)	B(3)-B(7)-B(6)	101.2(9)
B(5)-B(4)-Fe(1)	65.7(6)	B(4)-B(7)-Ir(2)	109.2(8)
B(3)-B(4)-Fe(1)	68.6(6)	B(5)-B(7)-Ir(2)	106.1(7)
B(7)-B(4)-Fe(1)	87.4(7)	B(3)-B(7)-Ir(2)	62.8(6)
B(4)-B(5)-B(6)	114.2(10)	B(6)-B(7)-Ir(2)	61.7(6)
B(4)-B(5)-B(7)	63.4(8)	B(6)-B(5)-P(2)	111.2(8)
B(6)-B(5)-B(7)	64.3(7)	B(7)-B(5)-P(2)	136.9(8)
B(4)-B(5)-P(2)	134.1(9)	B(4)-B(5)-Fe(1)	71.9(7)
		B(6)-B(5)-Fe(1)	71.0(6)

(CO)₂-2,4-(PPh₃)₂-*closo*-1,2-FeIrB₅H₄ (**1**) in 28.5% yield. Stirring the reaction mixture in CH₂Cl₂ for 24 h or refluxing for 2 h gave very low yields. NMR and IR spectroscopy suggested a *closo*-iridaborane cluster with iron incorporated, and this was confirmed by a single-crystal X-ray diffraction study. The structure (Figure 1) reveals a *closo*-bimetallaheptaborane cluster with an {Ir(CO)₂(PPh₃)} moiety in an equatorial position and an {Fe(CO)₃} moiety in the apical position. As such, **1** represented both the first pentagonal bipyramidal metallahexaborane to be structurally characterized and the first ferrairidaborane heterobimetallaborane cluster to be synthesized.¹² A system which may be considered to be a pentagonal

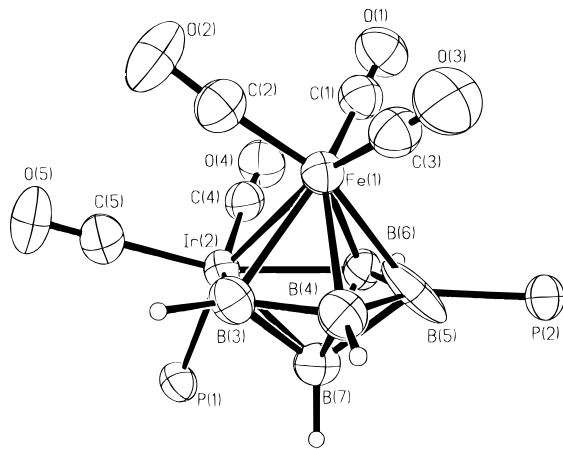


Figure 1. Projection view of **1** with the thermal ellipsoids drawn at the 50% probability level. Phenyl rings have been omitted for clarity.

bipyramidal structure was recently reported.¹⁷ The latter is $\{\text{Mo}(\eta^5\text{-C}_5\text{H}_4\text{Me})\}_2\text{B}_5\text{H}_9$, but it is described by the authors as a bicapped trigonal bipyramidal structure although it does resemble a distorted pentagonal bipyramid. Two other pentagonal bipyramidal metallahexaboranes, $[\{\eta^5\text{-C}_5\text{Me}_5\text{Ni}\}\text{B}_6\text{H}_6]^{2-}$ ¹⁸ and $\{\eta^5\text{-C}_5\text{Me}_5\text{Co}\}_2\text{B}_5\text{H}_7$,¹⁹ have been proposed from NMR evidence, and we recently prepared a second ferrairidaborane, 1,1-(CO)₂-2,2-(CO)₂-1,2-(PPh₃)₂-*nido*-1,2-FeIrB₂H₅.²⁰ The occurrence of both first- and third-row metals in a metallaborane is also rare although our work and that of Leach et al.,¹⁰ who prepared $\{\eta^5\text{-C}_5\text{H}_5\text{Fe}\}\{\text{Mo}(\text{PMe}_2\text{Ph})_3\text{H}\}\text{B}_5\text{H}_7$ and $\{\eta^5\text{-C}_5\text{H}_5\text{Fe}\}\{\text{W}(\text{PMe}_3)_3\text{H}\}\text{B}_5\text{H}_7$ suggest that perhaps such systems are not difficult to prepare.

The structure determination for **1** using the CCD detector resulted in a better quality data set than the one we originally reported,¹² which was determined using a point detector. Thus, isotropic refinement of the B(5) atom was possible although, due to unresolved disorder, the anisotropic displacement parameters for B(5) were large. The $\{(\text{CO})(\text{PPh}_3)_2\text{IrB}_5\text{H}_5\}$ portion of the molecule retains much of the overall geometry of a $(\text{PPh}_3)_2(\text{CO})\text{IrB}_5\text{H}_8$ cluster with the $\{\text{Fe}(\text{CO})_3\}$ moiety effectively capping the open face of the cluster. The plane Ir(2)B(3)B(4)B(5)B(6) is essentially completely planar; the mean deviation from the least-squares plane is only 0.073 Å. Compound **1**, therefore, conforms to geometrical and skeletal electron counting rules²¹ for a 16-electron *closo* seven-vertex cluster with the $\{\text{Fe}(\text{CO})_3\}^{2+}$ vertex capping a formal *nido*- $\{(\text{CO})_2(\text{PPh}_3)_2\text{IrB}_5\text{H}_4(\text{PPh}_3)_2\}^{2-}$ unit. Although there are several examples of $\text{Fe}(\text{CO})_3$ units replacing BH units in borane chemistry,²² as far as we are aware this is the first example of metallaborane compound in which a $\{\text{Fe}(\text{CO})_3\}$ moiety is η^5 bonded in a *closo*-borane cluster and thus caps a B₅ face. There are two structurally characterized examples of $\text{Fe}(\text{CO})_3$ capping C₂B₃ faces in metallacarboranes. These include the piano stool

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2**^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ir(2)	1493(1)	1988(1)	3755(1)	31(1)
Pt(7)	451(1)	1944(1)	5134(1)	34(1)
P(1)	1911(3)	3226(2)	3985(2)	38(1)
P(2)	581(2)	1954(2)	2579(2)	35(1)
P(3)	174(2)	1885(2)	6403(2)	39(1)
Cl(1)	-1021(3)	2299(3)	4810(2)	62(1)
C(1)	2481(9)	1823(7)	3209(7)	32(3)
O(1)	3108(6)	1712(6)	2877(6)	54(3)
B(1)	2096(11)	1143(8)	4573(9)	33(4)
B(3)	1822(10)	1926(10)	5051(9)	37(4)
B(4)	1452(12)	1122(9)	5421(9)	36(4)
B(5)	1278(13)	472(10)	4743(10)	44(5)
B(6)	1360(11)	799(9)	3837(11)	38(4)
C(2)	-651(10)	2507(9)	6707(9)	70(6)
C(3)	-258(11)	1018(9)	6663(9)	76(6)
C(4)	1751(10)	3847(7)	3195(8)	40(4)
C(5)	2106(11)	3703(8)	2481(10)	60(5)
C(6)	2089(13)	4158(10)	1868(11)	84(7)
C(7)	1633(12)	4803(10)	1938(10)	73(6)
C(8)	1280(14)	4963(10)	2615(12)	86(7)
C(9)	1321(11)	4493(9)	3242(10)	61(5)
C(10)	3095(9)	3333(7)	4172(9)	41(4)
C(11)	3449(11)	4020(10)	4041(10)	70(6)
C(12)	4298(12)	4160(11)	4227(12)	82(6)
C(13)	4845(12)	3615(11)	4517(10)	71(6)
C(14)	4520(9)	2930(10)	4575(9)	57(5)
C(15)	3643(9)	2800(8)	4426(8)	46(4)
C(16)	1468(11)	3697(8)	4829(9)	44(4)
C(17)	1967(11)	4050(9)	5384(11)	69(5)
C(18)	1570(13)	4409(11)	5976(11)	97(8)
C(19)	728(13)	4440(10)	6010(11)	76(6)
C(20)	187(11)	4100(9)	5475(9)	55(5)
C(21)	571(11)	3729(9)	4881(9)	56(5)
C(22)	1242(9)	1815(8)	1720(8)	40(4)
C(23)	1628(10)	1164(8)	1607(9)	54(5)
C(24)	2183(10)	1059(10)	1002(9)	56(5)
C(25)	2304(10)	1608(10)	514(10)	55(5)
C(26)	1925(11)	2263(11)	610(10)	66(6)
C(27)	1380(9)	2374(9)	1202(8)	47(4)
C(28)	-137(10)	2710(8)	2331(8)	39(4)
C(29)	-564(12)	2755(9)	1594(10)	70(6)
C(30)	-1130(11)	3320(11)	1437(11)	74(6)
C(31)	-1304(12)	3796(10)	1988(12)	74(6)
C(32)	-883(12)	3776(10)	2718(11)	84(7)
C(33)	-309(11)	3219(9)	2852(10)	68(6)
C(34)	-221(10)	1236(7)	2511(8)	37(4)
C(35)	-444(10)	866(8)	1824(8)	50(4)
C(36)	-1062(10)	363(8)	1785(10)	55(5)
C(37)	-1503(10)	178(9)	2420(11)	65(5)
C(38)	-1316(11)	539(9)	3120(10)	59(5)
C(39)	-670(9)	1060(8)	3180(8)	41(4)
C(40)	1063(9)	2057(9)	7076(8)	43(4)
C(41)	1624(11)	2608(10)	6902(9)	67(5)
C(42)	2330(12)	2801(11)	7410(12)	81(6)
C(43)	2428(14)	2460(14)	8132(12)	113(10)
C(44)	1876(13)	1925(13)	8284(11)	90(7)
C(45)	1183(11)	1723(10)	7769(9)	71(6)
C(1')	-3546(12)	873(11)	3706(12)	248(23)
C(2')	-4359(16)	1123(10)	3449(9)	145(12)
C(3')	-5031(10)	1147(10)	3958(16)	152(14)
C(4')	-4891(14)	920(12)	4724(14)	441(50)
C(5')	-4078(18)	671(12)	4981(8)	240(21)
C(6')	-3406(11)	647(10)	4472(14)	114(9)

^a *U*(eq) is defined as one-third of the orthogonalized *U*_{ij} tensor.

species 1,2,3-(CO)₃FeC₂B₃H₇²³ and the recently described icosahedral species *closo*-(CO)₃FeC₂B₉H₁₁.²⁴ **1** may be compared to *pileo*- $\{(\text{PPh}_3)_3(\text{CO})\text{Hf}\}\text{B}_5\text{H}_5\{(\text{PPh}_3)_2(\text{CO})\text{Os}\}$,¹¹ which we reported recently. Both are bimetallaheptaboranes containing

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Table 5. Selected Interatomic Distances (Å) and Angles (deg) for **2**

Ir(2)–C(1)	1.854(14)	P(2)–C(22)	1.852(14)
Ir(2)–B(6)	2.23(2)	P(3)–C(40)	1.782(14)
Ir(2)–B(3)	2.27(2)	P(3)–C(3)	1.81(2)
Ir(2)–B(1)	2.28(2)	P(3)–C(2)	1.815(14)
Ir(2)–P(2)	2.409(3)	C(1)–O(1)	1.16(2)
Ir(2)–P(1)	2.417(4)	B(1)–B(3)	1.73(2)
Ir(2)–Pt(7)	2.9297(8)	B(1)–B(6)	1.78(2)
Ir(2)–H(12)	1.68(12)	B(1)–B(4)	1.80(2)
Pt(7)–B(3)	2.13(2)	B(1)–B(5)	1.81(2)
Pt(7)–B(4)	2.21(2)	B(1)–H(1)	1.00(11)
Pt(7)–P(3)	2.246(3)	B(3)–B(4)	1.73(2)
Pt(7)–Cl(1)	2.406(4)	B(3)–H(3)	1.06(10)
Pt(7)–H(12)	1.94(12)	B(4)–B(5)	1.69(2)
P(1)–C(4)	1.792(14)	B(4)–H(4)	1.01(11)
P(1)–C(10)	1.85(2)	B(5)–B(6)	1.68(2)
P(1)–C(16)	1.85(2)	B(5)–H(5)	1.36(11)
P(2)–C(34)	1.821(14)	B(5)–H(56)	1.29(11)
P(2)–C(28)	1.83(2)	B(6)–H(6)	1.01(13)
		B(6)–H(56)	1.23(11)
C(1)–Ir(2)–B(6)	87.0(6)	B(3)–Pt(7)–B(4)	47.0(7)
C(1)–Ir(2)–B(3)	109.8(5)	B(3)–Pt(7)–P(3)	107.5(4)
B(6)–Ir(2)–B(3)	84.5(7)	B(4)–Pt(7)–P(3)	85.0(4)
C(1)–Ir(2)–B(1)	83.0(5)	B(3)–Pt(7)–Cl(1)	156.9(5)
B(6)–Ir(2)–B(1)	46.5(6)	B(4)–Pt(7)–Cl(1)	152.0(5)
B(3)–Ir(2)–B(1)	44.9(6)	P(3)–Pt(7)–Cl(1)	90.96(14)
C(1)–Ir(2)–P(2)	91.8(4)	B(3)–Pt(7)–Ir(2)	50.2(4)
B(6)–Ir(2)–P(2)	88.6(5)	B(4)–Pt(7)–Ir(2)	78.2(4)
B(3)–Ir(2)–P(2)	156.8(4)	P(3)–Pt(7)–Ir(2)	157.71(10)
B(1)–Ir(2)–P(2)	134.9(4)	Cl(1)–Pt(7)–Ir(2)	110.71(10)
C(1)–Ir(2)–P(1)	91.2(4)	B(3)–Pt(7)–H(12)	82(4)
B(6)–Ir(2)–P(1)	163.7(5)	B(4)–Pt(7)–H(12)	109(4)
B(3)–Ir(2)–P(1)	80.9(5)	P(3)–Pt(7)–H(12)	166(4)
B(1)–Ir(2)–P(1)	117.2(4)	Cl(1)–Pt(7)–H(12)	78(4)
P(2)–Ir(2)–P(1)	107.65(14)	Ir(2)–Pt(7)–H(12)	33(4)
C(1)–Ir(2)–Pt(7)	154.4(4)	O(1)–C(1)–Ir(2)	178.7(12)
B(6)–Ir(2)–Pt(7)	82.2(5)	B(3)–B(1)–B(6)	118.6(12)
B(3)–Ir(2)–Pt(7)	46.2(4)	B(3)–B(1)–B(4)	58.6(9)
B(1)–Ir(2)–Pt(7)	72.8(4)	B(6)–B(1)–B(4)	102.2(12)
P(2)–Ir(2)–Pt(7)	110.94(9)	B(3)–B(1)–B(5)	108.4(12)
P(1)–Ir(2)–Pt(7)	92.65(10)	B(6)–B(1)–B(5)	55.9(9)
C(1)–Ir(2)–H(12)	167(4)	B(4)–B(1)–B(5)	55.9(9)
B(6)–Ir(2)–H(12)	97(4)	B(3)–B(1)–Ir(2)	67.2(7)
B(3)–Ir(2)–H(12)	83(4)	B(6)–B(1)–Ir(2)	65.2(7)
B(1)–Ir(2)–H(12)	109(4)	B(4)–B(1)–Ir(2)	106.9(9)
P(2)–Ir(2)–H(12)	76(4)	B(5)–B(1)–Ir(2)	107.9(10)
P(1)–Ir(2)–H(12)	88(4)	B(4)–B(3)–B(1)	62.7(10)
Pt(7)–Ir(2)–H(12)	39(4)	B(4)–B(3)–Pt(7)	69.1(8)
B(6)–B(5)–B(4)	111.4(13)	B(1)–B(3)–Pt(7)	108.1(11)
B(6)–B(5)–B(1)	61.2(9)	B(4)–B(3)–Ir(2)	110.1(10)
B(4)–B(5)–B(1)	61.9(10)	B(1)–B(3)–Ir(2)	68.0(7)
B(6)–B(5)–H(56)	47(5)	Pt(7)–B(3)–Ir(2)	83.6(5)
B(4)–B(5)–H(56)	120(5)	B(5)–B(4)–B(3)	114.0(12)
B(1)–B(5)–H(56)	102(5)	B(5)–B(4)–B(1)	62.2(10)
H(5)–B(5)–H(56)	114(7)	B(3)–B(4)–B(1)	58.7(9)
B(5)–B(6)–B(1)	62.9(10)	B(5)–B(4)–Pt(7)	104.6(10)
B(5)–B(6)–Ir(2)	115.3(11)	B(3)–B(4)–Pt(7)	63.9(7)
B(1)–B(6)–Ir(2)	68.3(8)	B(1)–B(4)–Pt(7)	102.1(9)
B(5)–B(6)–H(56)	50(5)	Ir(2)–B(6)–H(56)	116(5)
B(1)–B(6)–H(56)	107(5)	H(6)–B(6)–H(56)	103(10)

group 8 and group 9 metals but with a major difference. The former contains two more skeletal electrons than the latter and is a conventional $2n + 2$ *closo* system containing 16 skeletal electrons whereas the latter is a $2n$ system containing 14 skeletal electrons and is thus a *pileo* system.²⁵ The Fe–Ir distance in **1**, of 2.706(2) Å, is slightly longer than the sum of the covalent radii and is in the middle of the range of Ir–Fe distances in iron–iridium metal clusters and bridged binuclear complexes,

(24) Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1991**, *10*, 670.

(25) (a) Mason, R.; Thomas, K. M.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1973**, *95*, 3802. (b) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1977**, 610. (c) Johnson, R. L.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1987**, 1445.

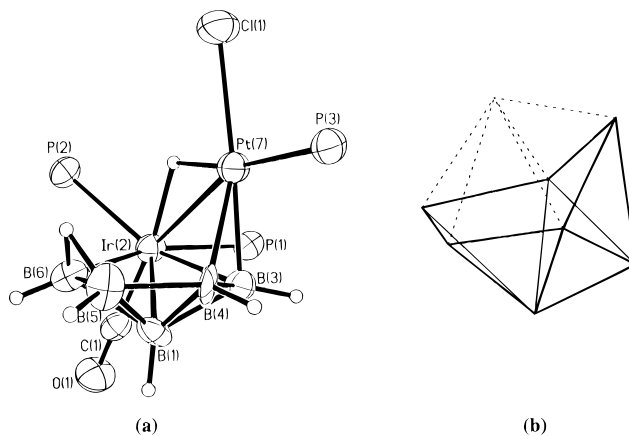
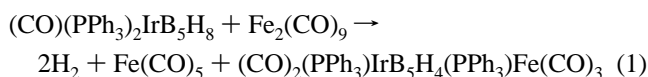


Figure 2. (a) Projection view of **2** with the thermal ellipsoids drawn at the 50% probability level. (b) Schematic description of an idealized *nido* seven-vertex cluster.

which has been taken in these compounds to indicate a significant bonding interaction.²⁶ The Fe–B distances of 2.12–2.23 Å, similar to or longer than the Ir–B_{equatorial} distances of 2.16 and 2.17 Å, perhaps reflect the η^5 coordination of the iron compared to the η^4 coordination of the iridium center. In line with this, the Ir–B_{axial} distance of 2.29 Å is *ca.* 0.1 Å longer. Similarly, the B_{axial}–B_{equatorial} distances (1.77–1.82 Å) are longer than the equatorial belt distances (1.57–1.69 Å).

NMR data for **1** are consistent with the structure. Two low-field ¹¹B resonances are assigned to B(3,6), which are bonded to the two metals. There are now several examples of systems in which boron atoms are bonded to more than one metal in clusters ranging all the way to encapsulated metal atoms, and the greater the number of metals bonded to the boron atom, the greater the deshielding and the lower the ¹¹B chemical shift.²⁷ The boron atom bonded to the phosphine, B(5), is easily identified in the selective decoupling experiments by the absence of the terminal H resonance although the resonance was too broad to observe coupling to ³¹P. Similarly, BH coupling was not measurable due to the broadness of the boron resonances. There is one borane system in the literature, with which we could compare our system, $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Co}\}_2\text{B}_5\text{H}_7$,¹⁷ and there are several *closo*-1,7-bimetalladicaheptaboranes,^{28a} formally described as triple-decker sandwich complexes, and 1-metalladicaheptaboranes,^{28b} but although they are structurally similar to **1**, comparisons of the NMR data are not so useful owing to the presence of the phosphine bonded to B(5) in **1** destroying the symmetry.

The stoichiometry of the reaction, indicated in eq 1, suggests that the product is formed via the initial addition of an Fe(CO)₄

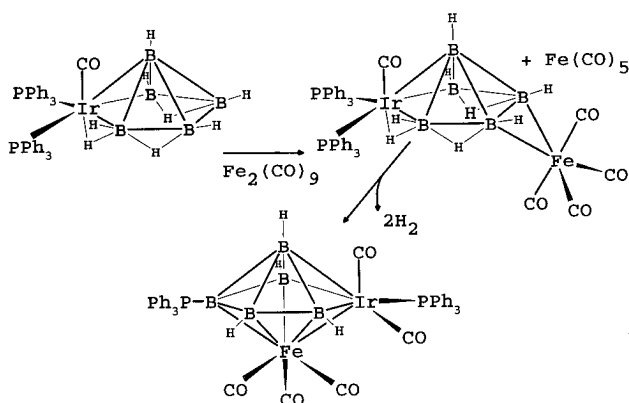


moiety to the iridaborane cluster which is followed by ligand

(26) Mague, J. T. *Organometallics* **1990**, *10*, 513 and references therein. Known Ir–Fe distances in cluster and binuclear complexes, from 12 published studies, range from 2.55 Å in $\{[\eta^5\text{-C}_5\text{Me}_5]\text{Ir}\}\{\text{C}(\text{Me})=\text{CHCH}=\text{C}(\text{Me})\}\{\mu\text{-SFe}(\text{CO})_4\}\{\text{Fe}(\text{CO})_2\}$ [Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2544] to 2.960 Å in $[\text{FeIr}(\mu\text{-PPh}_2)(\text{CO})_5(\text{PPh}_3)_2]$ [Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Dutter, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846].

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Scheme 1



rearrangement in which a carbonyl migrates to the iridium center and the PPh₃ moiety migrates to the borane cage together with concurrent hydrogen loss as suggested in Scheme 1. This would be analogous to the addition of Fe(CO)₄ to B₆H₁₀ to form B₆H₁₀-Fe(CO)₄ (illustration **IV**). The B–B bond to which the Fe(CO)₄ unit adds in B₆H₁₀ is very similar in length to the B–B connection in **4**, as determined by single-crystal X-ray diffraction (1.63 Å vs 1.65 Å in **4**),^{2,29} and thus the analogy is reasonable. The PPh₃ migration is not unusual. Iridaborane clusters with triphenylphosphine ligands on the metal have shown a very marked tendency to exhibit phosphine loss from the metal or migration of the phosphine to the borane cluster.^{11,20,30}

Treatment of the anion of **4**, [(CO)(PPh₃)₂IrB₅H₇][−], with [Pt(PMe₂Ph)Cl₂]₂ affords the species 2-(CO)-2,2-(PPh₃)₂-7-Cl-7-(PMe₂Ph)-*nido*-(2,7- μ -H)-2,7-IrPtB₅H₆, **2**, which is analogous to the known Os species (PPh₃)₂(CO)Os(PhMe₂P)Cl(μ H)PtB₅H₇ (**5**).⁷ NMR spectra for **2** and **5** are quite similar (see Table 6) and suggest that the structure of **2** is analogous to that of **5**. An X-ray structure determination confirmed that the structure of **2** retains the approximate overall geometry of the original *nido*-iridahexaborane **4** with a [PtCl(PMe₂Ph)] moiety bonded to two borons and the Ir atom such that the cluster resembles a classical seven-vertex *nido* system derived by the removal of a five-connectivity vertex from a triangulated dodecahedron. This is illustrated in Figure 2, where a projection of the structure of **2** and the idealized cluster are compared. A difference from the idealized structure is that the IrB(3)B(4)B(5)B(6) plane remains relatively flat in **2** with a dihedral angle between the two subplanes IrB(4)B(5)B(6) and IrB(3)B(4) of only 22°. For the idealized cluster, such as that in the structurally determined [Zn(NH₃)₄][B₈H₈], **6**, the fold is 39.9°.³¹ The angle between the two planes PtIrB(4) and B(3)IrB(4) is 83.3° in **2** and the corresponding angle in **6** is 79.6°, further indicating the similarity of the two clusters and supporting the assignment of **2** as a *nido* seven-vertex cluster. A comparison of the structure of **2** with the that for the iridahexaborane **4** is illustrative of the difference between *nido* six-vertex clusters and *nido* seven-vertex clusters. The IrB(3)B(4)B(5)B(6) plane in **4** is essentially flat with a deviation of only 4.3° from planarity between the two planes IrB(4)B(5)B(6) and IrB(3)B(4). This is consistent with the description of the two clusters. The iridahexaborane,

Table 6

¹¹B and ¹H NMR Data in ppm for **2** in CD₂Cl₂ Solution at 25 °C Together with Comparison Data for **5** (CDCl₃ Solution, 21 °C)

assignment	compd 2		compd 5	
	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$
3	+64.7	+6.88 ^a	+68	+7.57 ^a
5/6	+47.2 ^c	+6.62 ^a	+71.4	+8.56
6/5	+22.7 ^c	+5.29	+20.5	+5.14
4	0.0	+3.04 ^a	+0.9	+3.21 ^a
1	−13.7	+2.48 ^b	−31.1	+0.87 ^b
H _{$\mu_{2,7}$}		−13.45		−10.61
H _{$\mu_{4,5}$}				−0.10
H _{$\mu_{5,6}$}		−0.74		+0.53
CH ₃		+0.74, +0.68 ^a		+0.74, +0.61 ^a

³¹P Chemical Shift Data (ppm) and Coupling Constants (Hz)

	compd 2	compd 5
$\delta[\text{P}(1/2)]\text{ppm}$	−0.22 (d)	−0.3
$\delta[\text{P}(2/1)]\text{ppm}$	−7.2 (t)	2.22
$\delta[\text{P}(3)]\text{ppm}$	+4.78 (s)	−3.3
$^2J(^{31}\text{P}(1/2) - ^{31}\text{P}(2/1))$	12	28
$^3J(^{31}\text{P}(3) - ^{31}\text{P}(2/1))$	6	<i>d</i>
$J(^{195}\text{Pt} - ^{31}\text{P}(1/2))$	<i>d</i>	32
$J(^{195}\text{Pt} - ^{31}\text{P}(2/1))$	<i>d</i>	20
$J(^{195}\text{Pt} - ^{31}\text{P}(3))$	4018	3339.8
$J(^{195}\text{Pt} - ^{11}\text{B}(1))$	69	55
$^2J(^{31}\text{P}(2/1) - ^1\text{H}_{\mu_{2,7}}]_{\text{cis}}$	6	<i>d</i>
$^2J(^{31}\text{P}(1/2) - ^1\text{H}_{\mu_{2,7}}]_{\text{cis}}$	18	19
$^2J(^{31}\text{P}(1/2) - ^1\text{H}_{\mu_{2,7}}]_{\text{trans}}$	64	99
$J(^{195}\text{Pt} - ^1\text{H}_{\mu_{2,7}})$	420	555
$^2J(^{31}\text{P} - ^1\text{H}(6))$	11	11.5
$^2J(^{31}\text{P} - ^1\text{H}(4))$	28	<i>d</i>
$^2J(^{31}\text{P} - ^1\text{H}(3))$	21	11.5
$^2J(^{31}\text{P} - ^1\text{H}(\text{Me}))$	12	12

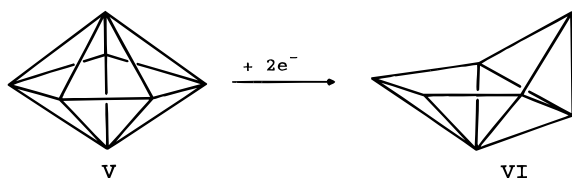
^a Doublet, probably due to coupling to phosphorus. See lower half of table. ^b Shows platinum satellites. See lower half of table. ^c ¹H{¹¹B_{selective}} irradiation of this resonance causes sharpening of H _{$\mu_{5,6}$} . ^d No coupling observed. Spectra recorded at −41 °C.

4, is a *nido* six-vertex cluster derived by removal of one of the apices from a pentagonal bipyramid, analogous to **1**, and thus the structure is expected to be that of a regular pentagonal pyramid with a planar five-membered-ring basal region. On the other hand, addition of a vertex to **4** should afford a *nido* seven-vertex cluster resulting in the folding of the plane by about 39°. There are small differences in the cage sizes for **2** and **4** which reflect the coordination of the Pt moiety. The fold in the five-membered plane results in the cage in **2** moving toward the B(5)–B(6) axis. The distances Ir–B(3)/B(3)–B(4) are slightly longer in **2** than in **4** and the apex, B(1) moves toward the B(5)–B(6) axis as reflected in the larger angles for B(3)–B(1)–B(5)/B(3)–B(1)–B(6) in **2** than in **4**. The coordination of the Pt moiety has the effect of tightening up the angle Ir–B(3)–B(4) in **2** with respect to **4** [110.1(10)° vs 117.3(3)°]. The structure of **2** is very similar to that of **5**, (PPh₃)₂(CO)Os(PhMe₂P)ClHPtB₅H₇, except that the Ir is replaced by Os and the additional electron is supplied by a bridging H atom between B(4) and B(5).^{7a,d} The species **5** is described as a *nido* seven-vertex cluster in which the metal atoms are considered as true vertices.⁷ The arguments are based on geometry and electronic factors, and the same may be said about **2**. The fold in the OsB(3)B(4)B(5)B(6) plane is represented by an interplanar angle of 28° in **5**, larger than in **2**, but other features of the two structures are quite similar. The related *nido*-carborane system, [Et₂C₂B₅H₆][−], to which we refer below, has a similar fold of 23.8°, which is closer to the value found for **2**.³²

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 (29) Barton, L.; Onak, T. P.; Shore, S. G. *Gmelin Handbook of Inorganic Chemistry, Boron Compounds 20*; Springer Verlag: Berlin, 1979; New Supplement Series Vol. 54, pp 52–79.
 (30) (a) Bould, J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1441. (b) Bould, J.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1992**, 563.
 (31) Guggenberger, L. *J. Inorg. Chem.* **1969**, 8, 2771.

NMR spectra for **2**, given in Table 6, are very similar to those for the related system **5**. Detailed coupling information was unobtainable for the boron resonances, but the ³¹P and ¹⁹⁵Pt couplings are summarized. Of interest is the H atom which bridges the two metals. It is observed at -13.45 ppm, and couplings to the three ³¹P atoms and ¹⁹⁵Pt are summarized in the table.

As described above, the cluster geometry of **2** conforms to that of a seven-vertex *nido* system. It is derived by the coordination of the Pt moiety to the atom triangle IrB(3)B(4). According to the PSEPT rules, it could also be obtained by the addition of two skeletal electrons to a pentagonal bipyramidal structure similar to **1**. Such a reaction would be analogous to the opening of the *closo*-carborane cage 2,3-Et₂C₂B₅H₅ with [BEt₃H]⁻ in the seminal work by Beck, Quintana, and Sneddon³² in the first report of a conventional non-metal-containing *nido* seven-vertex borane cluster, [Et₂C₂B₅H₆]⁻ (**6**). Such a transformation is depicted diagrammatically in illustrations **V** and **VI**. However there is a difference here in that cluster **2** is



formally two electrons short of the required 18 electrons for a classical *nido* structure based on a $2n + 4$ skeletal electron count where n is the number of vertices.^{21a,c,d} Thus **2** is analogous to **5** in this respect. The electron count in **5** led Sneddon and co-workers to suggest that it was a *closo* cluster.³² The rationale for the assignment of **5** as a *nido* cluster was based on the structure, which, as discussed above, conforms quite well to one derived from a triangulated dodecahedron minus a five-connected vertex. It has been pointed out that the electron count in **5** is acceptable for a *nido* system because the Pt center is not a conventional three-orbital two-electron conical vertex and the square planar Pt²⁺ moiety contributes only two orbitals and one electron to the skeletal electron count.^{7c,d} Similar arguments may be used to account for "anomalous" electron counts in other platinaboranes, for example 5,6-Me₂-7,7-(PEt₃)₂-7,5,6-PtC₂B₄H₄³³ and 7,7-(PMe₂Ph)₂-7-PtB₁₀H₁₂,³⁴ and related systems, and attempts have been made to account for the discrepancies in the latter systems using molecular orbital calculations.³⁵ The

carborane **6** is also unusual in that it is a *nido* cluster containing a BH₂ group and may be considered to be analogous to **2**. The (PhMe₂P)ClPt group is electronically and "lobally" equivalent to the BH₂ group in that both supply two orbitals and one electron to cluster bonding, proper, but the former does not have the additional electron pair in the *endo* terminal BH bond of the BH₂ moiety included for formal electron-counting purposes. On this basis, the skeletal electron counts for the carborane and the bimetalaboranes are equivalent and the conflict disappears.^{7c,32} In the case of 7,7-(PMe₂Ph)₂-7-PtB₁₀H₁₂, this species may be related to [B₁₁H₁₄]⁻ in the same way in which **2** is related to [Et₂C₂B₅H₆]⁻. The recently determined structure of the undecaborane [B₁₁H₁₄]⁻ reveals that it is another *nido* system which contains an *endo* terminal BH bond in a BH₂ group,³⁶ and the replacement of the latter by the [(PMe₂Ph)₂Pt] group to form the platinadecaborane 7,7-(PMe₂Ph)₂-7-PtB₁₀H₁₂,³⁴ which also has the "wrong" skeletal electron count for a *nido* system, represents a situation analogous to **2**. Again this phenomenon in 7,7-(PMe₂Ph)₂-7-PtB₁₀H₁₂ may be ascribed to the Pt moiety functioning as a two-orbital two-electron donor and adopting essentially a square planar configuration although contributions from higher valency Pt(IV) states have been proposed in these systems.^{34,37}

This work has demonstrated that standard chemistry which may be used to prepare metallaboranes from hexaborane(10) may also be utilized for metallahexaboranes to prepare hetero-bimetalboranes. Thus we have added a metal-containing acceptor to a basal B-B bond in (PPh₃)₂(CO)IrB₅H₈ to afford, after loss of H₂, the first example of a structurally characterized *closo*-heterobimetalloheptaborane. Also, by oxidative insertion of [(PMe₂Ph)ClPt]⁺ into the anion [(PPh₃)₂(CO)IrB₅H₇]⁻, we have isolated, in low yield, the *nido*-platinairidaheptaborane. The low yield of the latter may be due to difficulties in deprotonating (PPh₃)₂(CO)IrB₅H₈, so alternative approaches to deprotonation may afford better yields.

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Supporting Information Available: Tables giving X-ray experimental details, complete bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for the structures of 1,1,1-(CO)₃-2,2-(CO)₂-2,4-(PPh₃)₂-*closo*-1,2-FeIrB₅H₄ (**1**) and 2-(CO)-2,2-(PPh₃)₂-7-Cl-7-(PMe₂Ph)-*nido*-2,7-IrPtB₅H₇ (**2**) (14 pages). Ordering information is given on any current masthead page.

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