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Synthesis and Characterization of *nido*-[1,1,2,2-$(CO)_4$-1,2-$(PPh_3)_2$-1,2-$FeIrB_2H_5$]: A Heterobimetallaborane Analogue of *nido*-$[B_4H_7]^-$

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The synthesis and characterization of *nido*-[1,1,2,2-$(CO)_4$-1,2-$(PPh_3)_2$-1,2-$FeIrB_2H_5$] (**1**) is reported. **1** is formed in low yield as a degradation product from the reaction between $[\{\mu\text{-Fe(CO)}_4\}B_6H_9]^-$ and *trans*-Ir(CO)Cl$(PPh_3)_2$ in THF and is characterized from NMR, IR, and analytical data and by a single-crystal X-ray diffraction study. **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.8622(12)$, $b = 14.3313(12)$, $c = 23.579(3)$ Å, $\beta = 97.12(2)°$, $Z = 4$, $V = 4257.0(8)$ Å^3, $R_1 = 4.83\%$, and $wR_2(F^2) = 12.43\%$. The heterobimetallaborane structure may be viewed as a derivative of the binary boron hydride *nido*-$[B_4H_7]^-$ and is related to the known homobimetallatetraborane analogues $[Fe_2(CO)_6B_2H_6]$ and $[Co_2(CO)_6B_2H_4]$. **1** exhibits proton fluxionality in its ^{1}H NMR spectrum, which is related to that found in the latter two compounds.

Introduction

There has been much recent interest and activity in the preparation of polyhedral metallaboranes containing two boron atoms.[1] Species containing the $ML_nB_2H_5$ moiety have been prepared where the metal group is M$(CO)_4$ (M = Fe, Ru, Os),[2] CpM$(CO)_2$ (M = Fe, Ru),[3,4] Cp_2Mo(H),[5] and $(CpCo)_2(\mu\text{-PPh}_2)$.[6] These latter may be formally described as diborane(6) derivatives in which the metal coordinates to the B_2H_5 group and effectively replaces a proton. Systems containing the $ML_nB_2H_6$ moiety, including $[Fe_2(CO)_6B_2H_6]$,[7] $[Cp^*{}_2Ta_2(\mu\text{-X})_2(B_2H_6)]$,[8] and $Ru_3(CO)_9(B_2H_6)$,[9] are perhaps best considered as metal clusters wherein a BH moiety subrogates a metal vertex, and the additional H atoms (or halogens in the case of the Ta species) serve to provide the appropriate electron count. Similar arguments may be made for the species $[(\mu\text{-H})_3(CpCo)_4B_2H_2)]$,[10] $[(CpCo)_4PB_2H_2]$,[11] $[(Cp^*Co)_3B_2H_4]$,[12,13] $[(Cp^*Co)_4B_2H_4]$,[13] $[Co_2(CO)_6B_2H_4]$,[12,14] and $[Co_5(CO)_{14}B_2H]$.[12,14] Of major interest to this study are the species $[Fe_2(CO)_6B_2H_6]$, $[(Cp^*Co)_2B_2H_6]$, and $[Co_2(CO)_6B_2H_4]$. These latter compounds represent an isoelectronic series of tetrahedral clusters, and they are related to the structurally similar metal rich borane clusters of the general formula $H_nM_3(CO)_9BL_n$ (M = Fe, Ru, Os), pioneered by Fehlner, Housecroft, and Shore.[15] Although the chemistry of these M_2B_2 systems is very interesting, to this point they have proved not to be amenable to crystal structure determination, nor are there any examples which are heterobimetallic. In this paper we report that the major isolable product from the reaction between *trans*-Ir(CO)Cl$(PPh_3)_2$ and $[\mu\text{-}\{(CO)_4Fe\}B_6H_9]^-$ is the novel heterobimetallatetraborane *nido*-[1,1,2,2-$(CO)_4$-1,2-$(PPh_3)_2$-1,2-$FeIrB_2H_5$](**1**) and we also report a structure determination for the species.

Experimental Section

Reactions were carried out on a vacuum line using standard methods.[16] 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. $Fe_2(CO)_9$ (Aldrich) was used as received, and *trans*-Ir(CO)Cl$(PPh_3)_2$[17] and $[\{\mu\text{-Fe(CO)}_4\}B_6H_{10}]$[18] were prepared according to the literature methods. NMR spectroscopy was carried out on a Bruker ARX 500 spectrometer at 500.1 MHz for proton, 160.5 MHz for boron-11, and 202.5 MHz for phosphorus-31. Chemical shifts are reported in ppm 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

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for ^{31}P. Mass spectra were recorded by the Washington University, St. Louis, MO, mass spectrometry service. Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA.

Synthesis of *nido*-[1,1,2,2-(CO)$_4$-1,2-(PPh$_3$)$_2$-1,2-FeIrB$_2$H$_5$] (1). Fe$_2$(CO)$_9$ (0.66 g, 1.82 μmol) was placed in a round bottom flask together with a magnetic stir bar, the flask was attached to an extractor holding a two-neck flask on the other end, and the system was evacuated. B$_6$H$_{10}$ (0.2 mL, 1.82 mmol) and *ca.* 5 mL of pentane were condensed in at −196 °C, and the mixture was stirred at ambient temperature overnight. The extractor was inverted to filter the resultant yellow−brown solution into the two-neck flask placed in a −35 °C slush bath, and the system was pumped for 3−4 h and then was pumped at 0 °C for a further 2−3 h. Under a counter-current of nitrogen a tipper tube containing 85 mg, 1.82 mmol of KH (85% active) was attached to one arm of the flask. THF was condensed in, the KH was added, and deprotonation was carried out at −35 °C. After gas evolution had stopped the hydrogen was measured on a Toepler pump (*ca.* 1.2 mmol). The tipper tube was replaced with one containing *trans*-Ir(CO)Cl(PPh$_3$)$_2$ (1.56 g, 1.8 mmol), which was then added to the solution, and the stirring continued with slow warming to room temperature overnight. ^{11}B NMR spectra of the reaction mixture showed a number of new resonances, none of which corresponded to the starting materials. Analytical TLC of the mixture showed one bright yellow spot (70/30 CH$_2$Cl$_2$/pentane, R_f 0.8). Preparative TLC of the mixture gave one major yellow-orange band in the same position, and its ^{11}B NMR spectrum was essentially the same as that of the reaction mixture. A small amount of the title compound was apparent from the ^{1}H spectrum. Further preparative TLC resulted in the loss of all compounds other than the title compound, which was rechromatographed in benzene/pentane (50/50) and crystallized by diffusion of pentane into a CHCl$_3$ solution of the compound to give *nido*-[1,1,2,2-(CO)$_4$-1,2-(PPh$_3$)$_2$-1,2-FeIrB$_2$H$_5$] (**1**, 51 mg, 0.049 mmol, 2.7% yield). IR using a disposable teflon infrared card (3M)/cm^{-1}: ν(BH) 2546 w, br; ν(CO) 2034 s, 2003 s, 1986 s, 1980 s, 1962 s. Anal. for C$_{40}$H$_{35}$B$_2$O$_4$P$_2$FeIr·CHCl$_3$, obsd (calcd): C, 47.77 (47.78); H, 3.62 (3.52). HRMS: C$_{40}$H$_{36}$B$_2$O$_4$P$_2$FeIr, 913.1265 (obsd), 913.1254 (calcd). NMR, δ(^{11}B) (298 K): −17.2 ppm (resonance too broad to observe ^{1}H coupling). δ(^{1}H) (relative intensities in parentheses)/ppm (298 K): H[(3),(4)] +2.19(2), H(3,4) −4.34(1), H[(1,3),(1,4)] −13.77(2), phenyl resonances +7.24 to +7.61. δ(^{31}P) (213 K)/ppm: P(1) +60.5 (*s*), P(2) +19.8 (*s*). The high-temperature NMR behavior is described in the discussion section.

X-ray Structural Determination

A well-shaped crystal of dimensions 0.5 × 0.4 × 0.2 mm, obtained as described above, was mounted on a glass fiber in random orientation. Preliminary examination and data collection were performed on a Siemens P4 automated single crystal X-ray diffractometer using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) at 298 K. Autoindexing of 10 centered reflections from the rotation photograph indicated a monoclinic lattice. Equivalent reflections were checked to confirm the Laue symmetry; and a fractional index search was conducted to confirm the cell lengths.[19] Final cell constants and orientation matrix for data collection were calculated by least-squares refinement of the setting angles for 21 reflections ($10° < 2\theta < 30°$). Intensity data were collected using ω scans with variable scan speed. Three representative reflections measured every 97 reflections showed 11.3% 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.[20] An absorption correction was applied to the data using equivalent reflections and ψ scan reflections (XEMP). The structure was solved by the Patterson method and refined successfully in the monoclinic space group $P2_1/n$. 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 hydrogen atoms of the boron cage were located from difference Fourier syntheses, and the terminal hydrogens (two) were refined freely. The bridging hydrogen atoms could not be refined and were included in the final refinement in fixed positions. The phenyl group H atoms were refined using the riding model AFIX 43. The final residual values were $R(F) = 4.83\%$ for observed reflections $[I > 2(I)]wR(F^2) = 12.43\%$; s =1.015. Structure refinement parameters are listed in Table 1. The atomic coordinates for the non-hydrogen atoms and the geometrical parameters are listed in Tables 2, and 3 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 1.

Table 1. Crystal Data and Structure Refinement for **1**

empirical formula	C$_{40}$H$_{35}$B$_2$O$_4$P$_2$FeIr·CHCl$_3$
fw	1030.66
temp/K	298(2)
crystal system	monoclinic
space group	$P2_1/n$
a/Å	12.8622(12)
b/Å	14.3313(12)
c/Å	23.579(3)
β/°	97.12(2)
V/Å^{-3}	4257.0(8)
Z	4
D (calcd)/Mg m^{-3}	1.608
abs coeff/mm^{-1}	3.766
crystal size/mm	0.5 × 0.4 × 0.2
F(000)	2032
θ range for data collcn/deg	2.15 to 25.00
index ranges	$-15 \leq h \leq 15, -17 \leq k \leq 17, -28 \leq l \leq 27$
reflcns collcd	16 982
independent reflcns	7488 ($R_{\text{int}} = 0.0642$)
data/restraints/ parameters	7488/0/495
goodness-of-fit on F^2	1.015
final R indices [$I > 2\sigma(I)$]	
R_1	0.0483
$wR_2(F^2)$	0.01243
largest diff peak and hole/e Å^{-3}	1.332 to −1.088

Results and Discussion

The reaction of [{μ-Fe(CO)$_4$}B$_6$H$_9$]$^-$ with *trans*-Ir(CO)Cl(PPh$_3$)$_2$ at −35 °C in THF followed by thin layer chromatographic separation of the reaction mixture resulted in the isolation in *ca.* 3% yield of the air-stable, orange-red compound *nido*-[1,1,2,2-(CO)$_4$-1,2-(PPh$_3$)$_2$-1,2-FeIrB$_2$H$_5$] (**1**). The compound was characterized from NMR, IR, and mass spectrometries, elemental analysis, and a single-crystal X-ray diffraction study in which all heavy atoms were located and refined independently. Terminal borane hydrogen atoms were located and freely refined, but the bridging hydrogen atoms were refined in fixed positions. The geometric parameters for the bridging H atoms are reasonable with the metal-bridging hydrogen atoms occupying pseudo-octahedral positions approximately *trans* to the carbonyl ligands and are in accord with NMR data which are discussed below. Table 3 lists selected interatomic distances and angles for the compound.

Figure 1 shows a view of the cluster which may be regarded as having a trigonal pyramidal structure based on a closed trigonal bipyramid with one vertex missing (illustration **I**) and may be seen to be related to the proposed structure for the binary

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[19] XSCANS, Siemens Analytical Instruments, Madison, WI, 1994.

[20] Sheldrick, G. M., SHELXTL-PLUS, Siemens Analytical X-Ray Division, Madison, WI, 1994.

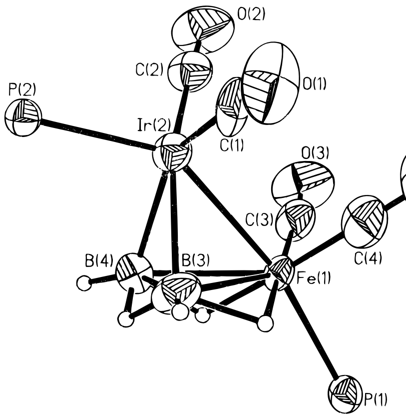
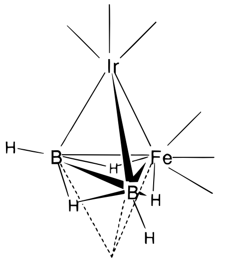


Figure 1. Molecular structure of *nido*-[1,1,2,2-$(CO)_4$-1,2-$(PPh_3)_2$-1,2-$FeIrB_2H_5$] (**1**) with 50% thermal ellipsoids. The phenyl groups are omitted for clarity.



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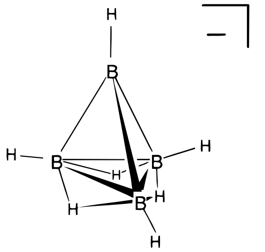

II

boron hydride analogue *nido*-$[B_4H_7]^-$ (**II**)[21] in which the $(PPh_3)(CO)_2Fe$ and $(PPh_3)(CO)_2Ir$ moieties supplant the isolobal BH and BH^- moieties, respectively.[22] The iridium vertex is thereby contributing three orbitals and three electrons to the bonding where the extra electron is centered on the iridium rather than as a relatively diffuse negative charge in the parent borane or in the diironborane, $[(CO)_6Fe_2B_2H_5]^-$,[7] described below, resulting in a large degree of two-center two-electron character to the interaction. This may be reflected in the Ir−Fe and Ir−B distances of *ca.* 2.621(1) and 2.16(1) Å. The latter is shorter than the Fe−B distances of *ca.* 2.23(1) Å, which are themselves in the middle of the range of multicenter-bonded hydrogen-bridged Fe−B bonds in other ferraboranes.[23] The Fe−B distances may be compared to the pentaborane(9) analogue $(CO)_6Fe_2B_3H_7$, where the unbridged "apical" $Fe(CO)_3$ unit exhibits significantly shorter Fe−B bonds than the H-bridged unit (*ca.* 2.06 *vs* 2.26 Å).[24] The 0.1 Å difference in the apical Ir−B and Fe−B distances in **1** and the latter compound is in line with the 0.1 Å difference in the covalent radii of iron and iridium.[25] The Ir−Fe distance is on the low end of a the range in a number of ferrairida metal clusters[26] and is shorter than the only other known ferrairidaborane compound, *closo*-$[(CO)_5(PPh_3)_2FeIrB_5H_4(PPh_3)]$ (2.706(2) Å), where the bimetalla unit is bridged by the much larger $[B_5H_4(PPh_3)]$ ligand.[27] The mixed metal ferrairida cluster **1** occupies a middle position between the known isoelectronic homobimetallaborane analogues, the group 8 system $[(CO)_6Fe_2B_2H_6]$ (**2**)[7] and the group 9 systems $[(CO)_6Co_2B_2H_4]$ (**3**)[12,14] and the related $[\eta^5\text{-}C_5Me_5)_2Co_2B_2H_6]$,[13] all of which were unsuitable for crystal structural characterization by X-ray diffraction.

Table 2. Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(eq)[a]
Ir(2)	1404(1)	−2824(1)	3480(1)	36(1)
Fe(1)	−245(1)	−2630(1)	3966(1)	28(1)
P(1)	−1458(2)	−2120(2)	4459(1)	35(1)
P(2)	2607(2)	−2087(2)	3036(1)	31(1)
Cl(1)	2726(7)	12012(4)	9177(3)	206(3)
Cl(2)	1926(6)	11819(7)	7990(3)	243(4)
Cl(3)	3858(7)	10996(5)	8459(5)	281(5)
B(4)	350(9)	−1627(7)	3376(5)	44(2)
B(3)	1188(9)	−1729(8)	4069(5)	48(3)
O(1)	3022(6)	−3751(6)	4434(3)	85(3)
O(2)	413(6)	−4236(5)	2565(3)	80(2)
O(3)	−1671(6)	−3724(6)	3108(3)	84(3)
O(4)	564(6)	−4208(6)	4675(4)	92(3)
C(1)	2417(8)	−3445(7)	4068(4)	51(2)
C(2)	805(7)	−3710(7)	2896(4)	46(2)
C(3)	−1127(7)	−3288(7)	3457(4)	51(2)
C(4)	248(8)	−3570(8)	4400(5)	60(3)
C(5)	2177(7)	−1712(6)	2282(3)	40(2)
C(6)	2851(8)	−1163(7)	2017(4)	54(3)
C(7)	2542(11)	−905(8)	1451(5)	76(4)
C(8)	1576(13)	−1187(9)	1140(4)	82(4)
C(9)	894(11)	−1711(9)	1382(5)	78(4)
C(10)	1196(9)	−1960(6)	1964(4)	54(3)
C(11)	3802(6)	−2777(6)	2997(3)	30(2)
C(12)	3748(6)	−3730(6)	2994(3)	36(2)
C(13)	4635(7)	−4283(6)	2961(4)	46(2)
C(14)	5583(7)	−3866(8)	2933(4)	54(3)
C(15)	5637(7)	−2903(7)	2928(4)	48(2)
C(16)	4763(7)	−2360(6)	2960(4)	47(2)
C(17)	3140(7)	−1020(6)	3421(3)	37(2)
C(18)	3922(8)	−1094(7)	3916(4)	55(3)
C(19)	4262(9)	−314(9)	4235(5)	74(3)
C(20)	3840(10)	535(8)	4056(6)	75(4)
C(21)	3082(10)	617(8)	3578(5)	72(3)
C(22)	2714(8)	−159(7)	3258(4)	55(3)
C(23)	−2187(6)	−1049(6)	4196(4)	37(2)
C(24)	−2509(7)	−929(6)	3600(4)	45(2)
C(25)	−3092(8)	−166(8)	3369(5)	63(3)
C(26)	−3347(8)	496(8)	3744(5)	69(3)
C(27)	−3007(8)	402(7)	4341(5)	66(3)
C(28)	−2448(7)	−378(6)	4563(4)	49(2)
C(29)	−2544(6)	−2950(6)	4497(3)	36(2)
C(30)	−3565(7)	−2658(7)	4485(4)	58(3)
C(31)	−4348(8)	−3307(9)	4505(5)	75(4)
C(32)	−4154(9)	−4225(8)	4521(4)	66(3)
C(33)	−3137(11)	−4524(8)	4554(5)	78(4)
C(34)	−2343(9)	−3881(7)	4522(5)	66(3)
C(35)	−911(7)	−1842(6)	5220(3)	38(2)
C(36)	−1264(7)	−2247(7)	5675(4)	52(2)
C(37)	−850(9)	−1984(8)	6239(4)	68(3)
C(38)	−89(8)	−1300(8)	6346(4)	64(3)
C(39)	250(8)	−888(7)	5900(4)	53(2)
C(40)	−128(7)	−1149(6)	5346(4)	43(2)
C(41)	3025(19)	11891(16)	8499(10)	183(9)

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

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(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 Cp·Ir(C(Me)═CHCH═C(Me))[μ-SFe(CO)$_4$]Fe(CO)$_2$ (Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2544) to 2.960 Å in FeIr(μ-PPh$_2$)(CO)$_5$(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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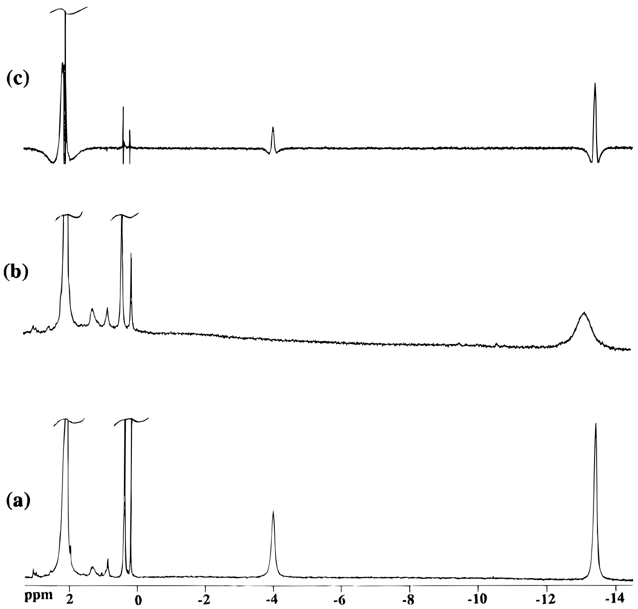
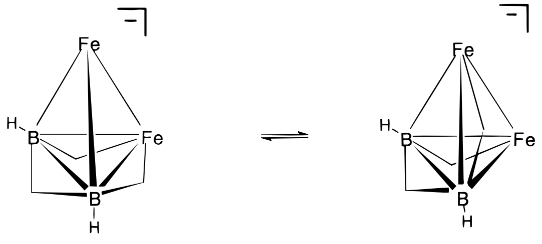


Figure 2. ^{1}H{^{11}B} NMR spectrum (in toluene-d_8) of **1** at (a) 298 K, showing the resonances Hμ(1,2), Hμ(1,4) at −13.77 ppm, Hμ(3,4) at −4.34, and H(3), H(4) at 2.19 ppm, and at (b) 350 K, showing broadening of the Hμ(1,2; 1,4) resonances and almost complete coalescence of the Hμ(3,4) and the H(3), H(4) resonances. (c) ^{1}H{^{11}B} NMR spectrum at 298 K with the ^{1}H spectrum subtracted, thus eliminating the solvent peaks in the region 0 to + 2.5 ppm.



III IV

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

Ir(2)−C(2)	1.917(9)	Fe(1)−C(4)	1.733(12)
Ir(2)−C(1)	1.919(11)	Fe(1)−C(3)	1.750(11)
Ir(2)−B(3)	2.150(11)	Fe(1)−B(3)	2.223(11)
Ir(2)−B(4)	2.169(11)	Fe(1)−B(4)	2.240(10)
Ir(2)−P(2)	2.294(2)	Fe(1)−P(1)	2.249(2)
Ir(2)−Fe(1)	2.6206(11)	Fe(1)−H(14)	1.5779(11)
P(1)−C(35)	1.834(8)	Fe(1)−H(13)	1.5376(10)
P(1)−C(23)	1.839(8)	P(2)−C(5)	1.832(8)
P(1)−C(29)	1.851(8)	P(2)−C(17)	1.839(8)
B(4)−B(3)	1.77(2)	P(2)−C(11)	1.845(8)
B(4)−H(4)	1.10(7)	B(3)−H(3)	0.83(9)
B(4)−H(14)	1.450(10)	B(3)−H(13)	1.390(11)
B(4)−H(34)	0.953(10)	B(3)−H(34)	1.300(13)
O(1)−C(1)	1.127(11)	O(3)−C(3)	1.152(11)
O(2)−C(2)	1.129(10)	O(4)−C(4)	1.147(12)
Cl(1)−C(41)	1.73(2)	Cl(2)−C(41)	1.66(2)
		Cl(3)−C(41)	1.69(2)
C(2)−Ir(2)−C(1)	109.1(4)	C(4)−Fe(1)−C(3)	95.4(5)
C(2)−Ir(2)−B(3)	149.5(4)	C(4)−Fe(1)−B(3)	101.0(5)
C(1)−Ir(2)−B(3)	91.7(5)	C(3)−Fe(1)−B(3)	142.8(4)
C(2)−Ir(2)−B(4)	106.9(4)	C(4)−Fe(1)−B(4)	137.4(4)
C(1)−Ir(2)−B(4)	140.1(4)	C(3)−Fe(1)−B(4)	100.1(4)
B(3)−Ir(2)−B(4)	48.4(4)	B(3)−Fe(1)−B(4)	46.8(4)
C(2)−Ir(2)−P(2)	100.8(3)	C(4)−Fe(1)−P(1)	99.0(3)
C(1)−Ir(2)−P(2)	97.0(3)	C(3)−Fe(1)−P(1)	96.2(3)
B(3)−Ir(2)−P(2)	98.4(3)	B(3)−Fe(1)−P(1)	113.6(3)
B(4)−Ir(2)−P(2)	92.8(3)	B(4)−Fe(1)−P(1)	118.2(3)
C(2)−Ir(2)−Fe(1)	98.1(3)	C(4)−Fe(1)−Ir(2)	86.8(3)
C(1)−Ir(2)−Fe(1)	103.0(3)	C(3)−Fe(1)−Ir(2)	96.5(3)
B(3)−Ir(2)−Fe(1)	54.5(3)	B(3)−Fe(1)−Ir(2)	51.9(3)
B(4)−Ir(2)−Fe(1)	54.8(3)	B(4)−Fe(1)−Ir(2)	52.3(3)
P(2)−Ir(2)−Fe(1)	146.19(6)	P(1)−Fe(1)−Ir(2)	165.47(7)
B(3)−B(4)−Ir(2)	65.2(5)	C(4)−Fe(1)−H(14)	177.5(3)
B(3)−B(4)−Fe(1)	66.1(5)	C(3)−Fe(1)−H(14)	85.6(3)
Ir(2)−B(4)−Fe(1)	72.9(3)	B(3)−Fe(1)−H(14)	76.9(3)
B(3)−B(4)−H(4)	148(4)	B(4)−Fe(1)−H(14)	40.1(3)
Ir(2)−B(4)−H(4)	130(4)	P(1)−Fe(1)−H(14)	83.13(7)
Fe(1)−B(4)−H(4)	140(4)	Ir(2)−Fe(1)−H(14)	90.85(4)
B(3)−B(4)−H(14)	96.7(6)	C(4)−Fe(1)−H(13)	82.7(4)
Ir(2)−B(4)−H(14)	115.1(6)	C(3)−Fe(1)−H(13)	178.1(3)
Fe(1)−B(4)−H(14)	44.5(3)	B(3)−Fe(1)−H(13)	38.2(3)
H(4)−B(4)−H(14)	99(4)	B(4)−Fe(1)−H(13)	81.4(3)
B(3)−B(4)−H(34)	45.7(6)	P(1)−Fe(1)−H(13)	84.03(7)
Ir(2)−B(4)−H(34)	106.8(8)	Ir(2)−Fe(1)−H(13)	83.50(4)
Fe(1)−B(4)−H(34)	95.2(7)	H(14)−Fe(1)−H(13)	96.29(6)
H(4)−B(4)−H(34)	105(4)	Fe(1)−B(3)−H(3)	130(7)
H(14)−B(4)−H(34)	95.8(8)	B(4)−B(3)−H(13)	105.0(8)
B(4)−B(3)−Ir(2)	66.3(5)	Ir(2)−B(3)−H(13)	107.2(6)
B(4)−B(3)−Fe(1)	67.1(5)	Fe(1)−B(3)−H(13)	43.1(3)
Ir(2)−B(3)−Fe(1)	73.6(4)	H(3)−B(3)−H(13)	89(6)
B(4)−B(3)−H(3)	161(7)	B(4)−B(3)−H(34)	31.6(4)
Ir(2)−B(3)−H(3)	122(7)		

The boron-11 NMR spectrum of **1** shows a single resonance indicating equivalent boron atoms, and the ^{1}H{^{11}B} spectrum at room temperature shows two equivalent terminal BH, one B−H−B, and two equivalent M−H−B resonances. (Figure 2a) The ^{31}P spectrum shows two singlets at +60.5 ppm, which is in the region characteristic for the [Fe(CO)$_2$(PPh$_3$)] moiety,[28] and +19.8 ppm from the PPh$_3$ groups on the Ir, which compares well to the values for the ^{31}P resonances in the [Ir(CO)(PPh$_3$)$_2$] moiety in *closo*-[(CO)$_5$(PPh$_3$)$_2$FeIrB$_5$H$_4$(PPh$_3$)].[27] No coupling of phosphorus to the metal-bridging hydrogen atoms was apparent such that selective phosphorus decoupling would confirm the bridging H atom positions found in the solid state. With the temperature raised to 250 K the B−H−B-bridging hydrogen and the terminal BH resonances broaden and disappear into the base line while the metal-bridging hydrogen resonance broadens (Figure 2). Upon cooling, the original spectrum reappears. It was not possible to resolve exactly the nature of the fluxional process, as further heating caused rapid decomposition of the complex before coalescence could be observed, and relative intensity measurements of the terminal and bridging hydrogen atom regions in the proton spectrum were unreliable due to overlapping protonic solvent impurities. However, the broadening of all resonances does suggest that all H atoms are interchanging in contrast to the diferraborane, **2a**, [B$_2$H$_5$Fe$_2$(CO)$_6$]$^-$, which also exhibits fluxionality albeit at a lower temperature (-90 to +20 °C). In this case the exchange process involves the terminal boron hydrogen atoms and the metal-bridging hydrogen atoms *via* rotation of a BH$_2$ fragment around the BH(bridge) axis.[7b] This effectively involves, using the trigonal prismatic description for **1** depicted above, an exchange of one of the M−H−B hydrogens between a "basal" and an "apical" position (**III** to **IV**). As may be seen, the structure of **1** corresponds to the conformation shown in illustration **III.** The dicobaltaborane, **3** (**V**), also shows a similar fluxional process which is proposed to involve three distinct stages: exchange of the Co−H−B proton between Co−B edge and face-bridging positions, Co−H−B, B−H(terminal) exchange, and exchange of the B−H−B proton with all others. There was no evidence of H exchange with the iridium vertex in **1** (although the possibility cannot be excluded), suggesting only a two-stage process in **1**. The structurally characterized and

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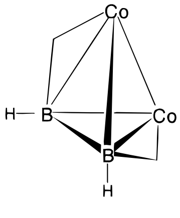
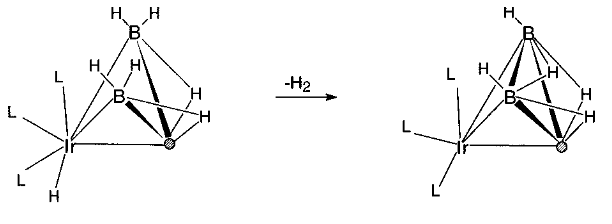
(28) For example, see: Howell, J. A. S.; Squibb, A. D.; Goldschmidt, Z.; Gottleib, H. E.; Almadhoun, A.; Goldberg, G. *Organometallics*, **1990**, *9*, 80.

related fused cluster $[(CO)_6Fe_2B_2H_4]_2$, which has a similar arrangement of "basal" bridging hydrogen atoms, shows no fluxionality of any kind.[29]



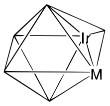
V

Although we choose to describe **1** as a heterobimetallaborane analogue of *nido*-$[B_4H_7]^-$ it is also possible to view **1** as structurally related to *arachno*-$[(CO)(PPh_3)_2HIrB_3H_7]$, the metallaborane analogue of *arachno*-B_4H_{10},[30] with a BH vertex subrogated by the $Fe(CO)_3$ moiety,[31] *via* loss of two hydrogen atoms. Although such a transformation (**VI** → **VII**) has not been observed in this case, such *arachno* → *nido* transitions with loss of H_2 have been experimentally observed in iridaborane systems,[32] thus it is possible that a stable monometalla-*nido*-iridatetraborane $[L_3IrB_3H_6]$ could be prepared from *arachno*-$[(CO)(PPh_3)_2HIrB_3H_7]$, although the facile loss of PPh_3 from iridium in these systems suggests that elimination of a mole of H_2 *via* thermolysis of the *arachno*-iridatetraborane may not be the best approach.

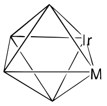


VI VII

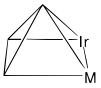
The cluster **1** may also be added to the series of heterometallaborane clusters that we recently[33] have prepared and structurally characterized containing iridium and a group 8 metal (osmium) with five (**VIII**), four (**IX**), three (**X**), and now two (**XI**) boron atom vertices. ^{11}B and ^{1}H NMR of the reaction mixture showed, in addition to small amounts of the title compound, the presence of other metallaborane species which were the main products of the reaction but which were not isolable using the chromatographic techniques employed. We hope that further work will extend the series (**VIII**−**XI**) shown above to include bimetallaoctaborane clusters.



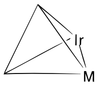
VIII



IX



X



XI

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Supporting Information Available: Tables of bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

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