Metallaborane Heteroatom Incorporation Reactions: Metallacarboranes, Metallathiaboranes, and an Iridaazaborane from Iridanonaborane Precursors

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Formation of metallaheteroboranes by insertion of heteroatoms into an existing metallaborane cluster, rather than adding the metal moiety to the heteroborane which is normally the case, has been achieved in the cases of carbon, nitrogen, and sulfur to produce nine-, ten-, and eleven-vertex metallaheteroborane clusters. Thus passage of acetylene through refluxing *p*-xylene solutions of either *arachno*-[$(PMe_3)_2(CO)HIrB_8H_{12}$] (**1a**) or *nido*-[$(PMe_3)_2(CO)IrB_8H_{11}$] (**2a**) afforded the 11-vertex cluster *nido*-[9,9,9-$(PMe_3)_2$(CO)-9,7,8-$IrC_2B_8H_{11}$] (**5a**) in up to 44% yield. With the cage substituted species *arachno*-[$(PMe_3)_2(CO)HIrB_8H_{11}Cl$] (**1b**), the analogous product is *nido*-[5-Cl-9,9,9-$(PMe_3)_2$(CO)-9,7,8-$IrC_2B_8H_{10}$] (**5b**) and the position of the Cl substituent in the product suggests that the acetylene moiety attacks across the open face of the intermediate *nido*-iridanonaborane species and that cage rearrangement does not occur during the course of the reaction. Similarly, reaction of **1a** with H_2S under identical conditions results in the formation *nido*-[2,2,2-$(PMe_3)_2$H-2,6-$IrSB_8H_{10}$] (**9a**), *closo*-[2,2,2-$(PMe_3)_2$H-2,1-$IrSB_8H_8$] (**10**), and *nido*-[$(PMe_3)_2HIrS_2B_8H_8$] (**11a**) in overall yields of 13%, 7%, and 20%, respectively. Additionally, refluxing a solution of **1a** and anhydrous hydrazine in xylene afforded a 10% yield of the novel iridaazanonaborane *nido*-[2,2,2-$(PMe_3)_3$-2,9-$IrNB_7H_9$] (**12**). The compound is the first metallaazanonaborane cluster to be described, and its formation indicates that methods similar to those used to generate azaboranes may be used on metallaboranes to generate metallazaboranes. In addition to characterization by a combination of ^1H, ^{31}P, and ^{11}B NMR and IR spectroscopy and high-resolution mass spectrometry, single-crystal X-ray diffraction studies were carried out on compounds **5a**, **9a**, **10**, and **12**.

Introduction

Syntheses of metallaheteroborane clusters are typically effected by the addition of metal complexes to heteroborane clusters.[1] The most ubiquitous metallaheteroboranes are metallacarborane complexes although much work is being done on metalla complexes of thia,[2,3] aza,[4] and other heteroatom species, but herein we focus only on those containing the atoms C, S, and N. Little attention has been given to the idea of producing metallaheteroborane clusters by the addition of the heteroatom to metallaborane clusters. Some carbon insertion products involving iridaboranes have been isolated in low yields as the unexpected degradation products from the reaction of $Ir(CO)Cl(PPh_3)_2$ and $[B_{10}H_{10}]^{2-}$ in refluxing methanol, *viz.* [$(PPh_3)(PPh_2P$-$C_6H_4)IrB_8H_6(OMe)C(OH)$] and [$(MeCOO)(PPh_3)\{HIrCB_8H_7(PPh_3)\}$],[5] and other work has been done on the reactions of iridadecaborane clusters with unsaturated molecules[6a−c] although only one of these, to our knowl-

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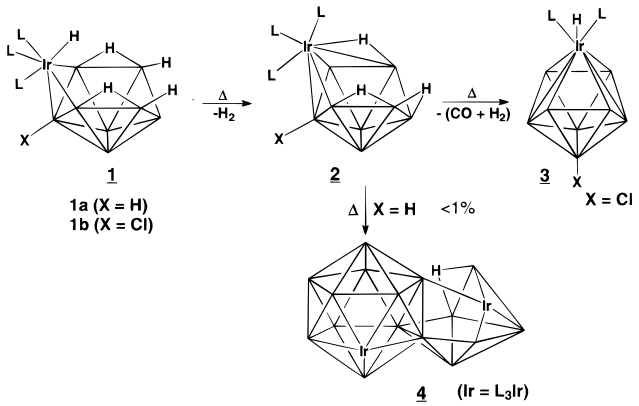
Scheme 1



edge, has been reported to result in heteroatom insertion.[6d,e] This latter example involves the incorporation of a RCN moiety into ruthena- and rhodadecaboranes, but it is less clear whether this reaction involves the metal center.

The iridanonaborane cluster *arachno*-[$(PMe_3)_2(CO)HIrB_8H_{11}X$] (X = H, **1a**; X = Cl, **1b**) is a unique example of a single metallaborane cluster compound which exhibits the classic *arachno* → *nido* → *closo* sequence (**1** → **2** → **3**, when X = Cl) of borane cluster chemistry.[7] The clusters exhibit an orbital and electronic flexibility that involves proposed changes in both the formal oxidation state of the metal (Ir(III) to Ir(V) during **2** → **3**) and in the orbital interaction of the metal with the cluster {two (**1**) to three (**2**) to four (**3**) orbitals}.[8] Conversely, when X = H, the *nido* → *closo* transition does not occur and low yields of larger clusters such as [$\{(PMe_3)_2(CO)Ir\}_2B_{16}H_{14}$] (**1** → **2** → **4**) have been observed.[9] Our initial studies on the work reported herein were based on the surmise that during the intracluster closure process (**1** → **3**) or intercluster condensation process (**1** → **4**) in which the iridium center essentially becomes more intimately bonded to the cluster, the iridium moiety would proceed through a transition state in which a coordinative site vacancy on the metal might be available to react with other, moderately nucleophilic species, rather than the cage itself. We chose to use acetylene rather than, for example, MeNC in order to reduce the possibility of simple ligand adduct formation although, in one case, as mentioned above, nitrile cage incorporation has been observed.[6] Some products of cage insertion of carbon involving group 6[10a] and 9[10b] metallaboranes wherein carbonyl insertion effectively occurs have been observed. Related to this, orthocycloboronation reactions have been observed in iridaborane and other metallaborane clusters in which the H atom and the associated electron pair in the aryl CH bond of PPh_3 ligands on the metal are added to a boron vertex in the cluster suggesting that the metal vertex could play a direct role in the interaction of borane clusters and unsaturated organic nucleophiles.[11] Important in the context of this report are reactions of alkynes and alkenes with metallaboranes in which reaction appears to take place at the metal center. Aromatization of norbornadiene at a Rh center in a rhodacarborane has been observed,[12] and recently reactions involving metal promoted alkyne[13a] and norbornadiene[13b] insertion into BH bonds have been described although carbon cluster incorporation was not observed in either case. Metallacarboranes are formed by the insertion of C_2H_2 into 2-(η^5-C_5H_5)CoB_4H_8 in a reaction analogous to the insertion of C_2H_2 into B_5H_9[14] and photolytic methods have also yielded carbon insertion products, *viz*. $(CH_3)_4C_4B_4H_4$ from the photolysis of B_4H_8-$Fe(CO)_3$ with $CH_3C{:}CCH_3$.[15] Also pertinent to this discussion is the pyrolytic incorporation of the (C_5H_5) moiety and cluster expansion in [(η^5-$C_5H_5)_2HMo(\eta^2$-$B_2H_5)$] to give [$CpMo(\eta^3{:}\eta^2$-$C_3H_3)C_2B_9H_9$)].[16] Various other low-yield carbon insertions related to this latter report have been observed. This article reports the incorporation of a C_2 unit into an iridanonaborane and also the incorporation of both one and two S atoms and also a N atom into an iridanonaborane.

Experimental Section

Solvents used were reagent grade and were dried before use. *p*-Xylene was dried by refluxing and storage over NaH. Reactions were carried out under a nitrogen atmosphere and 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). Acetylene gas and H_2S were commercial grade in cylinders. *arachno*-[$(PMe_3)_2(CO)HIrB_8H_{12}$] (**1a**) and *arachno*-[$(PMe_3)_2(CO)HIrB_8H_{10}Cl$] (**1b**) were prepared according to the literature method[8b] although extra purification steps in the preparation of *trans*-$Ir(CO)Cl(PMe_3)$[17] used in the synthesis of the metallaborane resulted in a yield of 41% compared to 30% previously of *arachno*-[$(PMe_3)_2(CO)HIrB_8H_{12}$] and a concomitant reduced yield of the Cl-substituted analogue. *nido*-[$(PMe_3)_2(CO)IrB_8H_{11}$] (**2a**)[8c] was prepared by heating the *arachno*-iridanonaborane in a tube under vacuum at 400 ± 2 K for *ca*. 1 h followed by the addition of a minimum quantity of cold $CHCl_3$ to give a colorless solution containing the *nido* component as an almost white powder which may be recovered by filtration. Remaining traces of **1a** in the filtrate were recycled or purified by TLC. NMR spectroscopy was carried out on a Bruker ARX 500 spectrometer at 500.1 MHz for proton and 160.5 MHz for boron-11 and 202.5 MHz for ^{31}P. 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 ^1H, and of 85% H_3PO_4 for ^{31}P. High-resolution mass spectra (HRMS) were recorded at the Analytical Sciences

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Center of the Monsanto Co., St. Louis, MO, on a Finnigan MAT-95 mass spectrometer in the FAB mode using a nitrobenzyl alcohol matrix and standardized with PEG1000. The masses reported are for the most abundant peak (100%) in the molecular ion envelope. Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA.

Reaction of *arachno*-[(PMe$_3$)$_2$(CO)HIrB$_8$H$_{12}$] (1a), *arachno*-[(PMe$_3$)$_2$(CO)HIrB$_8$H$_{11}$Cl] (1b), and *nido*-[(PMe$_3$)$_2$(CO)IrB$_8$H$_{11}$] (2) with Acetylene. Acetylene gas, direct from the cylinder, was passed through an 2-propanol/dry ice trap into a two neck flask fitted with a condenser and containing a 5 mL *p*-xylene solution of *arachno*-[(PMe$_3$)$_2$(CO)HIrB$_8$H$_{12}$] (**1a**) (79 mg, 0.17 mmol). The solution was degassed for 10 min and then heated to reflux for a further 40−45 min during which time the solution darkened. The solution was cooled, the solvent removed under vacuum, redissolved in CH_2Cl_2 and filtered through silica gel, and again reduced in volume, applied to a preparative TLC plate, and developed with 70% CH_2Cl_2/pentane. Two colorless bands, visible under UV illumination, were apparent; one, R_f 0.4, was identified as *nido*-[(PMe$_3$)$_2$(CO)IrC$_2$B$_8$H$_{11}$] (**5a**). The compound was removed from the silica gel with CH_2Cl_2. Pentane was added to the filtrate to give analytically pure, off white crystals. [Anal. Obsd (calcd): C, 21.93 (21.88); H, 5.78 (5.92). Yield: 36 mg, 0.073 mmol, 44%. IR/cm^{-1}: ν(CO) 1998 (s), ν(BH) 2517 (s).] Single crystals, suitable for X-ray analysis were grown by diffusion of pentane into a $CDCl_3$ solution of the compound. **5a** is air stable and sublimes at 150−200 °C *in vacuuo*. A second band at R_f 0.1−0.2 was characterized as *nido*-[(PMe$_3$)$_3$IrC$_2$B$_8$H$_{11}$] [compound **6**, HRMS (C$_{11}$H$_{38}$B$_8$IrP$_3$): *m*/*q* 542.2632 (obsd), 542.2615 (calcd)] by a comparison of the ^{1}H, ^{11}B, and ^{31}P NMR spectra with those of **5a**. In a similar reaction, 72 mg, 0.15 mmol, of *nido*-[(PMe$_3$)$_2$(CO)IrB$_8$H$_{11}$] was allowed to react with acetylene to give **5a** in 41% yield. Compound **6** was also detected and combined with the product from the previous reaction to give 8 mg, 0.015 mmol, *ca*. 5% yield per reaction. Small amounts of the known[18,19] *isonido* cluster type [(PMe$_3$)$_2$HIrC$_2$B$_8$H$_{10}$] {**7a**: NMR (ppm) ^{11}B [^{1}H] +50.6 [+7.53], +11.5 [+4.85], +1.8 [+2.16 {*doublet*, $^3J(^{31}P-^1H)$ = 13 Hz}], −7.4 [+1.32], −13.2 [−0.20], −22.3 [+1.80], −27.7 [+0.09], −45.8 [−2.75], Ir−H −7.83 (*doublet* of *doublets*, *J* = 17 and 30 Hz), cage C−H +3.81, +3.76; HRMS, (C$_8$H$_{28}$B$_8$Ir$_1$P$_2$) *m*/*q* 466.2147 (obsd), 466.2095 (calcd)} were also observed in the reaction products. Refluxing xylene solutions of **5a** for *ca*. 1 h gave **7a** in approximately 25% yield based on the amount of reactant consumed (38 mg of **5a** gave 3.5 mg of **7a**, and 24 mg of **5a** was returned).

Similarly to the above acetylene was passed through a xylene solution of 25 mg of *arachno*-[(PMe$_3$)$_2$(CO)HIrB$_8$H$_{11}$Cl] (**1b**) and the resultant mixture separated by TLC using 60:40 CH_2Cl_2/pentane as the mobile phase giving a band at R_f 0.3 containing 14.5 mg of material. The band was examined by NMR and seen to be a mixture of two compounds. The mixture could not be separated by chromatographic methods. Addition of pentane to a CH_2Cl_2 solution gave two crystalline species consisting of clumps of well-formed yellow crystals surrounded by colorless thin platelets. Separation was achieved by manually removing the yellow crystals from the clumps under a microscope giving a small amount (1.5 mg) of the colorless material which was identified as *nido*-[9,9,9-(PMe$_3$)$_2$(CO)-9,7,8-IrC$_2$B$_8$H$_{10}$-(5-Cl)] {**5b**: IR/cm^{-1} ν(CO) 2006 (s), ν(BH) 2485, 2535, 2577; HRMS showed two equal intensity fragmentation envelopes corresponding to the molecular ion C$_9$H$_{28}$B$_8$IrP$_2$OCl (*m*/*q* 528.1744 (obsd), 528.1731 (calcd)) and the molecular ion minus (CO + H) (499.1715 (obsd), 499.1704 (calcd))}. The yellow crystals identified as the *closo*-type cluster [(PMe$_3$)$_2$HIrC$_2$B$_8$H$_9$Cl] (**7b**) have been characterized by a single-crystal X-ray diffraction study and reported independently.[20]

Reaction of *arachno*-[(PMe$_3$)$_2$(CO)HIrB$_8$H$_{12}$] with 1-Heptyne. 1-Heptyne (110 μL, 0.83 mmol, Aldrich) was syringed into a toluene solution of **1a** (40 mg, 0.085 mmol) and the mixture refluxed for 54 min during which time it changed from colorless to dark yellow. After cooling the solvent was removed and the residue redissolved in CH_2Cl_2 and separated by TLC using 60:40 CH_2Cl_2/pentane. A number of boron-containing bands were observed on the TLC plate under UV light only one of which, a colorless band at R_f 0.25 yielding a pale yellow oil soluble in pentane, has so far been identified and partially characterized as *nido*-[(PMe$_3$)$_2$(CO)IrC$_2$B$_8$H$_{10}$-(C$_5$H$_{11}$)] {**8**, 13 mg, 0.022 mmol, *ca*. 25% yield; IR/cm^{-1} ν(CO) 1989(*s*), ν(BH) 2512 (br) 2563 (sh); HRMS (C$_{14}$H$_{39}$B$_8$IrP$_2$O) *m*/*q* 563.2921 (obsd), 563.2911 (calcd) [N.B. The most abundant peak at *ca*. *m*/*q* 564 was obscured by overlapping PEG calibrant peak] and molecular ion minus (H + CO) 535.2942 (obsd), 535.2881 (calcd)}. Boron-11 and ^{1}H NMR showed that the oil contained an amount of what was apparently a *nido*-iridadicarbaundecaborane isomer which could not be removed by TLC methods and thus preventing the definitive characterization of the compound.

Reaction of *arachno*-[(PMe$_3$)$_2$(CO)HIrB$_8$H$_{12}$] and *nido*-[(PMe$_3$)$_2$(CO)IrB$_8$H$_{11}$] with H$_2$S. Hydrogen sulfide gas, direct from the cylinder, was passed through a 5 mL *p*-xylene solution of **1a** (58.5 mg, 0.12 mmol) for 10 min and then heated to reflex for a further 40−45 min during which time the solution turned slightly red and some material deposited on the sides of the vessel. The mixture was allowed to cool, the solvent removed under vacuum, redissolved in CH_2Cl_2, and filtered through silica gel. The filtrate was again reduced in volume, applied to a preparative TLC plate and developed with 70% CH_2Cl_2/pentane. A number of almost colorless bands, visible under UV illumination were apparent. Among these, **A,** R_f 0.8, was identified as *nido*-[2,2,2-(PMe$_3$)$_2$H-2,6-IrSB$_8$H$_{10}$] [**9a**, 5 mg, 13% yield (all yields based amount of iridanonaborane consumed); mass spectrometry showed the molecular ion with loss of H$_2$, *m*/*q* (C$_6$H$_{27}$B$_8$IrP$_2$S) 472.1674 (obsvd), 472.1736 (calcd)]. Crystals of the product formed in $CDCl_3$ NMR solution when stored in the refrigerator overnight. A second band **B**, R_f 0.7, was isolated and identified as *nido*-[(PMe$_3$)$_2$HIrS$_2$B$_8$H$_8$] (**11a**, 9 mg 20% yield, HRMS for C$_6$H$_{27}$B$_8$Ir$_1$P$_2$S$_2$ *m*/*q* 504.1409 (obsvd) 504.1456 (calcd). ^{11}B NMR showed minor amounts of other species associated with **B**. A third band **C**, R_f 0.5, was identified as *closo*-[2,2,2-(PMe$_3$)$_2$H-2,1-IrSB$_8$H$_8$] [**10**, 2.6 mg, 7%; HRMS shows the molecular ion minus H, *m*/*q* (C$_6$H$_{26}$B$_8$IrP$_2$S) 471.1633 (obsd) 471.1658 (calcd)]. Finally, a band **D**, R_f 0.4, identified as the starting material *nido*-[(PMe$_3$)$_2$(CO)IrB$_8$H$_{11}$](20.5 mg, 35%) was isolated.

Each of the metallathiaborane compounds was found to react cleanly with the $CDCl_3$ NMR solvent, slowly at room temperature and more rapidly at elevated temperatures. A $CDCl_3$ solution of compound **9a** was left in a water bath at 50 °C for 4 days and showed *ca*. 60% conversion to product. TLC in 70% CH_2Cl_2/pentane showed two bands, the first at R_f 0.8 due to **9a** and the second, a pale yellow band at R_f 0.3, identified as *nido*-[2,2,2-(PMe$_3$)$_2$Cl-2,6-IrSB$_8$H$_{10}$] (**9b**). Pale yellow crystals were obtained from CH_2Cl_2/pentane solution. Mass spectroscopy showed two ion envelopes normalized to relative intensities of *ca*. 40% and 100%. The former was probably due to compound **9b** with loss of H [*m*/*q* for C$_6$H$_{27}$B$_8$IrP$_2$SCl 508.1422 (obsd), 508.1410 (calcd)], and the latter, due to the molecular ion with loss of HCl [*m*/*q* for C$_6$H$_{26}$B$_8$IrP$_2$S 472.1724 (obsvd), 472.1736 (calcd)].

The chloro-substituted derivative of compound **11a** was isolated similarly giving pale yellow crystals, R_f 0.3, as *nido*-[(PMe$_3$)$_2$ClIrS$_2$B$_8$H$_8$] (**11b**). HRMS gave two envelopes of equal

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Table 1. Crystal Data and Structure Refinement for Compounds 5a, 9a, 10, and 12

compd no.	**5a**	**9a**	**10**	**12**
empirical formula	$C_9H_{29}B_8IrOP_2$	$C_6H_{29}B_8IrP_2S$	$C_6H_{27}B_8IrP_2S$	$C_{10}H_{37}B_7IrCl_3NP_3$
fw	493.94	473.97	471.96	638.54
temp/K	295(2)	295(2)	295(2)	295(2)
cryst system	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1$
a/Å	8.769(3)	9.385(7)	9.046(3)	9.739(3)
b/Å	16.666(5)	9.485(7)	9.184(3)	9.865(2)
c/Å	13.511(4)	12.466(9)	12.508(8)	13.970(5)
α/deg	90	69.14(5)	70.66(4)	90
β/deg	97.12(2)	97.12(2)	74.90(4)	101.90(3)
γ/deg	90	63.63(3)	65.62(2)	90
V/Å^{-3}	1959.3(11)	921.1(12)	883.8(7)	1313.3(2)
Z	4	2	2	2
D(calcd)/Mg/m^3	1.674	1.709	1.774	1.615
abs coeff/mm^{-1}	6.967	7.511	7.828	5.569
cryst size/mm	0.5 × 0.3 × 0.2	0.4 × 0.2 × 0.1	0.4 × 0.5 × 0.1	0.03 × 0.1 × 0.5
F(000)	952	456	452	624
diffractometer used	Siemens P4(ST)	Siemens R3m	Siemens P4(ST)	Siemens P4(ST)
radiation used, Å	0.710 73	0.710 73	0.710 73	0.710 73
intensity collcn method	ω-2θ	ω	ω	ω
θ range for data collcn/deg	1.95−30.60	1.76−27.51	1.74−27.57	2.14−25.07
index ranges	$-12 \le h \le 12$, $0 \le k \le 23$, $-17 \le l \le 19$	$-10 \le h \le 12-10 \le k \le 11$, $-15 \le l \le 16$	$-11 \le h \le 11-11 \le k \le 44$, $-16 \le l \le 16$	$-11 \le h \le 9$, $-9 \le k \le 10$, $-13 \le l \le 15$
reflcns collcd	6016	7371	6888	2925
indepdt reflcns	5752 (R_{int} = 0.0433)	4157 (R_{int} = 0.0300)	4074 (R_{int} = 0.0681)	2448 (R_{int} = 0.0778)
data/restraints/params	5750/0/240	4153/0/213	4050/0/187	2445/1/137
goodness-of-fit on F^2	1.030	1.045	1.044	1.041
final R indices [$I > 2\sigma(I)$]				
R_1	0.0378	0.0298	0.0521	0.0882
wR_2	0.0766	0.0774	0.1389	0.2509
largest diff peak and hole/e Å^{-3}	1.672 and −0.751	0.890 and −1.717	3.845 and −2.777	2.600 and −2.119

intensity (m/q ($C_6H_{26}B_8IrP_2S_2Cl$) 539.0860 (obsd), 539.1052 (calcd); low resln m/q [rel. intensity obsd (calcd)] 535 [20 (19)], 536 [44 (46)], 537 [75 (77)], 538 [98 (99)], 539 [100 (100)], 540 [73 (73)], 541 [36 (34)], 542 [18 (18)]} and **11b** with loss of Cl (m/q, $C_6H_{26}B_8IrP_2S_2$ 503.1072 (obsd), 503.1378 (calcd); low resln m/q [rel. intensity obsd (calcd)] 500 [24 (22)], 501 [56 (52)], 502 [90 (84)], 503 [100 (100)], 504 [91 (90)], 505 [56 (53)], 506 [14 (11)]}.

Preparation of *nido*-[2,2,2-(PMe_3)$_3$-2,9-$IrNB_7H_9$] (12). To a dry, degassed xylene solution of **1a** (40 mg, 84 μmol) was added 0.054 mL of anhydrous hydrazine *via* syringe. The solution was heated to reflex for 40 min during which time a gray precipitate formed. After cooling, the solvent was removed and the mixture redissolved in CH_2Cl_2 and filtered giving 31.4 mg of insoluble solid. The filtrate was reduced in volume, applied to a preparative TLC plate, and developed using 70/30 CH_2Cl_2/pentane. A number of bands were apparent under UV illumination only one of which, the strongest, was amenable to isolation and was characterized as the title compound *nido*-[2,2,2-(PMe_3)$_3$-2,9-$IrNB_7H_9$] (**12**) (4.0 mg, 8 μmol, 10% yield, IR ν(BH) 2540, 2493 cm^{-1}) as an air-stable colorless crystalline solid. The high-resolution FAB mass spectrum for **12** showed two strong, almost equal intensity, envelopes corresponding to the molecular ion for **12** ($C_9H_{36}IrB_7NP_3$, m/q 519.2420 (obsd), 519.2390 (calcd)) and **12** with loss of (PMe_3 + H): ($C_6H_{26}IrB_7NP_2$, 442.1859 (obsd), 442.1869 (calcd)). NMR data are listed in Table 12. Crystals suitable for single-crystal X-ray diffraction purposes could only be grown from diffusion of pentane into a $CHCl_3$ solution of the compound although these tended to suffer from solvent loss following isolation.

X-ray Diffraction Analyses. A summary of crystal data, intensity data collection, and structure refinement parameters for compounds **5a, 9a, 10**, and **12** is listed in Table 1.

***nido*-[(PMe_3)$_2$(CO)$IrC_2B_8H_{11}$] (5a).** For compound **5a** data reduction and structure solution were carried out using the SHELXTL-PLUS (VMS) software package.[21] Least-squares refinement was achieved by using SHELXTL-5.0,[22] and the empirical absorption correction was applied to the data using ψ-scan reflections.[22] The structure was solved by the Patterson method and refined successfully in the 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 connected to boron atoms, including the single bridging hydrogen, were located from the difference Fourier synthesis and were refined isotropically. The methyl hydrogens were refined using a riding model. Selected interatomic distances and angles are listed in Table 2.

***nido*-[(PMe_3)$_2$$HIrSB_8H_{10}$] (9a).** Data reduction was carried out using XDISK, and structure solution and refinement were carried out using the SHELXTL-PLUS (5.0) software package.[22] Absorption correction was applied to the data using equivalent reflections and ψ scan reflections (SHELXA).[23] The structure was solved by the Patterson method and refined successfully in the space group $P\bar{1}$. The non-hydrogen atoms were refined anisotropically to convergence. All hydrogen atoms in the boron cage were located from difference Fourier syntheses and were refined isotropically. The methyl group H atoms were refined using a riding model. The hydride H was located and included in the final refinement. Geometrical parameters are listed in Table 6.

***closo*-[(PMe_3)$_2$$HIrSB_8H_8$] (10).** Data reduction was carried out using XSCANS. Structure solution and refinement was achieved as above for **9a**. All the hydrogen atoms in the boron cage were located from difference Fourier syntheses and were refined isotropically. The methyl group H atoms were refined using a riding model. It should be noted that the hydride atom H(2) was refined but it has a very short contact to the Ir atom of 1.36 Å and thus its reliability is questionable. Geometrical parameters are given in Table 8.

(21) Sheldrick, G. M. Siemens Analytical X-Ray Division, Madison, WI, 1991.

(22) Sheldrick, G. M. Siemens Analytical X-Ray Division, Madison, WI, 1994.

(23) Sheldrick, G. M. University of Göttingen, Germany.

(24) Sheldrick, G. M. Siemens Analytical X-Ray Division, Madison, WI, 1995.

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

Ir(9)−C(9)	1.870(6)	B(3)−B(4)	1.768(13)
Ir(9)−C(8)	2.182(7)	B(4)−C(8)	1.733(10)
Ir(9)−B(4)	2.232(7)	B(4)−B(5)	1.833(10)
Ir(9)−B(10)	2.235(6)	B(5)−B(10)	1.779(9)
Ir(9)−B(5)	2.239(7)	B(3)−C(8)	1.715(10)
Ir(9)−P(2)	2.331(2)	B(3)−C(7)	1.722(11)
Ir(9)−P(1)	2.341(2)	B(5)−B(6)	1.790(11)
B(1)−B(3)	1.748(13)	B(6)−B(11)	1.767(12)
B(1)−B(2)	1.753(14)	B(6)−B(10)	1.769(10)
B(1)−B(6)	1.771(11)	C(7)−C(8)	1.568(9)
B(1)−B(5)	1.780(12)	C(7)−B(11)	1.642(10)
B(1)−B(4)	1.786(11)	B(10)−B(11)	1.817(10)
B(2)−C(7)	1.703(11)	B(10)−H(101)	0.90(8)
B(2)−B(3)	1.732(11)	B(11)−H(101)	1.00(8)
B(2)−B(6)	1.734(12)	C(9)−O	1.153(8)
B(2)−B(11)	1.762(12)		
C(9)−Ir(9)−C(8)	93.3(3)	C(7)−B(3)−B(4)	102.9(5)
C(9)−Ir(9)−B(4)	89.6(3)	C(8)−B(4)−B(3)	58.6(4)
C(8)−Ir(9)−B(4)	46.2(3)	O−C(9)−Ir(9)	178.0(7)
C(9)−Ir(9)−B(10)	172.9(3)	C(8)−B(4)−B(1)	103.7(6)
C(8)−Ir(9)−B(10)	82.3(3)	C(8)−B(4)−B(5)	104.9(5)
B(4)−Ir(9)−B(10)	83.3(3)	C(8)−B(4)−Ir(9)	65.4(3)
C(9)−Ir(9)−B(5)	126.9(3)	B(3)−B(4)−Ir(9)	119.0(5)
C(8)−Ir(9)−B(5)	79.5(3)	B(1)−B(4)−Ir(9)	118.3(4)
B(4)−Ir(9)−B(5)	48.4(3)	B(5)−B(4)−Ir(9)	66.0(3)
B(10)−Ir(9)−B(5)	46.9(2)	B(10)−B(5)−Ir(9)	66.4(3)
C(9)−Ir(9)−P(2)	88.3(2)	B(1)−B(5)−Ir(9)	118.2(4)
C(8)−Ir(9)−P(2)	164.2(2)	B(6)−B(5)−Ir(9)	117.3(4)
B(4)−Ir(9)−P(2)	118.2(2)	B(4)−B(5)−Ir(9)	65.6(3)
B(10)−Ir(9)−P(2)	94.4(2)	C(8)−C(7)−B(11)	114.0(5)
B(5)−Ir(9)−P(2)	87.0(2)	C(8)−C(7)−B(2)	112.2(6)
C(9)−Ir(9)−P(1)	96.0(2)	B(11)−C(7)−B(2)	63.5(5)
C(8)−Ir(9)−P(1)	96.4(2)	C(8)−C(7)−B(3)	62.6(4)
B(4)−Ir(9)−P(1)	142.5(2)	B(11)−C(7)−B(3)	114.4(6)
B(10)−Ir(9)−P(1)	90.0(2)	B(2)−C(7)−B(3)	60.8(5)
B(5)−Ir(9)−P(1)	136.9(2)	C(7)−C(8)−B(3)	63.1(5)
P(2)−Ir(9)−P(1)	99.06(6)	C(7)−C(8)−B(4)	111.5(5)
C(7)−B(2)−B(3)	60.2(4)	B(3)−C(8)−B(4)	61.7(5)
C(7)−B(2)−B(6)	104.6(5)	C(7)−C(8)−Ir(9)	119.7(4)
C(7)−B(2)−B(1)	105.2(5)	B(3)−C(8)−Ir(9)	124.5(5)
C(7)−B(2)−B(11)	56.5(4)	B(4)−C(8)−Ir(9)	68.4(3)
C(8)−B(3)−C(7)	54.3(4)	B(6)−B(10)−Ir(9)	118.5(4)
C(8)−B(3)−B(2)	104.0(5)	B(5)−B(10)−Ir(9)	66.7(3)
C(7)−B(3)−B(2)	59.1(5)	B(11)−B(10)−Ir(9)	111.3(4)
C(8)−B(3)−B(1)	106.1(6)	C(7)−B(11)−B(2)	59.9(4)
C(7)−B(3)−B(1)	104.6(5)	C(7)−B(11)−B(6)	105.7(6)
C(8)−B(3)−B(4)	59.7(4)	C(7)−B(11)−B(10)	109.7(5)

***nido*-[(PMe$_3$)$_3$IrNB$_7$H$_9$] (12).** Data reduction was carried out using XSCANS, and structure solution and refinement were carried out using SHELXTL-PLUS (5.03) software.[24] 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 space group $P2_1$. The non-hydrogen atoms were refined anisotropically to convergence. The H atoms were refined using the appropriate riding model. Absolute configuration was determined by the Flack method (Flack x = 0.0095). Selected geometrical parameters are listed in Table 11.

Results and Discussion

Metallacarboranes. Passage of acetylene through refluxing *p*-xylene solutions of *arachno*-[(PMe$_3$)$_2$(CO)HIrB$_8$H$_{12}$] (**1a**, structure given in Scheme 1) with acetylene affords, after thin-layer chromatographic separation of the products, up to 44% yield of *nido*-[9,9,9-(PMe$_3$)$_2$(CO)-9,8,7-IrC$_2$B$_8$H$_{11}$] (**5a**, structure given in Scheme 2) according to eq 1. Similarly, the reaction

$$[(PMe_3)_2(CO)HIrB_8H_{12}] + C_2H_2 \rightarrow [(PMe_3)_2(CO)IrC_2B_8H_{11}] + 2H_2 \quad (1)$$

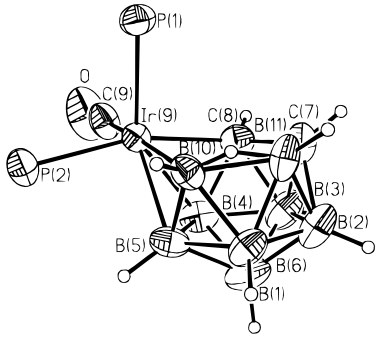


Figure 1. Molecular structure of *nido*-[9,9,9-(PMe$_3$)$_2$(CO)-9,8,7-IrC$_2$B$_8$H$_{11}$] (compound **5a**) with 50% probability thermal ellipsoids and with methyl groups omitted for clarity. All terminal boron hydrogen atoms and the bridging hydrogen atom μH(10,11) were located and refined satisfactorily.

of acetylene with *nido*-[(PMe$_3$)$_2$(CO)IrB$_8$H$_{11}$] (**2**, structure given in Scheme 1) gives a 41% yield of **5a**, indicating that the initial *arachno*, **1a** to *nido*, **2a** cluster closure step plays no direct role in the acetylene incorporation mechanism. Also identified in both reactions were minor amounts of *nido*-[9,9,9-(PMe$_3$)$_3$-9,8,7-IrC$_2$B$_8$H$_{11}$](**6**) in 5% yield. Compounds **5a** and **6**, which were obtained essentially pure in a combined yield of up to 49%, were identified by NMR and IR spectroscopy and, in the case of **5a**, by a single-crystal X-ray diffraction analysis (Figure 1). The NMR data for **5a** and **6** are listed in Table 3, and selected interatomic distances and angles for **5a** are listed in Table 2.

Species **5a** is clearly seen to be an 11-vertex *nido*-iridadicarbaundecaborane cluster incorporating two adjacent carbon atoms arising from the acetylene. The NMR data are in accord with the single crystal structural data, and the compound gives good ^{11}B−^{11}B COSY correlations although they were not sufficient to identify unambiguously the positions of the carbon atoms within the cluster. All interboron distances [ranging from 1.732(11) to 1.833(10) Å] are within the usual range, and the shorter distance between the carbon atoms, C(7)−C(8), of 1.568(9) Å is consistent with intercarbon distances in other metallacarboranes[25] confirming the atomic designations given. In addition to the terminal hydrogen atoms on the cage, the H atom bridging B(10)−B(11) was also located and refined.

In common with a broad range of *nido* metallaundecaborane clusters of this type,[26] the molecule features a fluxionality on the NMR time scale in both its boron and proton spectra. The exchange process involves a rotation of the {(PMe$_3$)$_2$(CO)Ir} moiety with respect to the B(4)−B(5)−C(8)−B(10) face of the carborane cage as is also observed in the L$_3$RhC$_2$B$_8$H$_{11}$ analogues.[18] The process was monitored by observation of the coalescence of the boron resonances assigned to vertex B(5) at δ(^{11}B) +8.9 and +7.2 ppm which are in a relative intensity ratio of 2:1 giving an approximate value for the fluxional process of $\delta G^{\ddagger}$(368 K) 71 kJ mol^{-1}. This

(25) For example see: (a) Barker, G. B.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 627. (b) Barker, G. B.; Godfrey, N. R.; Green, M.; Parge, H. E.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 277. (c) Lu, P.; Knobler, C. B.; Hawthorne, M. F. *Acta. Crystallogr.* **1984**, *C40*, 1704. (d) Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *Organometallics* **1987**, *6*, 2254.

(26) See: Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, *36*, 211 (specifically pp 349−375).

Table 3. ^{11}B, ^{1}H, and ^{31}P[a] NMR Data for *nido*-[$(PMe_3)_2(CO)IrC_2B_8H_{11}$] (5a) in $CDCl_3$ (298 K) and $CD_3C_6D_5$ Solutions (353 K) and for *nido*-[$(PMe_3)_3IrC_2B_8H_{11}$] (6) in $CDCl_3$ (298 K) Solution

	nido-[$(PMe_3)_2(CO)IrC_2B_8H_{11}$] (**5a**)[b]					*nido*-[$(PMe_3)_3IrC_2B_8H_{11}$] (**6**)		
assgnt	$\delta(^{11}B)$ (353 K)	$\delta(^{11}B)$ (298 K)	J(B−H) (298 K)	$\delta(^{1}H)$[c] (298 K)	^{11}B−^{11}B) COSY correlns (353 K)[d]	$\delta(^{11}B)$	J(B−H)	$\delta(^{1}H)$[c]
2	+12.5	+11.3	148	+5.28	(3) *w*, (1,6) *s*	+9.2	130	+4.87
5	+8.9, [+7.2]	+8.3, [+6.1]	132 [134]	+3.55[j] [+3.92]	(1,4,10) *s*	+7.7	129	+3.60[h]
4	[−7.0], −10.9	[−7.3], −11.6	[140] 163	[+2.41], +2.46	(1,5) *s*, (3) *vw*	−9.6	140	+1.99[i]
11	−12.2	−12.7	165	+2.60	(6) *s*	−14.2	131	+2.16
3	−17.9	−18.3	168	+2.38	(4) *vw*, (2) *w*, (1) *s*	−18.6	152	+2.09
10	−19.0	−19.8	141	+0.77	(5,6) *s*	−21.1	125	+0.50
6	−21.7	[−22.4], −22.7	130	+1.92	(1,2,5,10,11) *s*	−23.4	136	+1.57
1	−28.4	−29.3	138	+1.74	(2,3,4,5,6) *s*	−30.6	139	+1.26
H(10,11)				−4.35 [−3.78]				−4.02
H(7),(8)				+2.66 (2), [+2.97 (2)]				2.37, 2.40
P(CH_3)				1.87 [1.85],[e] 1.69 [1.65][f]				1.74,[g] 1.58,[g] 1.54[g]

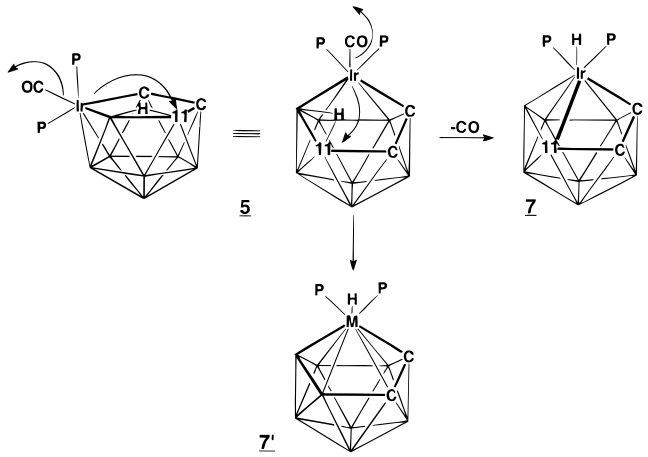
[a] ^{31}P NMR data in ppm ($CD_3C_6D_5$, 181 K): −41.1 (*s*), −46.9 (*s*), [−37.9, −49.2, $^2J(^{31}P-^{31}P)$ 18 Hz][b] for compound **5a** and −46(*br*), −47.5, −49.9 (*d*, J = 25.2 Hz) for compound **6**. [b] Figures in brackets refer to the data for the minor rotomer component (see text). [c] Boron−proton resonances related by (^{11}B−^{1}H) HETCOR experiments for compound **3a** and (^{1}H)−(^{11}B{selective}) experiments for compound **6**. [d] *s* = strong, *m* = medium, *w* = weak. [e] $^2J(^{31}P-^{1}H)$ = 9.3 [8.4] Hz. [f] $^2J(^{31}P-^{1}H)$ = 10.0 [9.3] Hz. [g] $^2J(^{31}P-^{1}H)$ 8.9 Hz. [h] Doublet, probably due to coupling to phosphorous, $^3J(^{31}P-^{1}H)$ 22 Hz. [i] Doublet, probably due to coupling to phosphorus, $^3J(^{31}P-^{1}H)$ 19 Hz. [j] Doublet, $^3J(^{31}P-^{1}H)$ 22 Hz, probably due to *cisoidal*-coupling to P(2).

Table 4. ^{11}B, ^{1}H, and ^{31}P[a] NMR Data for *nido*-[$(PMe_3)_2(CO)IrC_2B_8H_{10}Cl$] (5b, $CDCl_3$ Solution at 302 K)

assgnt	$\delta(^{11}B)$[b]	$\delta(^{1}H)$[b]	(^{11}B−^{11}B) COSY correlns (323 K)[c]
5	+18.1	*d*	(1, 4, 6/10) *s*
2	+8.5	+4.63	(3) *vw*, (1, 6/10) *m*
4	−7.0	+2.51	(5) *s*, (1) *w*
11	−12.8	+2.47	(1, 6/10) *s*
3	−18.1	+2.25	(1, 6/10) *s*
6/10	−20.2 (2)	+1.90, +1.45	(2) *s*, (1, 11) *m*
1	−26.8	+1.70	(2, 4, 3, 6/10) *s*, (5) *w*
H(10,11)		−3.30	
H(7),(8)		2.30(2)	
(CH_3)		+1.85(9), +1.73(9)[e]	

[a] ^{31}P NMR data ($CDCl_3$, 230 K): −35.0, −47.4 ppm, $^2J(^{31}P-^{31}P)$ 14 Hz. [b] Relative intensities in parentheses. Boron−proton resonances related by (^{11}B−^{1}H) HETCOR experiments and ^{1}H−{^{11}B(selective)} decoupling experiments. [c] *s* = strong, *m* = medium, *w* = weak, *vw* = very weak. [d] Site of chlorine substituent. [e] Doublets, $^2J(^{31}P-^{1}H)$ 9 Hz.

Scheme 2



compares well to calculated values for related compounds such as *nido*-[$(PPh_3)_2(CO)IrB_{10}H_{11}(PPh_3)$] (65 kJ mol^{-1} at 319 K)[27a] and *nido*-[(7,7,7-$(PMe_2Ph)_2PtB_{10}H_{11}$-(4-Cl)] (77 kJ mol^{-1}).[27b] Presumably the solid-state structure (Figure 1) with the carbonyl group *cis* to C(8) represents the major rotamer component. In the chloro-substituted compound **5b** described below where the chlorine is in the B(5) position, the ^{31}P and the bridging hydrogen resonances (Table 4) have chemical shift values very close to those of the minor component in **5a** and there is no evidence of fluxionality up to 380 K suggesting that steric interaction with the PMe_3 ligand results in the alternate configuration for **5b**.

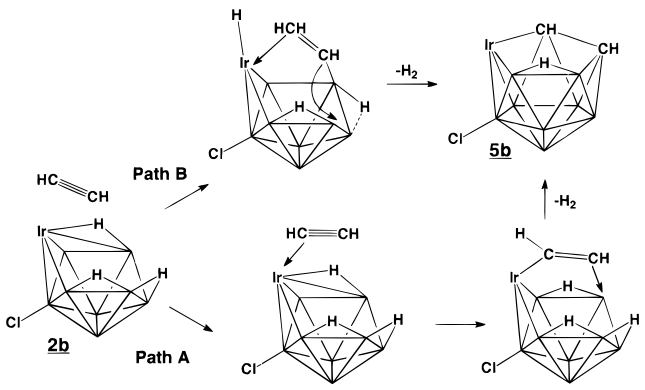
Compound **5a** (structure **5** in Scheme 2) may be compared to a similar rhodium species *nido*-$(PPh_3)_2$-$RhC_2B_8H_{11}$[25c] prepared more conventionally from the addition of the metal complex $RhCl(PPh_3)_3$ to the *nido*-carborane anion $[C_2B_8H_{11}]^-$. The major difference between the rhodium and iridium species lies in the coordinative unsaturation of the Rh species which undergoes a reversible addition of the metal to B(11) to afford what was the presumed to be *closo* species $[(PPh_3)_2HRhC_2B_8H_{10}]$ [18] (structure type **7′**, Scheme 2**)** on the basis of NMR spectroscopy but which was later shown to have an *isonido*-type structure with a four membered open face[19] (structure type **7**, Scheme 2). In the case of **5a** a nonreversible carbonyl loss occurs (structures **5** → **7**, Scheme 2) when refluxed for an extended period in xylene to give *isonido*-[$(PMe_3)_2$-$HIrC_2B_8H_{10}$], **7a**, in *ca.* 25% yield as illustrated in Scheme 2. The compound was characterized by NMR spectroscopy (see Experimental Section) and exhibits an equivalent cluster geometry to the rhodadicarbaundecaborane.

In an effort to obtain mechanistic information about the site of insertion of the C_2 moiety the reaction was repeated with the chloro-substituted iridanonaborane *arachno*-[$(PMe_3)_2(CO)HIrB_8H_{11}Cl$] (**1b**). This compound is obtained in low yield as a byproduct in the preparation of the unsubstituted analogue (**1a**). The *nido*-iridanonaborane formed on heating the *arachno* species (**1** → **2**, Scheme 1) has been previously characterized by NMR spectroscopy,[8c,28] and the chloro substituent is reasonably proposed to remain in its relative position during the *arachno* to *nido* transformation thereby providing a marker and supplying information on the mode of addition of the alkyne to the metallaborane cluster. Passage of acetylene through a refluxing solu-

(27) (a) See ref 26, p 353. (b) Reference 26, p 359.

(28) Beckett, M. A.; Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1969.

Scheme 3



tion of **1b** (25 mg) for 40 min followed by chromatographic separation of the reaction mixture resulted in the isolation of 14.5 mg of a mixture of two crystalline solids—the pale yellow *isonido*-type[20] compound $[PMe_3)_2HIrC_2B_8H_9Cl]$ (**7b**) and the colorless *nido*-$[9,9,9\text{-}(PMe_3)_2\text{-}(CO)\text{-}9,7,8\text{-}IrC_2B_8H_{10}\text{-}(5\text{-}Cl)]$ (**5b**). The structural characterization of **7b** is reported elsewhere.[20] The compounds were separated manually under a microscope, and thus the relative amounts were difficult to assess although we estimate them to be in a ratio of 60:40, respectively. The higher yield of the decarbonylated species compared to that for compound **1a** emphasizes the electronic effect on the metal vertex of the halogen substituent in **1b**. Compound **5b** (structure given in Scheme 3) was characterized by NMR and IR spectroscopy by comparison with compound **5a**. The position of the Cl substituent follows readily from [^{11}B−^{11}B] COSY NMR experiments (Table 4) which show a connectivity pattern for the singlet resonance at $\delta(^{11}B)$ +18.1 ppm similar to that for the resonance at +8.9 ppm in **5a** assigned to cluster vertex B(5). The downfield shift of *ca.* 10 ppm is reasonable for a chlorine atom.[28] The position of the chlorine substituent in the product suggests that it is unlikely that isomerization has occurred during the reaction and the observed product may be rationalized by a simple addition of the acetylene moiety to the open face of the *nido*-iridanonaborane cluster at the metal atom.

The opening of a vacant coordination site on the metal during the thermolysis and coordination of the alkyne to the metal cluster followed by insertion of the β-carbon into the cluster (Scheme 3, path **A**, **2b** → **5b**) is a possible initial step. Metal−alkyne coordination has been observed in the related *nido*-iridadecaborane system where the species *nido*-$[(PPh_3)(PPh_2\overline{C_6H_4})HIrB_9H_{12}]$ combines with acetylene affording a small yield of the iridacyclopentadiene species *isocloso*-$[(PPh_2\overline{C_6H_4})(C_4H_4)\text{-}\overline{IrB_9H_7(PPh_3)}]$.[6a,b] In the latter case, after the initial addition of the alkyne, the tendency of iridium to lose or transfer the more weakly bound PPh_3 ligand to the cage opens a vacant coordination site and presumably allows the reaction to proceed via coordination of a second acetylene molecule rather than via C_2 incorporation as reported herein and, additionally, the migrating phospine ligands effectively supply the extra electrons that any intermediate electron-deficient cluster might otherwise gain from the incoming alkyne moiety. A similar reaction with the PMe_3 ligated species might proceed quite differently. Alternatively, hydroboration of the alkyne,[29] by the metallaborane cluster, is also a possible initial step followed by coordination of the resultant alkenyl fragment to the metal vertex (Scheme 3, path **B**). However, in an attempted reaction of acetylene with *arachno*-$[(PMe_2Ph)_2PtB_8H_{12}]$, which might also be expected to undergo at least the initial hydroboration reaction, the only borane species we were able to identify was a low yield of the previously reported phosphine-substituted platinanonaborane *arachno*-$[4,4\text{-}(PMe_2Ph)_2\text{-}4\text{-}PtB_8H_{11}\text{-}6\text{-}(PMe_2Ph)]$,[30a] which is a simple thermal degradative product from the thermolysis of *arachno*-$[(PMe_2Ph)_2PtB_8H_{12}]$.[30b]

Presumably, if hydroboration were the initial step, then a substituted alkyne, RCCH, might be expected to undergo a normal anti-Markonikov addition and the R group would tend to be found adjacent to the metal in the product. In this vein we investigated the incorporation of the 1-substituted alkyne, 1-heptyne, into the iridaborane cluster. *nido*-$[(PMe_3)_2(CO)IrC_2B_8H_{10}(C_5H_{11})]$ (**8**), identified from NMR (Table 5), IR spectroscopy, and high-resolution mass spectrometry, was isolated in *ca.* 25% yield together with the corresponding *isonido*-type product produced by loss of the metal carbonyl group. However, although **8** could be readily identified as a substituted analogue of **5a**, the position of the pendant alkyl group on the α or β cluster carbon atom could not be determined directly from NMR spectroscopy and the compound, as isolated, appeared to be an oil thus discounting the possibility of a structural determination. An inseparable, small amount of a closely related species was present in the product and resultant overlapping NMR resonances confused attempts to characterize the species unambiguously.

It is interesting to note the change in the nature of the H atom positions, when viewed from the point of view of the metal vertex and the open face of the cluster. As shown in Scheme 1 the terminal iridium hydride in compound **1** is effectively incorporated into the cluster in the form of an Ir−H−B bond on transformation to **2**

Table 5. ^{11}B, ^{1}H, and ^{31}P[a] NMR Data for *nido*-$[(PMe_3)_2(CO)IrC_2B_8H_{10}(C_5H_{11})]$ (8) in C_7D_8 Solution at 373 K

assgnt	$\delta(^{11}B)$[b]	$\delta(^{1}H)$[b]	(^{11}B−^{11}B) COSY correlns (353 K)[c]
2	+15.4	+5.73	(3) *w*, (1,6) *s*
5	+8.0	+4.01	(4) *w*, (6) *m*, (1,10) *s*
4	−9.6	+2.98	(1,5) *w*
11	−10.9	+2.99	(6) *s*
3	−15.3	+2.63	(4) *vw*, (2) *w*, (1) *s*
10	−18.6	+0.96	(5,6) *s*
6	−21.6	+2.62	(5) *m*, (1,2,10,11) *s*
1	−27.2	+2.42	(4) *w*, (2,3,5,6) *s*
H(10,11)		−3.85	
H(7) or (8)		*d*	
$P(CH_3)$[e]		+1.90, +1.65	

[a] ^{31}P NMR data ($CDCl_3$, 223 K). Resonances due to two rotamers apparent in ca. 1:1 ratio, −38.3, −44.9 ppm, $^2J(^{31}P-^{31}P)$ 6 Hz, and −35.0, −47.4 ppm, $^2J(^{31}P-^{31}P)$ 14 Hz. [b] Boron−proton resonances related by (^{11}B−^{1}H) HETCOR experiments and ^{1}H−{^{11}B(selective)} decoupling experiments. [c] *s* = strong, *m* = medium, *w* = weak, *vw* = very weak. [d] Doublets, $^2J(^{31}P-^{1}H)$ 9 Hz. Broad multiplets due to C_5H_{11} substituent on C(7) or C(8) centered at +1.2 and +0.8 ppm (recorded at 223 K). [e] $^2J(^{31}P-^{1}H)$ = 9.3 Hz.

(29) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972; Chapter XV.

(30) (a) Salter, P. Ph.D. Thesis, University of Leeds, 1987. (b) Boocock, S. K.; Greenwood, N. N.; Hails, M. J.; Kennedy, J. D.; MacDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1981**, 1415.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for 9a

Ir(2)−B(3)	2.228(6)	B(1)−B(5)	1.767(9)
Ir(2)−B(1)	2.232(6)	B(1)−B(10)	1.797(9)
Ir(2)−B(5)	2.266(6)	B(1)−B(4)	1.815(9)
Ir(2)−B(7)	2.279(6)	B(1)−B(3)	1.873(9)
Ir(2)−P(1)	2.334(2)	B(1)−H(1)	1.27(5)
Ir(2)−P(2)	2.336(2)	B(4)−B(9)	1.726(10)
Ir(2)−S(6)	2.458(2)	B(7)−B(8)	1.936(9)
Ir(2)−H(2)	1.36(7)	B(8)−B(9)	1.770(10)
S(6)−B(7)	1.893(7)	B(8)−H(89)	1.32(7)
S(6)−B(5)	1.901(7)	B(9)−B(10)	1.764(10)
B(3)−B(7)	1.789(9)	B(9)−H(89)	1.25(7)
B(3)−B(8)	1.793(9)	B(9)−H(910)	1.37(7)
B(4)−B(8)	1.774(10)	B(10)−H(910)	1.27(7)
B(4)−B(10)	1.794(11)	B(3)−B(4)	1.801(10)
B(5)−B(10)	1.936(9)		

B(1)−Ir(2)−H(2)	86(3)	B(7)−S(6)−Ir(2)	61.6(2)
P(1)−Ir(2)−H(2)	89(3)	B(5)−S(6)−Ir(2)	61.1(2)
S(6)−Ir(2)−H(2)	163(3)	B(1)−B(5)−S(6)	116.7(4)
B(3)−Ir(2)−B(1)	49.7(2)	B(1)−B(5)−B(10)	57.8(4)
B(3)−Ir(2)−B(5)	80.3(2)	S(6)−B(5)−B(10)	113.1(4)
B(1)−Ir(2)−B(5)	46.2(2)	B(1)−B(5)−Ir(2)	65.8(3)
B(3)−Ir(2)−B(7)	46.8(2)	S(6)−B(5)−Ir(2)	71.7(2)
B(1)−Ir(2)−B(7)	80.5(2)	B(10)−B(5)−Ir(2)	118.5(4)
B(5)−Ir(2)−B(7)	76.8(2)	B(3)−B(7)−S(6)	116.1(4)
B(3)−Ir(2)−P(1)	150.7(2)	S(6)−B(7)−B(8)	113.8(4)
B(1)−Ir(2)−P(1)	103.0(2)	B(3)−B(7)−Ir(2)	65.1(3)
B(5)−Ir(2)−P(1)	86.0(2)	S(6)−B(7)−Ir(2)	71.5(2)
B(7)−Ir(2)−P(1)	152.4(2)	B(8)−B(7)−Ir(2)	117.6(3)
B(3)−Ir(2)−P(2)	104.1(2)	B(3)−Ir(2)−H(2)	80(3)
B(1)−Ir(2)−P(2)	152.3(2)	B(5)−Ir(2)−H(2)	128(3)
B(5)−Ir(2)−P(2)	151.3(2)	B(7)−Ir(2)−H(2)	119(3)
B(7)−Ir(2)−P(2)	85.7(2)	P(2)−Ir(2)−H(2)	80(3)
P(1)−Ir(2)−P(2)	100.40(6)	B(5)−B(1)−Ir(2)	67.9(3)
B(3)−Ir(2)−S(6)	83.5(2)	B(10)−B(1)−Ir(2)	127.3(4)
B(1)−Ir(2)−S(6)	83.4(2)	B(4)−B(1)−Ir(2)	121.2(4)
B(5)−Ir(2)−S(6)	47.2(2)	B(3)−B(1)−Ir(2)	65.1(3)
B(7)−Ir(2)−S(6)	46.9(2)	B(7)−B(3)−Ir(2)	68.1(3)
P(1)−Ir(2)−S(6)	105.81(7)	B(8)−B(3)−Ir(2)	127.4(4)
P(2)−Ir(2)−S(6)	104.45(7)	B(4)−B(3)−Ir(2)	122.1(4)
B(7)−S(6)−B(5)	96.1(3)	B(1)−B(3)−Ir(2)	65.3(3)

and, on addition of alkyne, the only remaining facial H atom is a B−H−B bridging hydrogen atom which then reverts to a terminal metal hydride in compound **7** (structure **7**, Scheme 2). This suggests that it would be interesting to prepare rhodium analogues of these compounds which might tend to exhibit features of reversibility.[18,31]

Following the success of the alkyne reactions it became evident that other small molecules might be amenable to incorporation and, rather than cultivate the further chemistry of carborane formation at this stage, we chose to explore this possibility as is described in the next two sections.

Metallathiaboranes. Passage of H_2S through refluxing xylene solutions of **1a** followed by repeated TLC separation affords a number of metallathiaboranes in a combined yield of 40%. The first, isolated in 13% yield was identified by NMR spectroscopy and high-resolution mass spectroscopy together with a single-crystal X-ray diffraction study as *nido*-[2,2,2-$(PMe_3)_2$H-2,6-$IrSB_8H_{10}$] (compound **9a**). NMR data are listed in Table 7 together with data for the heteroborane analogue *nido*-[6-SB_9H_{11}]. Selected interatomic dimensions are listed in Table 6. A projection of the structure is shown in Figure 2. As with the previous alkyne reactions we repeated the experiment with the *nido*-iridanonaborane compound **2** and obtained the similar results although subsequently, for convenience, we used the *arachno* complex. Compound **9a** clearly results, after initial dihydrogen loss in the *arachno*-**1a** → *nido*-**2a** step, from addition of H_2S to the *nido*-iridanonaborane with dihydrogen and carbonyl elimination according to eq 2. It

$$\underset{\textbf{2a}}{[(PMe_3)_2(CO)IrB_8H_{11}]} + H_2S \rightarrow \underset{\textbf{9a}}{[(PMe_3)_2HIrSB_8H_{10}]} + H_2 + CO \quad (2)$$

would appear that CO elimination is a key step in providing a coordination site on the Ir for attack by the sulfur atom, if indeed the incorporation of sulfur is metal-centered. The cluster is the first metallaborane analogue of the thiadecaborane *nido*-$[SB_9H_{11}]$ with the sulfur in the prow position in the open face of the cage and the iridium in the adjacent basal 2-position. The NMR data for **9a** (Table 7) are completely in accord with the structural information and show, with allowance for the effect of the metal atom, a similar shielding pattern and COSY connectivity pattern to that of *nido*-SB_9H_{11}[32] in contrast to those of the only other metallathiadecaborane analogues known all of which exhibit *arachno* structures as typified by [9,9-$(PPh_3)_2$-6,9-$PtSB_8H_{10}$].[33a] An analogue of **9a**, [2-{η^6-$C_6Me_3H_3$}Fe-6-OB_8H_{10}], has been structurally characterized but was obtained only in trace quantities, and NMR data are unavailable.[33b] Consistent with the *nido* descriptor for **9a**, the B(5)−B(10) and B(7)−B(8) distances of 1.936(9) Å are the longest cluster interboron distances mirroring those in decaborane(14) itself, obtained in a neutron diffraction study (1.973(4) Å).[34] Unfortunately the structure of *nido*-SB_9H_{11} has not been reported so a structural comparison is not possible. The structure of the related species *arachno*-[9-(Et_3N)-SB_9H_{11}] is available,[35] but the corresponding B−B bonds are H-bridged rendering comparisons less useful. The B(5)−B(10)/B(7)−B(8) distances contrast those in the platinathiadecaborane in which they exhibit the more normal interboron distances of ca. 1.845 Å[33] as has been discussed elsewhere.[36]

A comparison of the boron shielding patterns for the related species *nido*-$B_{10}H_{14}$,[37] *nido*-SB_9H_{11},[32] *nido*-[(η^6-C_6Me_6)-2-RuB_9H_{13}][38] (the 2-iridadecaborane species has not yet been synthesized but the shielding effects of third-row transition metals are very similar in metalladecaborane clusters[39]), and **9a** is given in Figure 3. The apparent close similarity of the shielding characteristics of compound **9a** and decaborane may be due to competing shielding-deshielding effects of the metal and sulfur moieties such that they tend to cancel. The relatively low-field resonance due to B(9), however,

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(36) Reference 26, p 268.

(37) Barton, L.; Onak, T. P.; Remmel, R. J.; Shore, S. G. *Gmelin Handbook of Inorganic Chemistry, Boron Compounds 20*; Springer Verlag: Berlin, 1979 (New Supplement Series Vol. 54), 134 and references therein.

(38) Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; MacKinnon, P. *J. Chem. Soc., Chem. Commun.* **1987**, 817.

(39) Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D. *J. Organomet. Chem.* **1987**, *325*, 233.

Table 7. ^{11}B, ^{1}H, and ^{31}P[a] NMR Data (in ppm) for *nido*-[$(PMe_3)_2$H-2,6-$IrSB_8H_{10}$] (9a) in $CDCl_3$ Solution at 298 K and [$(PMe_3)_2$Cl-2,6-$IrSB_8H_{10}$] (9b) in $CD_3C_6D_5$ at 373 K with *nido*-SB_9H_{11} Data for Comparison (CD_2Cl_2)[32]

	compd **9a**			compd **9b**		SB_9H_{11}	
assgnt	$\delta(^{11}B)$[b]	$\delta(^{1}H)$[b]	($^{11}B-^{11}B$) COSY correlns (323 K)	$\delta(^{11}B)$[b] (373 K)	$\delta(^{1}H)$[b] (373 K)	$\delta(^{11}B)$	$\delta(^{1}H)$
9	+24.1[c]	+5.49	(4) *s*	+24.6	+5.55	+17.7	+3.88
1,3	+12.6 (2)	+4.11 (2)	(8, 9, 10) *s*	+10.0 (2)	+4.06 (2)	+6.6 (2)	+3.55 (2)
5,7	+11.4 (2)	+3.37 (2)	(1, 3) *s* (8,10) *w*	+12.0 (2)	4.00 (2)	+25.3 (2)	+5.04 (2)
8,10	−5.5 (2)[c]	+2.88 (2)	(1, 3) *s*	−7.5 (2)	+3.01 (2)	−9.9 (2)	+2.64(2)
4	−32.7	+0.97	(1, 3, 8, 9, 10) *s*	−32.3	+1.40	−21.5	+1.76
2	Ir			Ir		−30.7	+0.64
(8,9), (9,10)		−1.46 (2)			−1.74 (2)		−2.86 (2)
(CH_3)		+1.76[d]			+1.71[d]		

[a] ^{31}P NMR data in ppm ($CDCl_3$, 213 K): −42.7 (*s*) ppm for compound **7a** and −30.0 (*d*), −35.99 (*d*) [^2J = 11.3 Hz] ppm for compound **9b** ($CDCl_3$, 233 K). [b] Boron and proton resonances related by ^{1}H−{^{11}B(selective)} spectroscopy. Relative intensities in parentheses. [c] ^{1}H−{^{11}B(selective)} irradiation of this resonance causes sharpening of bridging protons resonance at $\delta(^{1}H)$ −1.46 ppm. [d] Doublet $^2J(^{31}P-^{1}H)$ 9.6 Hz (**9a**), 10.3 (**9b**).

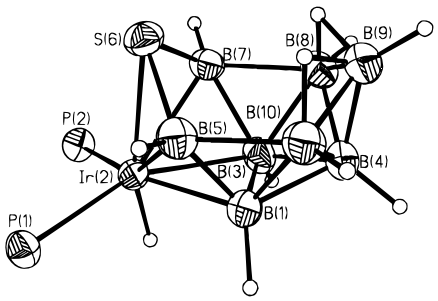

Figure 2. Molecular structure of *nido*-[2,2,2-$(PMe_3)_2$H-2,6-$IrSB_8H_{10}$] (compound **9a**) with 50% probability thermal ellipsoids and with methyl groups omitted for clarity. All terminal and bridging boron hydrogen atoms were located and refined satisfactorily. The terminal metal hydride was located from the X-ray data but was refined in a fixed position.

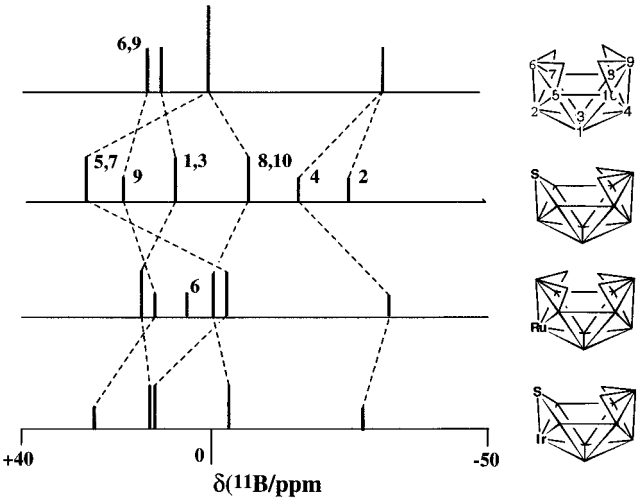

Figure 3. Stick diagram for the ^{11}B NMR positions for *nido*-$B_{10}H_{14}$,[37] *nido*-SB_9H_{11},[32] *nido*-[$(\eta^6$-$C_6Me_6)RuB_9H_{13}$],[38] and *nido*-[2,2,2-$(PMe_3)_2$H-2,6-$IrSB_8H_{10}$] (**9a**).

appears result from an additive antipodal deshielding effect of both nuclei.[40] Antipodal effects are also noted in compounds **10** and **12** described below.

Although compound **9a** and the *arachno*-platinathiaborane compounds are formally isoelectronic species with the metal vertices each contributing two electrons to the cluster bonding, the two metal fragments are not, however, isolobal. The two-orbital, two-electron {$(PPh_3)_2$Pt} moiety prefers to take up a 3-connected 6-position compared to the three-orbital, two-electron {$(PMe_3)_2$HIr} moiety which occupies the five-connected 2-position, and the compounds are thus an interesting example of the structural variance which may occur in clusters containing cluster fragments which are formally isoelectronic but not isolobal. The platinathiaborane could be considered to be two electrons short for the required 26 electrons for a classical *arachno* structure based on a $2n + 6$ skeletal electron count where n is the number of vertices.[41] This phenomenon is now quite common for metallaborane clusters containing the L_2M moiety (where M = Pt or Pd). Examples of "anomalous" electron counts in other platina- and palladaboranes include [5,6-Me_2-7,7-$(PEt_3)_2$-7,5,6-$PtC_2B_4H_4$][42] and [7,7-$(PMe_2Ph)_2$-7-$PtB_{10}H_{12}$],[43] [$(PPh_3)_2(CO)Os(PhMe_2P)$-$ClHPtB_5H_7$],[44] and [{$PhCH_2NMe_3$}$_2$($B_{10}H_{12})_2$Pd]·MeCN[45] and related systems, and attempts have been made to account for the discrepancies in the latter systems using molecular orbital calculations.[46] Again this phenomenon in [7,7-$(PMe_2Ph)_2$-7-$PtB_{10}H_{12}$] may be ascribed to be due to the Pt moiety functioning as a two orbital two electron donor and adopting effectively a square-planar configuration although contributions from higher valence Pt(IV) states have been proposed in these systems.[43,47]

A second compound isolated from the reaction mixture from which **9a** was obtained, *closo*-[2,2,2-$(PMe_3)_2$H-2,1-$IrSB_8H_8$] (compound **10**, 7% yield), was also characterized by NMR spectroscopy (Table 9) and by a single-crystal X-ray diffraction study. A projection view of the structure is shown in Figure 4 and selected interatomic dimensions are listed in Table 8. The cluster is seen to be based upon the conventional bicapped Archimedean antiprism in which sulfur occupies an apical position as also observed for the heteroborane analogue *closo*-

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Table 8. Selected Interatomic Distances (Å) and Angles (deg) for 10

Ir(2)−B(7)	2.255(11)	Ir(2)−B(6)	2.263(12)
Ir(2)−P(1)	2.304(3)	Ir(2)−P(2)	2.304(3)
Ir(2)−B(3)	2.322(11)	Ir(2)−B(5)	2.329(12)
Ir(2)−S(1)	2.365(3)	Ir(2)−H(2)	1.68
S(1)−B(4)	1.91(2)	S(1)−B(5)	1.957(13)
S(1)−B(3)	1.974(12)	B(3)−B(8)	1.80(2)
B(3)−B(7)	1.84(2)	B(3)−B(4)	1.93(2)
B(4)−B(8)	1.76(2)	B(4)−B(9)	1.74(2)
B(5)−B(6)	1.86(2)	B(4)−B(5)	1.91(2)
B(6)−B(10)	1.66(2)	B(5)−B(9)	1.80(2)
B(6)−B(7)	1.90(2)	B(6)−B(9)	1.86(2)
B(7)−B(10)	1.68(2)	B(7)−B(8)	1.87(2)
B(8)−B(9)	1.84(2)	B(8)−B(10)	1.70(2)
B(9)−B(10)	1.71(2)		
B(7)−Ir(2)−B(6)	49.9(4)	B(7)−Ir(2)−P(1)	104.0(3)
B(6)−Ir(2)−P(1)	152.0(3)	B(7)−Ir(2)−P(2)	149.9(3)
B(6)−Ir(2)−P(2)	103.8(3)	P(1)−Ir(2)−P(2)	97.59(10)
B(7)−Ir(2)−B(3)	47.4(5)	B(6)−Ir(2)−B(3)	78.7(4)
P(1)−Ir(2)−B(3)	89.8(3)	P(2)−Ir(2)−B(3)	154.4(3)
B(7)−Ir(2)−B(5)	79.4(4)	B(6)−Ir(2)−B(5)	47.7(4)
P(1)−Ir(2)−B(5)	149.7(3)	P(2)−Ir(2)−B(5)	92.4(3)
B(3)−Ir(2)−B(5)	70.1(4)	B(7)−Ir(2)−S(1)	91.9(3)
B(6)−Ir(2)−S(1)	91.6(3)	P(1)−Ir(2)−S(1)	100.41(11)
P(2)−Ir(2)−S(1)	104.63(11)	B(3)−Ir(2)−S(1)	49.8(3)
P(1)−Ir(2)−H(2)	77.80(8)	B(5)−Ir(2)−S(1)	49.3(3)
B(3)−Ir(2)−H(2)	129.6(3)	P(2)−Ir(2)−H(2)	75.96(9)
B(6)−Ir(2)−H(2)	89.9(3)	B(5)−Ir(2)−H(2)	132.5(3)
S(1)−Ir(2)−H(2)	178.19(7)	B(7)−Ir(2)−H(2)	88.3(3)
B(4)−S(1)−B(5)	59.2(5)	B(4)−S(1)−B(3)	59.3(6)
B(5)−S(1)−B(3)	85.6(5)	B(4)−S(1)−Ir(2)	99.4(4)
B(5)−S(1)−Ir(2)	64.4(4)	B(3)−S(1)−Ir(2)	64.0(3)
B(8)−B(3)−B(7)	61.9(8)	B(8)−B(3)−B(4)	56.4(7)
B(7)−B(3)−B(4)	101.6(8)	B(8)−B(3)−S(1)	113.4(7)
B(7)−B(3)−S(1)	121.0(6)	B(4)−B(3)−S(1)	58.8(6)
B(8)−B(3)−Ir(2)	112.7(7)	B(7)−B(3)−Ir(2)	64.4(5)
B(4)−B(3)−Ir(2)	100.6(6)	S(1)−B(3)−Ir(2)	66.2(3)
B(9)−B(4)−B(8)	63.3(8)	B(9)−B(4)−B(5)	58.6(7)
B(8)−B(4)−B(5)	102.2(9)	B(9)−B(4)−S(1)	118.1(8)
B(8)−B(4)−S(1)	118.2	B(5)−B(4)−S(1)	61.5(6)
B(9)−B(4)−B(3)	101.6(9)	B(8)−B(4)−B(3)	58.2(7)
B(5)−B(4)−B(3)	88.2(7)	S(1)−B(4)−B(3)	61.9(6)
B(9)−B(5)−B(6)	61.2(7)	B(9)−B(5)−B(4)	56.0(7)
B(6)−B(5)−B(4)	100.7(8)	B(9)−B(5)−S(1)	113.4(7)
B(6)−B(5)−S(1)	120.8(8)	B(4)−B(5)−S(1)	59.3(6)
B(9)−B(5)−Ir(2)	112.1(7)	B(6)−B(5)−Ir(2)	64.3(5)
B(4)−B(5)−Ir(2)	100.7(6)	S(1)−B(5)−Ir(2)	66.3(4)
B(10)−B(6)−B(9)	57.7(8)	B(10)−B(6)−B(5)	110.7(9)
B(10)−B(6)−B(7)	55.6(7)	B(5)−B(6)−B(9)	57.8(7)
B(9)−B(6)−B(7)	89.6(7)	B(5)−B(6)−B(7)	102.1(8)
B(5)−B(6)−Ir(2)	68.0(5)	B(10)−B(6)−Ir(2)	118.8(8)
B(7)−B(6)−Ir(2)	64.8(5)	B(9)−B(6)−Ir(2)	112.4(7)
B(10)−B(7)−B(3)	109.9(9)	B(10)−B(7)−B(8)	56.7(8)
B(3)−B(7)−B(8)	58.0(7)	B(10)−B(7)−B(6)	54.9(6)
B(3)−B(7)−B(6)	101.8(7)	B(8)−B(7)−B(6)	88.5(7)
B(10)−B(7)−Ir(2)	118.6(7)	B(3)−B(7)−Ir(2)	68.2(5)
B(8)−B(7)−Ir(2)	112.7(7)	B(6)−B(7)−Ir(2)	65.3(5)
B(10)−B(8)−B(3)	111.0(8)	B(10)−B(8)−B(4)	111.8(10)
B(10)−B(8)−B(9)	57.7(8)	B(4)−B(8)−B(3)	65.4(7)
B(3)−B(8)−B(9)	102.9(8)	B(4)−B(8)−B(9)	57.8(8)
B(4)−B(8)−B(7)	106.7(8)	B(10)−B(8)−B(7)	55.8(7)
B(9)−B(8)−B(7)	91.1(8)	B(3)−B(8)−B(7)	60.1(6)
B(10)−B(9)−B(4)	112.0(10)	B(10)−B(9)−B(5)	111.6(9)
B(4)−B(9)−B(5)	65.4(8)	B(10)−B(9)−B(8)	56.9(8)
B(4)−B(9)−B(8)	58.9(7)	B(5)−B(9)−B(8)	103.9(8)
B(10)−B(9)−B(6)	55.4(7)	B(4)−B(9)−B(6)	107.4(8)
B(5)−B(9)−B(6)	61.1(7)	B(8)−B(9)−B(6)	90.8(8)
B(6)−B(10)−B(8)	103.3(9)	B(6)−B(10)−B(7)	69.5(7)
B(6)−B(10)−B(9)	66.9(8)	B(7)−B(10)−B(8)	67.5(8)
B(8)−B(10)−B(9)	65.4(9)	B(7)−B(10)−B(9)	103.0(9)

$[SB_9H_9]$[48] with the iridium in an adjacent equatorial position. The compound is, as far as we are aware, the first *closo*-metallathiadecaborane cluster to be synthesized, but it is of interest to note that an isostructural iridacarbadecaborane cluster[5] with a similar apical (C)−equatorial (Ir) arrangement has been isolated in low yield where the carbon vertex was introduced via cluster incorporation of the methanol reaction solvent. We were unable to assign the NMR spectra completely although the boron resonance due to the apical B(10) vertex appears at very low field (+68.8 ppm) and is comparable to that found in *closo*-$[SB_9H_9]$ (+74.5 ppm) which results from the antipodal deshielding effect of the sulfur.[48]

(48) Pretzer, W. R.; Rudolph, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 931.

Table 9. ^{11}B, ^{1}H, and ^{31}P[a] NMR Data (in ppm) for *closo*-[2,2,2-$(PMe_3)_2$H-2,1-$IrSB_8H_8$] (10)

assgnt[c]	$\delta(^{11}B)$[b] (373 K)	J(B−H)/ Hz	$\delta(^{1}H)$[b] (297 K)	(^{11}B−^{11}B) COSY correlns (323 K)
10	+68.8	150	+9.0	(b, d) *s*
3,5 (a)	−0.86(2)	150	+2.72 (2)	(10, b, c) *s*
4 (a)	−0.86	150	+3.27	
(6,7) or (8,9) (b)	−9.0(2)	160	+0.80 (2)	(a) *s*, (c) *m*
(8,9) or (6,7) (c)	−30.2(2)	160	−1.28 (2)	(10, a) *s*, (b) *m*
H(2)			−9.51[d]	
(CH_3)			+1.70[e]	

[a] ^{31}P NMR data in ppm ($CDCl_3$, 213 K): −31.6 (*s*) ppm. [b] Boron and proton resonances related by ^{1}H−{^{11}B(selective)} spectroscopy. Relative intensities greater than unity in parentheses. [c] Letters identify resonances for (^{11}B−^{11}B) COSY purposes. See last column in this table. [d] Triplet, $^{2}J(^{31}P-^{1}H)$*cis* 24.9 Hz. [e] Doublet, $^{2}J(^{31}P-^{1}H)$ 10.2 Hz.

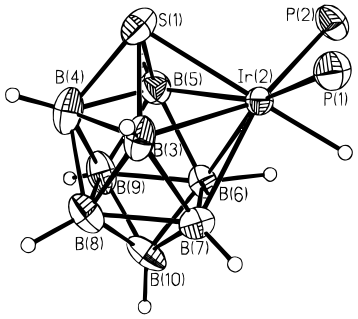


Figure 4. Molecular structure of *closo*-[2,2,2-$(PMe_3)_2$H-2,1-$IrSB_8H_8$] (compound **10**) with 50% probability thermal ellipsoids and with methyl groups omitted for clarity. All terminal boron hydrogen atoms were located and refined satisfactorily. The terminal metal hydride was located from the X-ray data and refined in a fixed position.

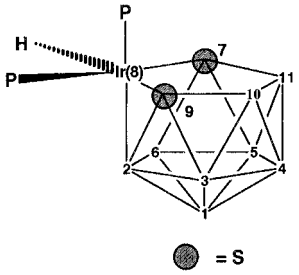


Figure 5. Proposed structure of *nido*-[8,8,8-$(PMe_3)_2$H-8,7,9-$IrS_2B_8H_8$] (**11a**).

The third and major component of the reaction, isolated in 20% yield, was tentatively identified as the 11-vertex cluster *nido*-[7,7,7-$(PMe_3)_2$H-8,7,9-$IrS_2B_8H_8$] (**11a**, Figure 5) by a comparison of its multinuclear magnetic resonance data (Table 10) with those of the structurally characterized rhodadithiaundecaborane *nido*-[7,7,7-$(PPh_3)_2$H-8,7,9-$RhS_2B_8H_8$].[3o] Assignment of the resonances is, again, uncertain as very little coupling information was available from [^{11}B−^{11}B] COSY experiments, but a comparison of the ^{11}B and ^{1}H NMR

Table 10. ^{11}B, ^{1}H, and ^{31}P[a] NMR Data (in ppm) for *nido*-[$(PMe_3)_2HIrS_2B_8H_8$] (11a) and *nido*-[$(PMe_3)_2ClIrS_2B_8H_8$] (11b) in $CDCl_3$ Solution at 298 K with Comparison Data for *nido*-[$(PPh_3)_2HRhS_2B_8H_8$][30]

	compd **11a**				compd **11b**		$[(PPh_3)_2HRhS_2B_8H_8]$	
assgnt[j]	$\delta(^{11}B)$[b]	J(B−H)/Hz	$\delta(^{1}H)$[b]	(^{11}B−^{11}B) COSY correlns (323 K)	$\delta(^{11}B)$[b]	$\delta(^{1}H)$[b]	$\delta(^{11}B)$[b]	$\delta(^{1}H)$[b]
a	+12.9	141	+6.09	(e,f) *s*, (g) *m*	+13.1	+5.92	+12.0	+4.07
2 or 6	+3.2	151	+3.12[e]	(c) *s*, (g) *s*	+5.4	+3.93[k]	+3.4 (2)	+3.53, +3.35
6 or 2	−0.7	169	+3.51	(b) *s*, (g) *s*	+6.6	+3.75		
d	−5.7(2)	*i*	+2.97, +2.85		−5.1 (2)	+2.63, +3.14	−4.1 (2)	+2.46, +2.05
e	−13.8	169	+2.53	(g) *s*	−15.6	+2.88	−13.7	+2.00
f	−16.9	160	+2.55	(g) *s*	−16.2	+2.23	−16.8	+2.03
l	−32.9	141	+1.68	(a) *m* (b,c,d,e,f) *s*	−32.5	+1.65	−28.1	+1.72
H(2)			−14.26[d]					−11.98
(CH_3)	−32.9		+1.85,[g] +1.75[h]			+1.83, +1.74[l]		

[a] ^{31}P NMR data in ppm ($CDCl_3$, 213 K): −28.0 (*d*), −37.9 (*d*) [^2J = 10.8 Hz] ppm for compound **11a** and −31.6 (*s*) ppm for compound **11b**. [b] Boron and proton resonances related by ^{1}H−{^{11}B(selective)} spectroscopy. Relative intensities in parentheses. [d] Doublet of doublets $^2J(^{31}P-^{1}H)$*cis* 18.7, 23.7 Hz. [e] Doublet, J = 15.6 Hz. [f] Triplet, $^2J(^{31}P-^{1}H)$*cis* 24.9 Hz. [g] Doublet, $^2J(^{31}P-^{1}H)$ 10.2 Hz. [h] Doublet, $^2J(^{31}P-^{1}H)$ 10.8 Hz. [i] Boron resonance too broad to exhibit coupling to terminal proton. [j] Letters identify resonances for (^{11}B−^{11}B) COSY purposes. [k] Doublet, $^2J(^{31}P-^{1}H)$ 13 Hz. [l] Both doublets, $^2J(^{31}P-^{1}H)$ 10 Hz.

chemical shift data with those of the rhodadithiaundecaborane species shows a striking similarity giving us a high degree of confidence in the proposed structure. Attempts to confirm the proposed structure with an X-ray diffraction study were unsuccessful as crystals showed an unresolveable positional disorder.

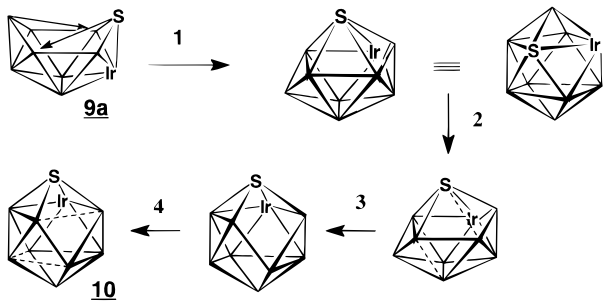
Finally, it may be noted that compounds **9a**, **10**, and **11a** were found to react slowly and cleanly at room temperature with the $CDCl_3$ NMR solvent, and more rapidly at elevated temperatures, effecting a replacement of the terminal iridium hydride with Cl. A solution of **9a** in $CDCl_3$ at 50 °C for 4 days showed 60% conversion (by integrated ^{11}B NMR spectroscopy) to *nido*-[2,2,2-$(PMe_3)_2$Cl-2,6-$IrSB_8H_{10}$] (compound **9b**). Correspondingly, compound **11a** gave *nido*-[7,7,7-$(PMe_3)_2$-Cl-8,7,9-$IrS_2B_8H_8$] (compound **11b**). NMR data are listed in Tables 7 and 10, respectively. **10** was also noted to react similarly, but the chloro species was not isolated.

Compound **9a** clearly results, after initial dihydrogen loss in the *arachno*-**1a** → *nido*-**2a** step, from addition of H_2S to the *nido*-iridanonaborane according to eq 3.

$$[(PMe_3)_2(CO)IrB_8H_{11}] + H_2S \rightarrow \underset{\textbf{2a}}{} \qquad [(PMe_3)_2HIrSB_8H_{10}] + H_2 + CO \quad (3)$$
$$\textbf{9a}$$

Unlike the case of alkyne addition it is not possible to postulate a straight-forward addition of sulfur to the cluster which would give the observed positions of S and Ir in the product and a cluster rearrangement seems likely. Further dihydrogen elimination from **9a** would then, in principle, yield the *closo*-metallathiaborane species **10**. Interestingly, pyrolysis of *nido*-[6-SB_9H_{11}] at 450 °C leads to *closo*-[1-SB_9H_9].[48] As pointed out by Pretzer and Rudolph,[48] a simple closure step of the *nido* cluster would not result in an apical position for the S atom in the *closo* species or, in the case of **9a**, in the observed 2,3 position for the sulfur and iridium vertices in **10** (Step **1**, Scheme 4).[32a] However, in the manner proposed by Pretzer and Rudolph to account for the apical heteroatom disposition in the *closo*-thiadecaborane, a diamond-square-diamond rearrangement on two faces would also result in the observed S(1) and Ir(2) dispositions in compound **10** (steps **2** to **4**, Scheme 4). We have not observed any tendency for H_2 loss directly

Scheme 4



in **9a** at the temperatures reached during NMR spectroscopic investigation of the species (up to *ca.* 90 °C) although it may be noted that high-resolution mass spectroscopic measurements on the chloro-substituted compound **9b** showed two ion envelopes of relative intensities 40:100 with the former being due to the parent ion with loss of H [m/q 508.1422 (obsd), 508.1410 (calcd)] and the latter, more intense envelope corresponding to the parent ion mass with loss of HCl [m/q 472.1724 (obsd), 472.1736 (calcd)]. This corresponds to the calculated mass for compound **10** suggesting that the *closo* species could be formed in the mass spectrometer as shown in eq 4. Further reaction with H_2S must

$$\underset{\textbf{9b}}{(PMe_3)_2ClIrSB_8H_{10}} \rightarrow \underset{\textbf{10}}{(PMe_3)_2HIrSB_8H_8} + HCl \quad (4)$$

take place with either **9a** or **10** to afford the metalladithiaborane species **11a** again with H_2-elimination (eqs 5 and 6). This two-stage heteroatom cluster assembly

$$[(PMe_3)_2HIrSB_8H_{10}] + H_2S \rightarrow \underset{\textbf{9a}}{} \qquad [(PMe_3)_2HIrS_2B_8H_8] + 2H_2 \quad (5)$$
$$\textbf{11a}$$

$$[(PMe_3)_2HIrSB_8H_8] + H_2S \rightarrow \underset{\textbf{10}}{} \qquad [(PMe_3)_2HIrS_2B_8H_8] + H_2 \quad (6)$$
$$\textbf{11a}$$

process contrasts with that of the one-boron atom degradation process from an unisolated metalla-S_2B_9 intermediate which gives the rhodium analogue.[30]

Reaction in the iridanonaborane system appears to proceed in alternate directions depending on the nature of the substituent in the iridanonaborane $[(CO)(PMe_3)_2IrB_8H_{10}X]$ (compound **2**). When X = H (**2a**) the cluster, on thermolysis, undergoes condensation to afford the species $[\{(PMe_3)_2(CO)Ir\}_2B_{16}H_{14}]$ (**4**)[9] with retention of CO or it degrades completely. If X = Cl (**2b**), it goes on to form *isocloso*-$(PMe_3)_2HB_8H_7Cl$ (**3**).[8a] It appears that, after CO loss, unless there is a suitable reactant present with which to form a more thermally stable species, the system with X = H falls apart. Thus, with H_2S or with alkynes reaction takes place to afford a series of products which are the result of heteroatom incorporation. Interestingly, reaction of **2a** with excess $B_{10}H_{14}$ in refluxing xylene affords the unsubstututed *isocloso*-$[(PMe_3)_2HIrB_8H_8]$ in up to 16% yield[49] and therefore the unisolated 50% of starting metallaborane may also play a role in some of these reactions whereas reaction with C_2H_4 affords a low yield of a product which NMR and IR spectra suggest is *isonido*/*closo*-$[(PMe_3)_2(CO)IrB_8H_7(PMe_3)]$.[50] Clearly the system is complex and the potential role of the unisolated 50% of starting metallaborane cannot be discounted.

The proximity of the heteroatoms and the metal centers in the metallacarborane and metallathiaborane products implies that the metal is intimately involved in the process although similar reactions of non-metal-containing borane clusters allow other possibilities. Examples include the classical reaction of C_2H_2 with $L_2B_{10}H_{12}$ to form $C_2B_{10}H_{12}$,[51] the addition of nitriles to SB_9H_{11} to afford monocarbon heteroborane species,[52] and the synthesis of cobaltathiaboranes from H_2S in a metal atom vapor reactor.[2]

Metallaazaborane. Reaction of **1** with a 10-fold molar excess of anhydrous hydrazine in refluxing xylene, followed by chromatographic separation of the products, gave a *ca.* 10% yield of the iridaazaborane cluster *nido*-[2,2,2-$(PMe_3)_3$-2,9-$IrNB_7H_9$] (compound **12**) identified by NMR spectrometry (Table 12), high-resolution mass spectroscopy, and a single-crystal X-ray diffraction study. Figure 6 shows a projection of the molecule. Selected interatomic distances and angles are listed in Table 11. The quality of the X-ray data were low due to decomposition of the crystal in the X-ray beam such that only heavy atoms were located and with high estimated standard deviations. However, together with the other data, the cluster is unambiguously seen to be a *nido*-nine vertex cluster based on the bicapped Archimedean antiprism of *closo*-$[NB_9H_{10}]$[53] with an equatorial boron vertex missing and is thus isostructural with the probable precursor *nido*-$[(PMe_3)_2(CO)IrB_8H_{11}]$[8b] (**2a**; see Scheme 1 and Figure 8) and with *nido*-$[B_9H_{12}]^-$.[54] There are similar azaboranes in the literature which do not contain metals. For example, concurrent with this work, substituted derivatives of the azaborane analogue *nido*-NB_8H_{11}, RNB_8H_9 (R = *p*-ClC_6H_4, *p*-MeC_6H_4, $PhCH_2$) were reported[55] and an *arachno*-azanonaborane, NB_8H_{13}, was synthesized and structurally characterized some time ago.[56] The position of the heteroatom N(9) in the *pseudo*-apical position is clear from the significantly shorter interatomic distances of 1.44(8)−1.47(7) Å to that vertex compared to the boron−boron distances [1.63(7)−1.93(7) Å] and is in the position that might be expected for an NH moiety which is subrogating a $HB(H_{bridging})_2$ unit in the iridanonaborane congener. The distances, allowing for the large estimated standard deviations, are in line with those in other azaboranes.[53a,56,57] The dimensions associated with the iridium environment are quite similar

Table 11. Selected Interatomic Distances (Å) and Angles (deg) for 12

Ir(2)−B(1)	2.06(5)	B(3)−B(7)	1.84(9)
Ir(2)−B(6)	2.13(5)	B(3)−B(4)	1.83(8)
Ir(2)−B(3)	2.19(6)	B(4)−B(7)	1.75(8)
Ir(2)−P(1)	2.232(14)	B(4)−B(8)	1.81(7)
Ir(2)−P(2)	2.307(13)	B(4)−B(5)	1.85(7)
Ir(2)−P(3)	2.309(11)	B(5)−B(8)	1.75(9)
Ir(2)−B(5)	2.51(6)	B(6)−N(9)	1.47(7)
B(1)−B(3)	1.63(7)	B(6)−B(7)	1.81(9)
B(1)−B(4)	1.74(7)	B(7)−N(9)	1.48(8)
B(1)−B(5)	1.93(7)	B(7)−B(8)	1.77(10)
B(3)−B(6)	1.84(6)	B(8)−N(9)	1.44(8)
B(1)−Ir(2)−B(6)	88(2)	B(1)−B(3)−Ir(2)	63(3)
B(1)−Ir(2)−B(3)	45(2)	B(6)−B(3)−Ir(2)	63(2)
B(6)−Ir(2)−B(3)	50(2)	B(7)−B(3)−Ir(2)	111(3)
B(1)−Ir(2)−P(1)	102.4(13)	B(4)−B(3)−Ir(2)	102(3)
B(6)−Ir(2)−P(1)	99.5(14)	B(8)−B(5)−Ir(2)	101(3)
B(3)−Ir(2)−P(1)	85(2)	B(4)−B(5)−Ir(2)	91(3)
B(1)−Ir(2)−P(2)	88.7(14)	B(1)−B(5)−Ir(2)	53(2)
B(6)−Ir(2)−P(2)	165.1(14)	N(9)−B(6)−B(7)	52(3)
B(3)−Ir(2)−P(2)	131.9(14)	N(9)−B(6)−B(3)	107(4)
P(1)−Ir(2)−P(2)	95.4(5)	N(9)−B(6)−Ir(2)	119(4)
B(1)−Ir(2)−P(3)	159.1(13)	B(7)−B(6)−Ir(2)	116(3)
B(6)−Ir(2)−P(3)	81.3(14)	B(3)−B(6)−Ir(2)	67(2)
B(3)−Ir(2)−P(3)	131.0(14)	N(9)−B(7)−B(4)	107(5)
P(1)−Ir(2)−P(3)	97.2(5)	N(9)−B(7)−B(8)	52(3)
P(2)−Ir(2)−P(3)	96.7(4)	B(4)−B(7)−B(8)	62(3)
B(1)−Ir(2)−B(5)	49(2)	N(9)−B(7)−B(6)	52(4)
B(6)−Ir(2)−B(5)	79(2)	N(9)−B(7)−B(3)	106(5)
B(3)−Ir(2)−B(5)	71(2)	N(9)−B(8)−B(7)	54(4)
P(1)−Ir(2)−B(5)	150.9(12)	N(9)−B(8)−B(5)	117(6)
P(2)−Ir(2)−B(5)	88.4(14)	N(9)−B(8)−B(4)	106(5)
P(3)−Ir(2)−B(5)	111.1(11)	B(8)−N(9)−B(7)	75(5)
B(3)−B(1)−Ir(2)	72(3)	B(8)−N(9)−B(6)	116(5)
B(4)−B(1)−Ir(2)	111(3)	B(7)−N(9)−B(6)	76(4)
B(5)−B(1)−Ir(2)	78(2)		

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(50) The data for the compound *isonido*/*closo*-$[(PMe_3)_2(CO)IrB_8H_7(PMe_3)]$ are as follows. NMR shifts in ppm ($CDCl_3$ at 300 K) are given in the order assignment, $\delta(^{11}B)$ [(δ^1H) of directly attached hydrogen atom in square brackets] and are as follows: B(4,5) +24.1 [+5.52], B(2,3) −1.2 [+3.35, *doublet of doublets* ^nJ = *ca.* 6.5 Hz], B(8) −18.2 [*doublet*, ^2J(B−P) 184 Hz], B(6,7) −21.9 [+1.00], B(9) −30.3 [−0.85]; PMe_3 on iridium +1.64 {^2J(P−H) = 16.0 Hz}, on B(8), +1.72 {^2J(P−H) = 19.5 Hz}; $\delta(^{31}P)$ ($CDCl_3$ at 223 K) P(1,2) −49.8 *sharp*, P(3) −7.9 vbr. IR (3M Teflon IR card)/cm^{-1}): ν(CO) 1964 s, ν(BH) 2462 s. The data are consistent with the following structure:

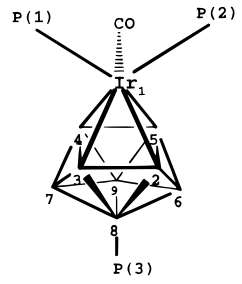

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Table 12. ^{11}B, ^{1}H, and ^{31}P[a] NMR Data for *nido*-[$(PMe_3)_3IrNB_7H_9$] (11) in $CDCl_3$ (298 K) Solution and Comparison Data for *nido*-[$(PMe_3)_2(CO)IrB_8H_{11}$] (2) ($CDCl_3$ Solution, 298 K)[8b,28]

[$(PMe_3)_3IrNB_7H_9$] (**11**)				[$(PMe_3)_2(CO)IrB_8H_{11}$] (**2a**)		
assgnt	$\delta(^{11}B)$	$\delta(^{1}H)$[b]	J(B−H)	assgnt	$\delta(^{11}B)$	$\delta(^{1}H)$[b]
1	+41.2	+6.44	156	1	+23.1	+5.04
6 }	+4.2	+3.70	136	4	+8.8	+4.90
4[c] }	−1.3	+4.14	152	6	−5.3	+2.94
8 }	−2.8	+1.96	147	8	−13.6	+1.02
9[d]				9	−14.5	+2.99
3	−23.6	+0.49[e]	130	3	−15.3	+0.83
7	−43.6	−0.55	151	5	−39.9	−0.51
5	−54.6	−2.30	*f*	7	−52.5	−1.48
H(2,5)		−13.23[g]		*H*(2,5)		−14.50[h]
				H(6,9), (8,9)		−2.10, −2.96
N(*H*)		+5.12				
P(CH_3)		+1.68 (9), +1.60 (9), +1.56 (9)[i]		P(CH_3)		+1.76 (9), +1.73 (9)[j]

[a] $\delta(^{31}P)$ NMR data in ppm ($CDCl_3$, 233 K (**12**) and 223 K for [$(PMe_3)_2(CO)IrB_8H_{11}$]): −40.9 [(*q*), $^2J(^{31}P-^{31}P)$ 20 Hz or *d*,*d*, J = 20, 40 Hz], −51.9 (*br*), −53.7 (*br*) for compound **12** and −39.5 (*d*), −50.5 (*d*) (^2J = 19 Hz) for [$(PMe_3)(CO)IrB_8H_{11}$]. [b] Relative intensities greater than unity in parentheses. [c] Relative assignments are uncertain although the most probable positions are as shown. B(4) is assigned on the basis of the generally sharper linewidths for nonfacial boron atoms *versus* those in the open face of boron clusters (see Figure 7). [d] Site of heteroatom N(9). See Figure 6. [e] Doublet probably due to coupling to phosphorus $^3J[^{31}P-^{1}H] = 22$ Hz. [f] Too broad to measure. [g] $^2J[^{31}P-^{1}H]$*trans* = 57 Hz. The resonance is also selectively sharpened on irradiation of the boron resonance at $\delta(^{11}B)$ −54.6 ppm. [h] $^2J[^{31}P-^{1}H]$*trans* = 62 Hz. [i] Doublets, $^2J[^{31}P-^{1}H] = 8$, 9, and 11 Hz, respectively. [j] Doublets, $^2J[^{31}P-^{1}H] = 9.5$ and 10.5 Hz, respectively.

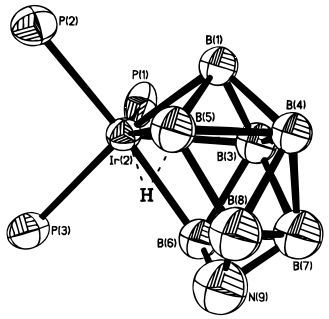

Figure 6. Molecular structure of *nido*-[2,2,2-$(PMe_3)_3$-2,9-$IrNB_7H_9$] (compound **12**) with 30% probability thermal ellipsoids and with methyl groups omitted for clarity. All heavy atoms were located. NMR spectroscopy shows terminal hydrogen atoms on all the boron atoms and nitrogen atom N(9) and an additional hydrogen atom bridging Ir(2)−B(5) which is indicated by dashed lines.

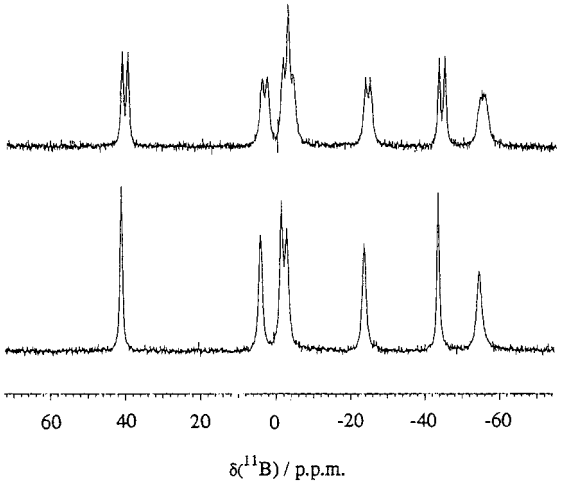

Figure 7. 96 MHz ^{11}B (upper trace) and $^{11}B\{^1H\}$ (lower trace) spectra for *nido*-[2,2,2-$(PMe_3)_3$-2,9-$IrNB_7H_9$] (compound **12**).

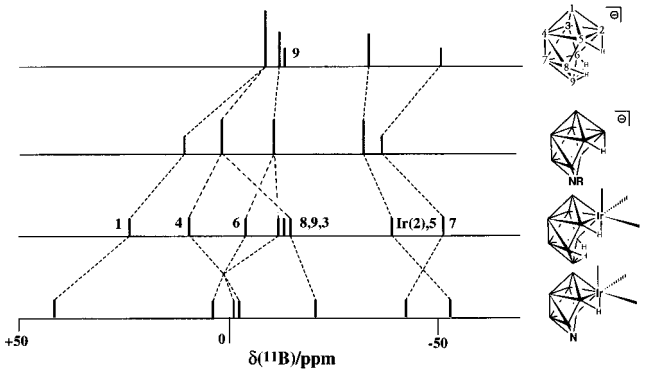

Figure 8. Stick diagram for the ^{11}B NMR positions for the isostructural and effectively isoelectronic series $[B_9H_{12}]^-$,[54] $[B_8H_9NR]^-$,[55] [$(PMe_3)_2(CO)IrB_8H_{11}$] (**2a**), and *nido*-[2,2,2-$(PMe_3)_3$-2,9-$IrNB_7H_9$] (**12**).

to those in *nido*-[$(PMe_3)_2(CO)IrB_8H_{11}$]; in particular the Ir(2)−B(5) separation of 2.51(6) Å compares well to that in the iridanonaborane of 2.500(6) Å[8c] and an analogous rhenanonaborane [$(PMe_2Ph)_3H_2ReB_8H_{11}$] [2.527(13) Å].[28] In each compound the M(2)−B(5) vector is the site of a hydrogen atom bridging the metal and the boron approximately *trans* to phosphorus atom P(1). The presence of the bridging hydrogen atom in **12** is apparent from the ^{1}H NMR spectrum where it appears at quite high field for a bridging H-atom in almost the same position as that in the iridanonaborane again demonstrating the essential similarity of the two species [$\delta(^1H)$ −13.23 ppm, $^2J(^{31}P-^{1}H)_{trans}$ = 57 Hz in compound **12** versus −14.50 ppm, J = 62 Hz in **2a**]. Insufficient sample prevented the attainment of useful information from ($^{11}B-^{11}B$) COSY experiments, but we are quite confident of our assignments. The atoms B(5) and B(7) are distinguishable on the basis of their relative peak widths and B(3) on the basis of coupling of its exo-terminal proton to ^{31}P. The ^{11}B NMR spectrum of **12** is given in Figure 7 and a ^{11}B chemical shift correlation diagram for **12** and the isostructural and effectively isoelectronic species $[B_9H_{12}]^-$,[54] $[B_8H_9NR]^-$,[55] and [$(PMe_3)_2(CO)IrB_8H_{11}$] (**2a**) is given in Figure 8. The correlation between the chemical shifts of the metallaborane **2a** and the parent binary borane $[B_9H_{12}]^-$ has been described previously.[28] The azaboranes fit into the picture quite well. As with the *nido*-iridathiadecaborane, **9a**, the shielding effects of the heteroatom and iridium tend to cancel although in the case of the apical B(10) vertex they appear to be precisely additive such that the chemical shift of that vertex in compound **12** is the resultant of the two shielding effects and the

extent of spreading out of the chemical shifts in **12** is an indication of the opposing effects on the electronic distribution in the molecule of the metal center and the nitrogen heteroatom.[40]

Other species were present in the product mixture although we have been unable to characterize them fully. Clearly the reaction is not clean and involves replacement of the metal carbonyl by phosphine arising from other species in solution (as does compound **6**). However, the overall stoichiometry (equation 7) can be

$$L_3IrB_8H_{11} + N_2H_4 \rightarrow L_3IrNB_7H_9 + \{NH_3{\cdot}BH_3\} \quad (7)$$

rationalized by loss of the elements of BH_3 and NH_3 suggesting a simple deboronation of the cluster by base and incorporation of {NH} with no direct role for the metal atom.

Conclusion

Our initial hypothesis that the redox-flexible iridanonaborane system would be a suitable substrate for heteroatom incorporations has been shown to be viable. It is clear that with alkynes the reaction occurs directly with the *nido*- rather than the *arachno*-iridanonaborane and before carbonyl elimination although whether dihydrogen is lost before or after coordination of the alkyne cannot be determined at this stage. It is tempting to hypothesize that the elimination step provides the coordination vacancy for the ethyne moiety. It is interesting that in all four processes **2** → **5**, **2** → **9**, **2** → **10**, and **2** → **11** one, one, two, or three molecules of dihydrogen are eliminated giving an effective incorporation of C_2, S, S, and S_2, respectively. In the case of the incorporation of nitrogen the reaction appears to proceed differently. As in the case of the deboronation reactions by amines, reported by Paetzold,[55] coordination of the N_2H_4 moiety and deboronation by loss of the elements of ammine−borane is followed by incorporation of the remaining N atom. In this case it appears that the presence of the metal is not required and thus the redox flexibility of the starting iridaborane is not important. The results reported here suggest that further heteroatom incorporation reactions are likely to succeed in this system. Thus reaction with H_2Se, H_2Te, and HCN among other heteroatom reagents may lead to new metallaheteroboranes. Further, it is possible that related metallaborane clusters such as *nido*-[(PMe_3)-$HIrB_9H_{13}$][58] may undergo similar reactions. Finally there is the potential to construct novel catalytic systems in this area. The iridaborane system tends to behave differently depending on the identity of cluster substituents and appropriate choice and site of substituent may allow modification of reactions taking place through the metal center, a feature we hope to invesitigate in the future.

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Supporting Information Available: Listings of atomic coordinates, bond distances and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and experimental details for compounds **5a**, **9a**, **10**, and **12** (23 pages). Ordering information is given on any current masthead page. Structure factor tables are available from the authors.

OM960313W

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