(2) D. F. Dustin, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 805 (1973).

(3) D. F. Dustin and M. F. Hawthorne, *J. Am. Chem. Soc.*, **96**, 3462 (1974).

(4) For a recent review, see D. O. Cowan, C. Le Vanda, J. Park, and F. Kaufman, *Acc. Chem. Res.*, **6**, 1 (1973).

(5) C. J. Jones, W. J. Evans, and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 543 (1973), and references therein.

(6) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 7633 (1973).

(7) (a) D. F. Dustin and M. F. Hawthorne, *Inorg. Chem.*, **12**, 1380 (1973); (b) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *ibid.*, **13**, 1393 (1974).

(8) We are grateful to Professor C. E. Strouse and Mr. Gordon Hardy for this information received prior to publication.

(9) This is in accord with previous observations[10] that a low-coordinate boron atom adjacent to one metal will occur at low field (ca. −40 to −80 ppm) in the ^{11}B spectrum. It is also apparent from the few examples available[10a,11] that a low-coordinate boron adjacent to two metals will occur between ca. −85 and −145 ppm (the above arguments seem to hold for 8-vertex and larger polyhedra).

(10) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 2830 (1973); (b) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *ibid.*, **95**, 4565 (1973); (c) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, H. Gong, S. Chan, and M. F. Hawthorne, *ibid.*, **96**, 3085 (1974).

(11) Note compounds II and IV of this work, and see also (a) K. P. Callahan, W. J. Evans, F. Y. Lo, C. E. Strouse, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **97**, 296 (1975); (b) W. J. Evans, C. J. Jones, B. Štibr, R. A. Grey, and M. F. Hawthorne, *ibid.*, **96**, 7405 (1974).

(12) The nomenclature conforms to the latest IUPAC rules; see R. M. Adams, *Pure Appl. Chem.*, **30**, 683 (1972).

(13) (a) W. J. Evans and M. F. Hawthorne, *Inorg. Chem.*, **13**, 869 (1974); (b) *J. Chem. Soc., Chem. Commun.*, 38 (1974).

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(15) (a) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U.S.A.*, **48**, 729 (1962); (b) W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 5434 (1964); (c) W. H. Knoth, W. R. Hertler, and E. L. Muetterties, *Inorg. Chem.*, **4**, 280 (1965).

(16) (a) P. M. Garrett, J. C. Smart, G. S. Ditta, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 1907 (1969); (b) J. Plešek and S. Heřmánek, *Chem. Ind. (London)*, 1267 (1971); (c) R. R. Rietz, R. Schaefer, and E. Walter, *J. Organomet. Chem.*, **63**, 1 (1973).

(17) We have not considered possibilities containing a low-coordinate cobalt vertex, as this has not yet been observed in closo-metallocarboranes having eight or more vertices.

(18) R. N. Leyden and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 310, (1975).

(19) This, as well as subsequent statements concerning rearrangement, can be verified with the use of models.

(20) (a) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes", Marcel Dekker, New York, N.Y., 1968; (b) R. J. Wiersema and M. F. Hawthorne, *Inorg. Chem.*, **12**, 785 (1973).

(21) Low field carborane C–H resonances seem to correlate only with low-coordinate carbon atoms, usually adjacent to one or more metals. We have previously mentioned this observation,[22] as have other workers.[23]

(22) C. G. Salentine, R. R. Rietz, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 3025 (1974).

(23) V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 3090 (1974).

(24) It is possible, and has been experimentally observed,[25] that halogenated carboranes do not rearrange by the same mechanism as their unhalogenated counterparts. However, recent studies[28] on halogenated icosahedral carboranes suggest that the major rearrangement products do follow the same mechanism as the parent carborane, $C_2B_{10}H_{12}$. We can only assume an analogous result here, as no studies of this kind have been performed on 10-vertex polyhedra.

(25) See, for example, H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **89**, 4218 (1967).

(26) H. V. Hart and W. N. Lipscomb, *Inorg. Chem.*, **12**, 2644 (1973).

(27) M. F. Hawthorne, K. P. Callahan, and R. J. Wiersema, *Tetrahedron*, **30**, 1795 (1974).

(28) For example, 1,2-$C_2B_{10}H_{12}$ thermally rearranges to the more stable 1,7 isomer. However, two-electron reduction of 1,7-$C_2B_{10}H_{12}$ followed by oxidation produces a high yield of 1,2-$C_2B_{10}H_{12}$ (see G. B. Dunks, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 3174 (1973), and references therein).

(29) It has been observed[30] in cobaltacarboranes of the formula $(C_5H_5Co)_2C_2B_nH_{n+2}$ (n = 6,7,8) that positions of bands in the visible spectrum, and hence the color of the complex, can be correlated with the presence or absence of metal–metal bonds. A similar situation may exist here, noting that I and II are green while III is red and IV is orange.

(30) W. J. Evans, C. J. Jones, B. Stibr, and M. F. Hawthorne, *J. Organomet. Chem.*, **60**, C27 (1973).

(31) It has generally been established[10b,27] that carbon–metal separation will increase upon thermal rearrangement and has been shown[32] for the monocarbon system $(C_5H_5)NiCB_{10}H_{11}$.

(32) R. R. Rietz, D. F. Dustin, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1580, (1974).

(33) (a) E. L. Hoel, C. E. Strouse, and M. F. Hawthorne, *Inorg. Chem.*, **13**, 1388 (1974); (b) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *ibid.*, **13**, 1397 (1974).

(34) This metal–naphthalene bonding mode has been shown crystallographically for $(C_{10}H_8)Cr(CO)_3$, which also contains a formal d^6 transition metal, see V. Kunz and W. Nowacki, *Helv. Chim. Acta*, **50**, 1052 (1967).

(35) M. R. Churchill, *Prog. Inorg. Chem.*, **11**, 53 (1970).

(36) F. A. Cotton, *Acc. Chem. Res.*, **2**, 240 (1969).

(37) T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **94**, 4882 (1972).

(38) R. B. King, "Organometallic Synthesis", Vol. 1, New York, N.Y., 1965, p 72.

(39) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **95**, 1109 (1973).

(40) Reference 23 describes metallocarboranes containing metal–metal bonds which are stable at the temperature of their synthesis (230–280°), but no attempt was made to rearrange these complexes at higher temperatures. It has been demonstrated in this report and many times previously that temperatures far in excess of 300° may be required for carborane or metallocarborane rearrangement.

Preparation of *B*-σ-Carboranyl Iridium Complexes by Oxidative Addition of Terminal Boron–Hydrogen Bonds to Iridium(I) Species

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Abstract: A number of *B*-σ-carboranyl iridium complexes have been prepared by both intra- and intermolecular oxidative addition of terminal boron–hydrogen bonds to iridium(I) species. The products from reactions between 1,2-, 1,7-, or 1,12-$C_2B_{10}H_{12}$ and L_2IrCl (L = PPh_3 or $AsPh_3$) are trigonal bipyramidal complexes of iridium(III) with axial hydride and chloride ligands, two equatorial L ligands, and an equatorial carboranyl ligand σ-bonded to the metal through one of the boron atoms closest to the carbon atoms. The preparation, characterization, and structures of these complexes are discussed, as well as their significance as model intermediates for transition metal catalyzed deuterium exchange at terminal boron–hydrogen bonds.

The class of metallocarboranes and metalloboranes in which the metal atoms are π-bonded to the carborane or borane ligand has been widely studied in the last decade.[2] Complexes of boranes and carboranes in which the metal is bonded to boron or carbon by two-center, two-electron σ-bonds are less well known. A number of *C*-σ-carboranyl metal complexes have been prepared by reactions between transition metal halide complexes and *C*-lithiocarboranes;[3-6] however, complexes with boron σ-bonded to a metal atom are much less prevalent.

In addition to the work reported herein, Grimes has prepared a B-σ-complex with germanium by thermal rearrangement of a compound containing a bridging trimethylgermyl group, although similar bridging tin and lead congeners failed to rearrange.[7] Gaines and Iorns prepared two *B*-σ-boranyl metal complexes by the nucleophilic displacement of chloride or bromide from halo derivatives of B_5H_9 using $NaM(CO)_5$ (M = Mn, Re) nucleophiles.[8] Also, a number of complexes of boron halides were prepared by oxidative addition of B-X bonds in Ph_2BCl, BCl_3, BBr_3, or BI_3 to certain metal complexes including $[(\eta\text{-}C_5H_5)_2Ti]_2$ and $[Me_2PCH_2CH_2PMe_2]_2Co$.[9] Very recently, oxidative addition of B-Br and B-H bonds in B_5H_8Br and B_5H_9 to $(PMe_3)_2(CO)IrCl$ was reported.[10]

Herein we report the preparation of a series of *B*-σ-carboranyl iridium complexes by oxidative addition of carboranyl boron-hydrogen bonds to certain iridium(I) species. Preliminary reports of part of this work have appeared elsewhere.[11,12]

Results and Discussion

The Preparation of a *B*-σ-Carboranyl Iridium Complex by an Intramolecular Oxidative Addition. Although oxidative addition of carbon-hydrogen bonds to low-valent, coordinatively unsaturated metal complexes is a well-known reaction, especially in the form of intramolecular reactions such as ortho metalation,[13,14] oxidative addition of a boron-hydrogen bond had not been reported when we initiated the research described in this paper. We decided to explore the feasibility of synthesizing *B*-σ-carboranyl metal complexes by oxidative addition of terminal boron-hydrogen bonds to suitable transition metal complexes, and we chose to model our test system after the facile intramolecular ortho metalation observed with $(PPh_3)_3IrCl$, a system extensively studied by Bennett and Milner.[14] It seemed possible that an L_3IrCl complex, with L being a carboranyl phosphine, might upon heating undergo an intramolecular oxidative addition similar to that found with the arylphosphine complexes.[14]

To minimize steric factors, which might inhibit the desired expansion of the coordination sphere due to the presence of such bulky groups as icosahedral carboranyls, and to enhance the basicity of the phosphine ligand, thus enhancing the probability of oxidative addition, we decided to restrict the other two groups present on the phosphine ligand to small alkyl groups such as methyl. Thus, $1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{11}$ (Ia) was chosen as the desired ligand, and it was synthesized by modification of existing procedures[15] used in the synthesis of diphosphinocarboranes (eq 1).

$$1\text{-}Li\text{-}1,2\text{-}C_2B_{10}H_{11} + Me_2PBr \xrightarrow[-LiBr]{} 1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{11} \qquad (1)$$

Bennett and Milner had previously prepared a wide variety of L_3IrCl complexes by the addition of an excess of the desired ligand to a suspension of $[Ir(C_8H_{14})_2Cl]_2$ in petroleum ether (eq 2).[14] When excess Ia was added to a yellow-orange suspension of $[Ir(C_8H_{14})_2Cl]_2$ in petroleum ether or cyclohexane the color of the suspended powder changed immediately to yellow, presumably forming $(Ia)_3IrCl$ according to eq 2. However, even if the yellow powder was immediately collected by filtration, its infrared spectrum exhibited a band at 2220 cm^{-1}, assigned to ν_{IrH}, which indicated that further reaction had begun (vide infra). Thus, $(Ia)_3IrCl$ was not isolated in a pure state.

$$[Ir(C_8H_{14})_2Cl]_2 + 6L \rightarrow 2L_3IrCl + 4C_8H_{14} \qquad (2)$$

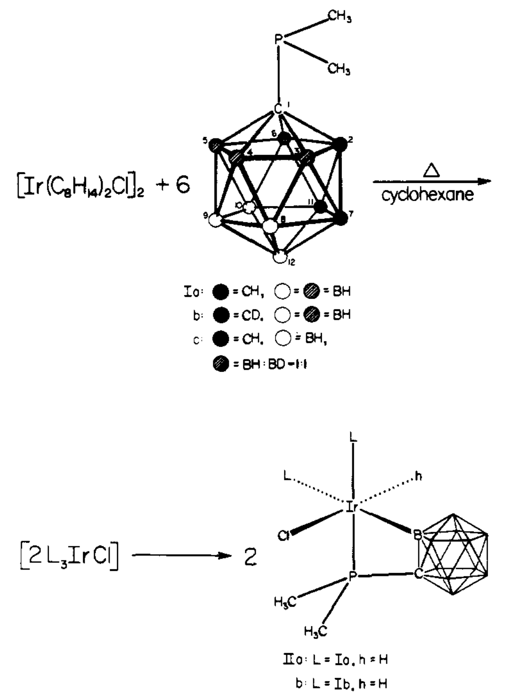

Figure 1. Preparation of *B*-σ-carboranyl iridium complexes by intramolecular oxidative addition.

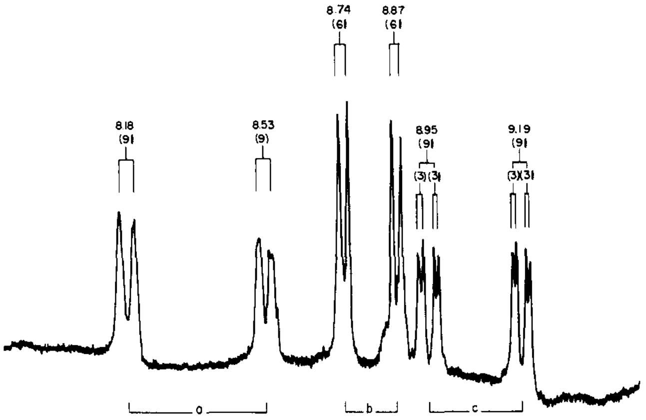

Figure 2. The methyl region of the 251-MHz ^1H NMR of IIa taken in C_6D_6. Partial decoupling of ^{31}P indicated that the pair of resonances labeled "a" belong to the same phosphine, as do those labeled "b" and "c". The numbers above the resonances are the chemical shifts in units of τ and the numbers in parentheses are coupling constants in Hz. The resonances labeled "a" showed evidence for unresolved, fine coupling in addition to that indicated.

Heating the cyclohexane suspension at the reflux temperature for 2 hr converted the yellow powder to a white, air-stable, and cyclohexane insoluble product. By analogy to the arylphosphine work of Bennett and Milner, and as confirmed by analysis, molecular weight, and spectral data, this product was determined to be $Ir(1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{11})_2[1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{10}]HCl$ (IIa), the product of an intramolecular oxidative addition in $(Ia)_3IrCl$ (Figure 1).

The infrared spectrum of IIa exhibited bands at 2600 and 2220 cm^{-1} assigned to ν_{BH} and ν_{IrH}, respectively. The presence of an iridium hydride was confirmed by the 251-MHz ^1H NMR spectrum which contained a quartet at τ 30.9 (J_{PIrH} (apparent) = 12.3 Hz). The other features of the

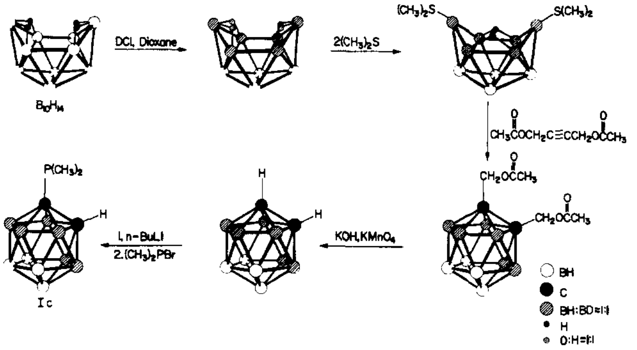

Figure 3. Preparation of Ic, 1-$P(CH_3)_2$-3,4,5,6,7,11-D_6-1,2-$C_2B_{10}H_5(d_3)$.

proton NMR spectrum were three broad singlets of area 1 at τ 4.79, 5.48, and 6.11 assigned to carboranyl C-H resonances and the six sets of area 3 methyl resonances shown in Figure 2. Heteronuclear double resonance was used to partially decouple ^{31}P from the methyl region signals at 100 MHz. In this manner it was determined that there were indeed six methyl resonances and that the two lowest field methyl resonances belong to the same phosphine, as do the two middle field and the two highest field resonances, but the spin-coupling pattern was not completely unraveled. These data imply the presence of three nonequivalent Ia ligands.

The stereochemistry of the complex about the iridium atom may be assigned from the spectral data.[16] The chemical shifts of iridium hydrides trans to phosphines are usually in the range τ 20-25, while hydrides trans to chloride appear in the τ 26-32 region. Furthermore, J_{PIrH} for cis phosphines is usually on the order of 10-20 Hz while for trans phosphines it is generally 100-170 Hz. These data strongly imply a configuration for IIa with the three phosphines cis to the hydride and the chloride trans. The high ν_{IrH} value is also indicative of a trans chloride. The proposed stereochemistry about the iridium atom is shown in Figure 1.

Examination of the ligand Ia (Figure 1) reveals that there are five sites "ortho" to the carbon atom bearing the dimethylphosphino group and therefore sterically available for participation in the reaction. However, there are only three chemically nonequivalent types of bonds: the carbon-hydrogen bond and the chemically equivalent pairs of boron-hydrogen bonds at positions 3,6 and 4,5.

To confirm that the reaction did not occur at the carbon atom, the ligand Ib, 1-PMe_2-2-D-1,2-$C_2B_{10}H_{10}$, was prepared from 1,2-D_2-1,2-$C_2B_{10}H_{10}$ according to eq 3 and was heated with $[Ir(C_8H_{14})_2Cl]_2$ in cyclohexane to afford IIb.

$$\text{1,2-}D_2\text{-1,2-}C_2B_{10}H_{10} + n\text{-BuLi} \xrightarrow{C_6H_6} \text{1-Li-2-D-1,2-}C_2B_{10}H_{10} \xrightarrow{Me_2PBr} \underset{\text{Ib}}{\text{1-PMe}_2\text{-2-D-1,2-}C_2B_{10}H_{10}} \quad (3)$$

The infrared spectrum of IIb exhibited a ν_{IrH} band at 2210 cm^{-1} and ν_{CD} bands at 2270 and 2290 cm^{-1}, but contained no evidence of a ν_{IrD} band in the 1500-1700-cm^{-1} region. This proved that the carboranyl C-H was not the source of the metal hydride.

Chatt and Davidson reported a reaction in which a C-H bond in a methylphosphine underwent oxidative addition,[17] producing a ruthenium hydride by what has recently been shown to be a dimerization reaction.[18] Although osmometric molecular weight measurements showed IIa to be monomeric (calcd mol wt = 840, found = 829 ± 24), the methyl groups still remained as a possible source of iridium hydride. To prove that the source of the hydride was a boron-hydrogen bond, the ligand Ic, containing approximately 50 atom % D at each of the 3, 4, 5, 6, 7, and 11 positions in the cage, was prepared via the carborane from μ,5,6,7,8,9,10-$D_{10}B_{10}H_4(d_5)$[19] (Figure 3). The "ortho" metalated complex IIc was prepared from Ic and its infrared spectrum was found to exhibit, as expected, both ν_{IrH} at 2250 cm^{-1} and ν_{IrD} at 1610 cm^{-1} (ν_{IrH}/ν_{IrD} = 1.40, theoretical = 1.41) with about equal intensities.

The one stereochemical question which remained was whether iridium showed any stereospecificity for attack at either the 3,6 or 4,5 positions. Attempts to prepare carboranylphosphine ligands stereospecifically labeled with deuterium at one of these pairs of sites were unsuccessful.

From the study of para-substituted triphenylphosphine complexes, Bennett and Milner found that electron donating groups accelerated the rate of ortho metalation.[14] This behavior is consistent with either of two competing effects: (1) enhanced electron density in the aromatic ring should promote electrophilic aromatic substitution, but (2) enhanced basicity of the ligand should promote electron density on the metal, making it a better nucleophile. At the time of our initial report,[11] the electrophilic substitution interpretation was favored on the basis of substituent effects for an analogous ortho-palladation of azobenzene complexes,[20] which strongly suggested electrophilic aromatic substitution.[13,20] Thus, the 4,5 positions were predicted to be the favored sites for B-H oxidative addition since known patterns of electrophilic substitution on carboranes indicate that the sites farthest from the carbon atoms are those most susceptible to electrophilic attack.[15] More recent studies of oxidative addition of B-H (vide infra) and C-H[21] bonds indicate that the nucleophilic substitution interpretation is probably the correct one. The site of attachment of the iridium atom to the carborane cage in IIa-c is therefore most probably the 3,6 positions.

The Preparation of *B*-σ-Carboranyl Iridium Complexes by Intermolecular Oxidation Addition. The Preparation and Characterization of 3-[$(PPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$ (III). The work described above showed that oxidative addition of terminal boron-hydrogen bonds to suitable metal complexes was a feasible route to *B*-σ-carboranyl metal complexes, at least in the intramolecular reaction. Our related work on the isotopic exchange of deuterium gas with terminal boron-hydrogen bonds catalyzed by transition metal complexes[22] strongly implied that intermolecular oxidative addition could also be a facile reaction; however, no stable *B*-σ-carboranyl metal complexes were isolated under the exchange conditions.

Since four-coordinate iridium(I) complexes with strong σ-donor ligands are among the complexes most susceptible to oxidative addition,[23] we decided to attempt the synthesis of *B*-σ-carboranyl metal complexes by intermolecular oxidative addition of carboranyl boron-hydrogen bonds to suitable iridium(I) complexes.

Prolonged treatment of $(PPh_3)_2(CO)IrCl$ with 1,2-$C_2B_{10}H_{12}$ in refluxing toluene failed to yield a stable oxidative adduct. However, $(PPh_3)_2(CO)IrD_2Cl$ was found to be an effective catalyst for deuterium exchange in this carborane.[22b] This implied that the oxidative addition occurred but the product was not thermodynamically favored. Similar reaction of $(PPh_3)_3IrCl$, a complex even more susceptible to oxidative addition than $(PPh_3)_2(CO)IrCl$,[14] with 1,2-$C_2B_{10}H_{12}$ resulted in the first intermolecular synthesis of a *B*-σ-carboranyl metal complex.[12]

The reaction of 1,2-$C_2B_{10}H_{12}$ with $(PPh_3)_3IrCl$ in refluxing toluene afforded a small yield of III, a yellow crystalline B-σ-carboranyl iridium complex;[12] the major product was $Ir(PPh_3)_2[(o-C_6H_4)PPh_2]HCl$, the result of intramolecular ortho metalation in $(PPh_3)_3IrCl$.[14] Analogous reactions with $1,7-C_2B_{10}H_{12}$ and $1,12-C_2B_{10}H_{12}$ failed to yield any B-σ-carboranyl containing products. On the basis of elemental analysis and spectral data (vide infra), III was identified as $3-[(PPh_3)_2IrHCl]-1,2-C_2B_{10}H_{11}$ (Figure 4), a five-coordinate iridium(III) complex with only two triphenylphosphine ligands. It seemed probable that III was formed either by oxidative addition of $1,2-C_2B_{10}H_{12}$ to $(PPh_3)_3IrCl$ followed by loss of PPh_3, or by prior dissociation of PPh_3 followed by oxidative addition to $(PPh_3)_2IrCl$. In either case, the low yield of III was presumably due to the strength of the Ir-P bond which inhibits dissociation of a phosphine,[14,24] and to the presence of a facile competing reaction, the ortho metalation. Thus, it was found that $(PPh_3)_2IrCl$, formed in situ from $[Ir(C_8H_{14})_2Cl]_2$ and 2 equiv of PPh_3 in various solvents,[24] reacted readily with $1,2-C_2B_{10}H_{12}$ according to eq 4

$$\tfrac{1}{2}[Ir(C_8H_{14})_2Cl]_2 + 2PPh_3 + 1,2-C_2B_{10}H_{12} \rightarrow \underset{\text{III}}{3-[(PPh_3)_2IrHCl]-1,2-C_2B_{10}H_{11}} \quad (4)$$

to afford III in good yield (Table I).

The infrared spectrum of III (Table III) exhibited a strong band at 2560 cm^{-1} assigned to ν_{BH} and a pair of sharp, medium intensity bands at 2209 and 2199 cm^{-1} assigned to ν_{IrH}. The 251-MHz ^{1}H NMR spectrum consisted of resonances in the τ 2.0–2.8 region assigned to coordinated PPh_3, a typically broad carboranyl C-H singlet at τ 7.29, and a 1:2:1 triplet at τ 28.08 (J_{PIrH} = 14.3 Hz), assigned to the hydride. As only one hydride resonance was found, the two bands for ν_{IrH} in the Nujol mull ir spectrum are believed to be an artifact of the solid state spectrum. In CH_2Cl_2 solution III exhibited a single ν_{IrH} at 2203 cm^{-1}. The 80.53-MHz ^{11}B NMR spectrum (Figure 4) consisted of an unresolved set of broad, overlapping resonances between 0.0 and +20.0 ppm (from $BF_3 \cdot O(C_2H_5)_2$) of relative area 9.1 and a broad singlet (width at half-height ca. 300 Hz) at +34.4 ppm of relative area 0.9.

These spectral data and the elemental analysis (Table IV) support the trigonal bipyramidal structure about the iridium atom depicted in Figure 4. The symmetrical hydride triplet is consistent with two equivalent phosphines cis to the hydride and the chemical shift and position of ν_{IrH} are consistent with chloride trans to the hydride.[16] Although a square pyramidal structure with an axial hydride would also have phosphine cis to the hydride, Shaw and coworkers have shown that such species exhibit ν_{IrH} at ca. 2000 cm^{-1} and the hydride resonance at ca. τ 60.[25]

The position of substitution on the carborane cage is not readily apparent from the ^{11}B NMR spectrum. The resonance at +34.4 ppm, a singlet shifted far upfield, clearly represents the boron atom to which the iridium atom is bonded; the remainder of the spectrum is very similar to that of $1,2-C_2B_{10}H_{12}$,[12] but small shifts and extensive line broadening[26] preclude definite assignments in this region. However, the existence of only one carboranyl C-H resonance in the ^{1}H NMR spectrum (assuming it does not represent the coincidental overlap of resonances for two chemically different C-H groups) requires the metal atom to be substituted on the plane of symmetry between the carbon atoms, i.e., at either B(3,6) or B(8,10). Rates of transition metal catalyzed deuterium exchange on $1,2-C_2B_{10}H_{12}$ have been found to follow the nucleophilic substitution pattern B(3,6) > B(4,5,7,11) > B(8,10) > B(9,12).[22] Since this isotopic exchange is proposed to proceed via a rate-determining oxidative addition, the expected position of substitution in III would be B(3,6).

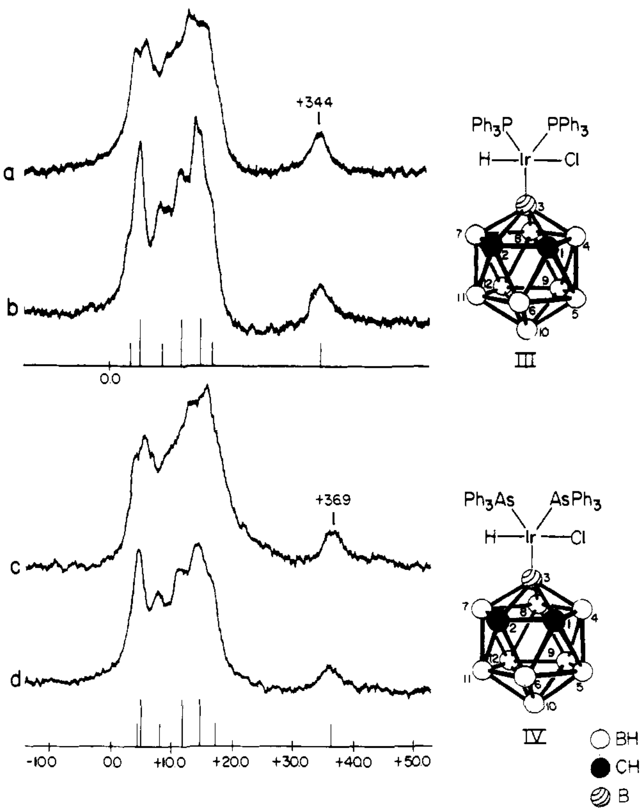

Figure 4. The proposed structures and 80.53-MHz ^{11}B NMR spectra of $3-[(PPh_3)_2IrHCl]-1,2-C_2B_{10}H_{11}$ (III) and $3-[(AsPh_3)_2IrHCl]-1,2-C_2B_{10}H_{11}$ (IV). Spectra (b) and (d) are proton decoupled and can be rationalized by resonances with the required symmetry as illustrated by the line spectra below them.

The position of substitution on the carborane cage of III was experimentally determined by deuterium labeling experiments. The reaction of $(PPh_3)_2IrCl$ with $1,2-C_2H_2B_{10}D_{10}$ yielded IX, a complex with ν_{IrD} at 1580 and 1570 cm^{-1} (ν_{IrH}/ν_{IrD} = 1.40, theoretical = 1.41), which confirmed that the product arises from oxidative addition of a carboranyl B-H bond to the metal atom. When $3,6-D_2-1,2-C_2B_{10}H_{10}(d_{1.6})$ was used, the product (X) gave an infrared spectrum which exhibited both ν_{IrH} and ν_{IrD} bands with a ratio of absorbances of ca. 1:2, respectively. This proved that substitution was indeed at the B(3,6) sites.

Preparation of Other B-σ-Carboranyl Iridium Complexes. Table I lists a series of complexes, III–VIII, prepared from L_2IrCl (L = PPh_3 or $AsPh_3$) and each of the three icosahedral $C_2B_{10}H_{12}$ carboranes. Unlike syntheses with $1,2-C_2B_{10}H_{12}$, which yielded nearly analytically pure crude products with a stoichiometric quantity of carborane, syntheses with 1,7- or $1,12-C_2B_{10}H_{12}$ required a large excess of carborane. Also, VI or VIII, products prepared from $(AsPh_3)_2IrCl$ and 1,7- or $1,12-C_2B_{10}H_{12}$, respectively, could not be prepared in refluxing cyclohexane but were successfully prepared at room temperature in benzene solution. The complexes III–VIII are all yellow, crystalline compounds and are indefinitely stable to air in the solid state. In solution, the PPh_3 complexes rapidly decompose upon exposure to air, V and VII within minutes and III within hours, while the $AsPh_3$ complexes are stable for at least several hours.

NMR and infrared spectral data for III–VIII are recorded in Tables II and III, respectively, and Table IV lists the results of elemental analyses. Although VII did not survive recrystallization attempts, one crude sample was obtained

Table I. Conditions for and Results of Selected Syntheses of *B*-*o*-Carboranyl Iridium Complexes

Product[a]	Ir[b]:L[c]:carb[d] (mmol)	Solvent (ml)[e]	Time[f]	% yield[g]	Recryst[h]	Mp,[i] °C
III	0.112:0.446:0.290	$C_6H_6(10)$ $+ C_6H_{14}(30)$	5 min	84		
	0.112:0.446:0.229	$C_6H_{12}(10)$	5 min	86		
	0.115:0.442:0.277	$C_6H_{14}(10)$	12 hr	91		
	0.114:0.446:0.243	$C_2H_5OH(10)$	45 min	61	B/H (59%)	
	1.12:4.46:2.36	$C_6H_{12}(100)$	1 hr	93	D/E (80%)[j]	250 (210)
IV	0.558:2.23:1.38	$C_6H_{12}(50)$	30 min	88	D/E (74%)[j]	235 (200)
V	0.569:2.23:6.93	$C_6H_{12}(40)$	5 min	80		
	0.223:0.891:1.38	$C_2H_5OH(10)$	40 min	60	D/H,D/E (36%)	220 (195)
VI	0.558:2.23:2.50	$C_6H_6(30)$	18 hr[l]	58	D/E (61%)	215 (190)
VII	0.114:0.446:0.693	$C_6H_{12}(10)$	1 hr	66	*k*	240 (200)
VIII	0.334:1.34:2.00	$C_6H_6(30)$ $+ C_5H_{12}(60)$	18 hr[l]	62	D/E (63%)	215 (185)
IX	0.117:0.477:0.233	$C_6H_{12}(10)$	5 min	87		
X	0.112:0.447:0.274	$C_6H_{12}(10)$	5 min	84		
XI	0.112:0.447:0.379	$C_6H_{12}(10)$	5 min	80		

[a] See Table II for formulas of III–VIII, IX = 3-[$(PPh_3)_2IrDCl$]-1,2-$C_2H_2B_{10}D_9$, X = 3-[$(PPh_3)_2IrDCl$]-6-D-1,2-$C_2B_{10}H_{10}(d_{1,6})$, XI = 2-[$(PPh_3)_2IrDCl$]-3-D-1,7-$C_2B_{10}H_{10}(d_1)$. [b] Ir = $[Ir(C_8H_{14})_2Cl]_2$. [c] For III, V, VII, IX, X, and XI: L = PPh_3, for IV, VI, and VIII: L = $AsPh_3$. [d] For III and IV, carb = 1,2-$C_2B_{10}H_{12}$; for V and VI, carb = 1,7-$C_2B_{10}H_{12}$; for VII and VIII, carb = 1,12-$C_2B_{10}H_{12}$; for IX, carb = 1,2-$C_2H_2B_{10}D_{10}$; for X, carb = 3,6-D_2-1,2-$C_2B_{10}H_{10}(d_{1,6})$; for XI, carb = 2,3-D_2-1,7-$C_2B_{10}H_{10}(d_1)$. [e] Where a second solvent is indicated, it was added to the cooled solution in the first solvent to crystallize the product. [f] Except where noted, time is for reflux in indicated solvent. [g] Crude yield. [h] Solvent mixture for recrystallization by rotary evaporation in drybox (except where noted): D = dichloromethane, E = ethanol, B = benzene, H = hexane. Recovery from recrystallization is given in parentheses. [i] Began to darken at temperature in parentheses, melted with decomposition at indicated temperature. [j] Recrystallized by rotary evaporation in air. [k] Crude product analytically pure. Attempts to repeat this synthesis gave impure product which decomposed upon attempted recrystallization in the drybox. [l] At room temperature.

Table II. NMR Data for *B*-σ-Carboranyl Iridium Complexes III–VIII

	^{1}H NMR[a]		^{11}B NMR[b]
Compound	Carborane C–H, τ[c]	Hydride, τ (J_{P-H}, Hz)[d]	Ir–B, ppm[e]
III, 3-[$(PPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$	7.29[f]	t, 28.08 (14.3)[f]	+34.4
IV, 3-[$(AsPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$	7.40	s, 30.17	+36.9
V, 2-[$(PPh_3)_2IrHCl$]-1,7-$C_2B_{10}H_{11}$	7.99	t, 28.96 (14)	+40.8
VI, 2-[$(AsPh_3)_2IrHCl$]-1,7-$C_2B_{10}H_{11}$	7.91	s, 31.17	+42.8
VII, 2-[$(PPh_3)_2IrHCl$]-1,12-$C_2B_{10}H_{11}$	8.27, 9.32	t, 29.08 (14)	+36.2
VIII, 2-[$(AsPh_3)_2IrHCl$]-1,12-$C_2B_{10}H_{11}$	7.55, 8.21	s, 31.23	+38.4

[a] Except where noted, taken in supersaturated CH_2Cl_2 solution at 100 MHz. [b] Taken in supersaturated CH_2Cl_2 solution at 80.53 MHz. [c] Broad singlets. [d] Sharp 1:2:1 triplets (t) or singlets (s). [e] Relative to $BF_3 \cdot O(C_2H_5)_2$. [f] Taken in CD_2Cl_2 at 251 MHz.

which was spectroscopically free of impurities and the analysis of this sample was satisfactory. These data are all in accord with the same stereochemistry for IV–VIII about the iridium atom as was found for III. The remaining unknown is the site of substitution on the carborane cage.

The expected site of substitution in IV is the same as that found in III, B(3,6). The ^{11}B NMR spectra in Figure 4 show a great deal of similarity making it highly probable that the site of substitution is the same, and that IV is 3-[$(AsPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$. Although the individual resonances cannot be resolved, except for those assigned to the boron atoms bonded to the metal, the envelopes of the proton decoupled spectra can at least be rationalized as peaks with the relative areas required by the symmetry of the proposed structures. This is shown by the line spectra in Figure 4.

The ^{11}B NMR spectra of V and VI were similar to each other, but even less well resolved than those of III and IV. Both complexes exhibited only one carboranyl C–H resonance in the ^{1}H NMR spectra, indicating that substitution had occurred at B(2,3) or B(9,10). On the basis of the observed order of rates for deuterium exchange on 1,7-$C_2B_{10}H_{12}$ catalyzed by transition metal complexes,[22] which was B(2,3) > B(4,6,8,11) > B(5,12) > B(9,10), and by analogy to the course of reaction with 1,2-$C_2B_{10}H_{12}$, the site of substitution was assigned as B(2,3). This assignment was confirmed for V by the observation of a ν_{IrD} band at 1573 cm^{-1} in the infrared spectrum of XI, the product from the reaction of $(PPh_3)_2IrCl$ with 2,3-D_2-1,7-$C_2B_{10}H_{10}(d_1)$. Figure 5 depicts the proposed structures of V and VI, 2-[$(PPh_3)_2IrHCl$]-1,7-$C_2B_{10}H_{11}$ and 2-[$(AsPh_3)_2IrHCl$]-1,7-$C_2B_{10}H_{11}$, respectively.

Since all boron atoms in 1,12-$C_2B_{10}H_{12}$ are chemically equivalent, there can be only one isomer for a monosubstitution product. The proposed structures of VII and VIII, 2-[$(PPh_3)_2IrHCl$]-1,12-$C_2B_{10}H_{11}$ and 2-[$(AsPh_3)_2IrHCl$]-1,12-$C_2B_{10}H_{11}$ respectively, are also shown in Figure 5.

Attempts to prepare *B*-σ-carboranyl rhodium complexes from reactions between 1,2-$C_2B_{10}H_{12}$ and $(PPh_3)_3RhCl$ or $[(PPh_3)_2RhCl]_2$ failed to yield stable oxidative adducts.

Reactions of 3[$(PPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$ (III). Carbon Monoxide. The rapid reaction of III with excess CO in benzene solution at room temperature produced *trans*-$(PPh_3)_2(CO)IrCl$ and 1,2-$C_2B_{10}H_{12}$ (eq 5). As mentioned above, even prolonged heating of *trans*-$(PPh_3)_2(CO)IrCl$

$$\text{3-[(PPh}_3)_2\text{IrHCl]-1,2-C}_2\text{B}_{10}\text{H}_{11} + \text{CO} \rightarrow \textit{trans}\text{-(PPh}_3)_2\text{(CO)IrCl} + \text{1,2-C}_2\text{B}_{10}\text{H}_{12} \quad (5)$$

with 1,2-$C_2B_{10}H_{12}$ in toluene solutions produced no stable *B*-σ-carboranyl iridium complexes. However $(PPh_3)_2(CO)IrCl$ is an active deuteration catalyst for carboranes,[22b] implying that the carborane does undergo oxidative addition but that the product is not thermodynamically favored.

Triphenylphosphine. Upon heating III with an excess of PPh_3 in toluene, a reaction similar to that observed with CO occurred. The carborane was reductively eliminated with complexation of the new ligand; however, under the vigorous conditions employed, the $(PPh_3)_3IrCl$ produced was partially converted to the ortho metalation product.[14] These processes are shown in eq 6.

Table III. Infrared Spectra *B*-σ-Carboranyl Iridium Complexes III–VIII[a]

Compound	ν_{IrH}[b]	Other bands[c]
III	2208 (m), 2198 (m), 2203 (m)[f]	3010 (m),[d] 2570 (s),[d] 1970 (w),[d] 1910 (w),[d] 1820 (w),[d] 1780 (w),[d] 1680 (w),[d] 1590 (w),[d] 1570 (w),[d] 1475 (s),[d] 1430 (s),[d] 1310 (w),[d] 1220 (w), 1190 (m),[d] 1160 (m),[d] 1130 (w), 1100 (s),[d] 1075 (w),[d] 1030 (m),[d] 1005 (m),[d] 990 (w), 960 (w), 950 (w), 930 (w), 910 (w), 854 (w), 832 (sh), 814 (m), 790 (m), 754 (s),[d] 749 (s),[d] 709 (s),[d] 695 (vs)[d]
IV	2195 (w), 2179 (m), 2201 (m)[f]	3000 (m),[e] 2570 (s),[e] 1960 (w),[e] 1900 (w),[e] 1820 (w),[e] 1770 (w),[e] 1660 (w),[e] 1575 (m),[e] 1475 (s),[e] 1430 (s),[e] 1305 (m),[e] 1270 (w),[e] 1220 (w),[e] 1190 (m),[e] 1155 (m),[e] 1130 (w), 1075 (m),[e] 1025 (m),[e] 1000 (m),[e] 988 (w), 960 (w), 950 (w), 925 (w), 910 (w), 895 (w), 850 (w), 835 (w), 815 (m), 751 (m), 740 (s),[e] 720 (w), 692 (s)[e]
V	2214 (m)	*d*, 1150 (sh), 1060 (w), 976 (w), 940 (m), 894 (w), 850 (w), 837 (m), 818 (m), 775 (w), 732 (m)
VI	2203 (m)	*e*, 1060 (w), 992 (w), 972 (w), 941 (w), 890 (w), 850 (w), 835 (sh), 818 (m), 777 (w)
VII	2200 (m)	*d*, 1120 (w), 1075 (m), 980 (w), 948 (w), 926 (w), 906 (w), 861 (sh), 847 (sh), 840 (m), 800 (m), 790 (m), 783 (sh), 731 (m)
VIII	2190 (m)	*e*, 1120 (w), 1110 (w), 1030 (sh), 978 (w), 945 (w), 919 (w), 904 (w), 860 (sh), 848 (sh), 839 (m), 802 (m), 782 (m)

[a] Nujol mull, cm^{-1} (intensity: w = weak, m = medium, s = strong, vs = very strong, sh = shoulder). [b] Recorded on Perkin-Elmer 421 spectrophotometer. [c] Recorded on Perkin-Elmer 137 spectrophotometer. [d] Absorptions in the spectrum of III are common to V and VII also. [e] Absorptions in the spectrum of IV are common to VI and VIII also. [f] Recorded in CH_2Cl_2 solution using Perkin-Elmer 421.

Table IV. Elemental Analyses for *B*-σ-Carboranyl Iridium Complexes III–VIII[a]

Compound		% C	% H	% B	% P/As	% Cl	% Ir
III, 3-[$(PPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$	Calcd	50.91	4.72	12.06	6.91	3.95	21.44
	Found	50.86	4.99	11.82	6.59	4.21	20.85
IV, 3-[$(AsPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$	Calcd	46.37	4.30	10.98	15.22	3.60	19.52
	Found	46.20	4.40	-----	15.02	----	-----
V, 2-[$(PPh_3)_2IrHCl$]-1,7-$C_2B_{10}H_{11}$	Calcd	50.91	4.72	12.06	6.91	3.95	21.44
	Found	50.58	4.81	-----	6.61	----	-----
VI, 2-[$(AsPh_3)_2IrHCl$]-1,7-$C_2B_{10}H_{11}$	Calcd	46.37	4.30	10.98	15.22	3.60	19.52
	Found	46.35	4.33	10.82	15.55	3.61	19.12
VII, 2-[$(PPh_3)_2IrHCl$]-1,12-$C_2B_{10}H_{11}$	Calcd	50.91	4.72	12.06	6.91	3.95	21.44
	Found	50.61	4.86	11.80	6.86	3.91	21.72
VIII, 2-[$(AsPh_3)_2IrHCl$]-1,12-$C_2B_{10}H_{11}$	Calcd	46.37	4.30	10.98	15.22	3.60	19.52
	Found	46.20	4.56	-----	14.95	----	------

[a] Analyses were of those products in Table I for which melting point data are given.

$$3\text{-}[(PPh_3)_2IrHCl]\text{-}1,2\text{-}C_2B_{10}H_{11} + PPh_3 \xrightarrow[\Delta]{-1,2\text{-}C_2B_{10}H_{12}}$$

$$(PPh_3)_3IrCl \xrightarrow[\Delta]{} Ir(PPh_3)_2[o\text{-}(C_6H_4)PPh_2]HCl \quad (6)$$

No reaction occurred between III and the weaker ligands acetonitrile and triethylamine.

Conclusion

Oxidative addition of terminal boron–hydrogen bonds to suitable low valent metal species appears to be a useful technique for the synthesis of complexes with a metal-boron σ-bond. It is anticipated that other B-H containing substrates and other metal complexes will be found to undergo similar reactions. Indeed, B_5H_9 has been found to oxidatively add to $(PMe_3)_2(CO)IrCl$, although not to $(PPh_3)_2(CO)IrCl$.[10] This latter result is in accord with our failure to obtain stable products from oxidative addition of carboranes to $(PPh_3)_2(CO)IrCl$. However, in the light of the reaction between III and CO, and in view of the efficacy of $(PPh_3)_2(CO)IrCl$ as a catalyst for deuterium exchange on carboranes,[22b] this apparent failure is most probably due to unfavorable thermodynamic stability of the products rather than a prohibitive activation energy.

The *B*-σ-carboranyl iridium complexes are models for intermediates postulated for transition metal catalyzed deuterium exchange at terminal boron–hydrogen bonds in a wide variety of B-H containing species and are themselves the most active agents thus far discovered for such exchange reactions.[22b] The many transition metal species which have been found to catalyze this deuterium exchange,[22] including Pd on charcoal, $(PPh_3)_3RuHCl$, $(PPh_3)_3RhCl$, and several hydridometallocarboranes,[27] indicate that such oxidative addition is a more facile reaction than the number of reported stable adducts would imply.

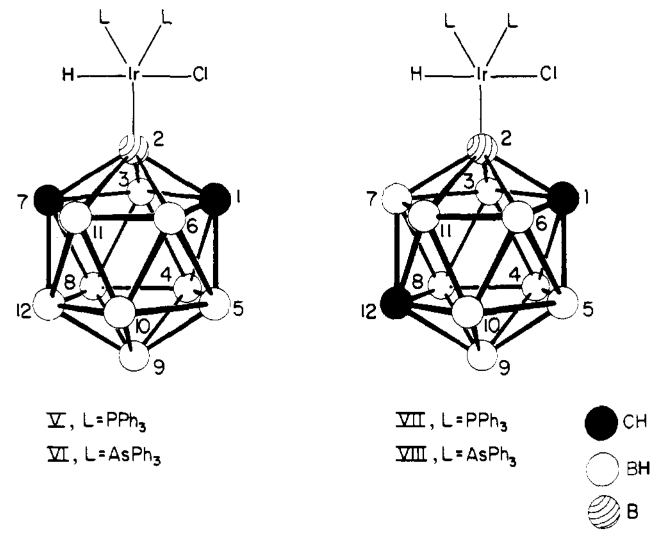

Figure 5. The proposed structures of V–VIII.

Experimental Section

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen and solvents were saturated with nitrogen just prior to use. Unless otherwise noted, isolation and purification of products were accomplished under an inert atmosphere.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 137 sodium chloride spectrophotometer in the range of 4000-700 cm^{-1} with KBr pellets or Nujol mulls. The 100-MHz proton NMR spectra were obtained on a Varian HA-100 spectrometer with samples which had been greatly supersaturated in CH_2Cl_2. These samples were prepared in the drybox by rotary evaporation of solvent from less than saturated solutions. The supersaturated solutions slowly deposited crystals, so all spectra were obtained within 1 hr of sample preparation. The chemical shifts were converted to τ values by addition of 4.65 ppm to the shift from CH_2Cl_2. The 251-MHz proton and 80.53-MHz ^{11}B NMR spectra were obtained on a superconducting, Fourier-transform instrument designed and constructed by Professor F. A. L. Anet and coworkers of this department. The ^{11}B NMR spectra of B-σ-carboranyl iridium complexes were taken on supersaturated samples prepared as described above. Mass spectra were obtained with an Associated Electrical Industries MS-9 spectrometer. Molecular weights were determined in tetrahydrofuran with a Mechrolab osmometer calibrated against benzil. Melting points (uncorrected) were taken in sealed, evacuated capillary tubes on a Unimelt Thomas-Hoover apparatus. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and by Galbraith Laboratories, Knoxville, Tenn.

Materials. Decaborane(14), $1,2\text{-}C_2B_{10}H_{12}$,[28] and $1,7\text{-}C_2B_{10}H_{12}$[29] were purified by sublimation prior to use; $1,12\text{-}C_2B_{10}H_{12}$[30] was purified by chromatography with 30-60° petroleum ether on basic alumina according to the suggestion of Sieckhaus et al.[31] n-Butyllithium in hexane was purchased from Ventron, D_2O (99.8% isotopic purity) from Bio-Rad Laboratories, and D_2 (99.7% isotopic purity) from Liquid Carbonic. Triphenylphosphine and triphenylarsine were recrystallized from ethanol prior to use. Hexane and dichloromethane (technical grade) were distilled from Drierite, dioxane (Matheson Coleman and Bell, reagent grade) was purified by a literature method,[32] and benzene and toluene (Mallinckrodt, reagent grade) were distilled from CaH_2 and stored under nitrogen. Reagent grade cyclohexane from Matheson Coleman and Bell and anhydrous ether from Mallinckrodt were used as received. Deuterium chloride,[33] Me_2PBr,[34] $[Ir(C_8H_{14})_2Cl]_2$,[35] $1,2\text{-}C_2H_2B_{10}D_{10}$,[22] and $(PPh_3)_3RuHCl\cdot C_6H_5CH_3$[36] were prepared by literature methods.

$1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{11}$ (Ia). A slurry of $1\text{-}Li\text{-}1,2\text{-}C_2B_{10}H_{11}$ was prepared by addition of 50 ml of 2.0 M n-butyllithium in hexane (0.1 mol) to 14.4 g (0.1 mol) of $1,2\text{-}C_2B_{10}H_{12}$ dissolved in 400 ml of benzene. The slurry was added, over a period of 15 min, to 14.1 g (0.1 mol) of Me_2PBr suspended in 100 ml of ether. After addition was complete, the mixture was stirred for 30 min at ambient temperature and then rotary evaporated to remove solvents. The residue was treated with 100 ml of hexane and filtered. The filtrate was washed with water (100 ml) and dried ($MgSO_4$). Removal of solvent by rotary evaporation yielded a yellow syrup. This syrup was sublimed/distilled under high vacuum with a 200° oil bath, yielding a white semisolid on the 0° cold finger and a colorless liquid in the receiver. Both products were mixtures of $1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{11}$ and $1,2\text{-}C_2B_{10}H_{12}$. The mixtures were combined, dissolved in 10 ml of CH_2Cl_2, and separated by preparative GLC with an Aerograph gas chromatograph on a 10 ft by ⅜ in. 20% Apiezon L on Chromosorb P, AW-DMCS column operated at 220°. The yield of $1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{11}$ was 5.8 g (28%) and 6.5 g of $1,2\text{-}C_2B_{10}H_{12}$ was recovered (45%).

The phosphine is a colorless, waxy solid, mp 50-51°. It has a pungent odor and must be stored in the absence of air to prevent its slow oxidation. The 60-MHz proton NMR (CCl_4) consisted of a broad, area 1 singlet at τ 6.51 assigned to the carboranyl C-H, and a sharp, area 6 doublet τ 8.71 (J_{PCH_3} = 5 Hz) assigned to the methyl protons. The 80.53-MHz $^{11}B\text{-}\{^1H\}$ NMR spectrum (CCl_4) was similar to that of $1,2\text{-}C_2B_{10}H_{12}$, consisting of four resonances of relative areas 2:2:4:2 at +2.0, +7.7, +12.6, and +13.6 ppm from $BF_3\cdot O(C_2H_5)_2$, respectively. The 101-MHz ^{31}P NMR spectrum (CCl_4) exhibited a single phosphorus resonance at +140.3 ppm from $P(OC_2H_5)_3$ as a broad singlet (width at half-height ca. 38 Hz). The ir spectrum (neat melt on NaCl) exhibited the following bands above 1200 cm^{-1}: 3035 (w), 2950 (w), 2890 (w), 2600 (s), 1420 (m), 1295 (m), 1283 (m). The relative intensities of the molecular ions in the mass spectrum at 15 eV were all within 5% of theoretical[37] for $C_4H_{17}B_{10}P$. Anal. Calcd for $C_4H_{17}B_{10}P$: C, 23.52; H, 8.39; B, 52.93; P, 15.16. Found: C, 23.26; H, 8.56; B, 52.61; P, 14.90.

$1,2\text{-}D_2\text{-}1,2\text{-}C_2B_{10}H_{10}$. Excess n-butyllithium (160 ml of 1.6 M in hexane) was added to a solution containing 14.4 g (0.1 mol) of $1,2\text{-}C_2B_{10}H_{12}$ in 250 ml of ether. After 20 min, D_2O (10 ml) was slowly added. The mixture was stirred for 15 min and the ether layer then separated and dried ($MgSO_4$). Solvent was removed by rotary evaporation and $1,2\text{-}D_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ was sublimed (60° to 0° cold finger under high vacuum) from the residue. The yield was 13.5 g (93%). The ir spectrum lacked the ν_{CH} band at 3050 cm^{-1} in $1,2\text{-}C_2B_{10}H_{12}$ and exhibited only the following absorptions: 2570 (s, ν_{BH}); 2295 (m, ν_{CD}; ν_{CH}/ν_{CD} = 1.33, theoretical = 1.36), 1080 (m), 954 (m), 909 (m), 831 (m), 749 (m), 736 (w), 724 (w), 708 (w). The mass spectrum at 15 eV was nearly identical with that of $1,2\text{-}C_2B_{10}H_{12}$, but with an increase of two mass units for each peak. The ^{11}B NMR spectrum was identical with that of the undeuterated carborane.

$1\text{-}D\text{-}2\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ (Ib). Ib was prepared as described for Ia, but with $1,2\text{-}D_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ as the starting carborane. Ib lacked the τ 6.51 carboranyl C-H resonance found in the ^1H NMR spectrum of Ia, but had an identical ^{11}B NMR spectrum. The ir spectra above 1200 cm^{-1} were identical for the two phosphines except for the shift of ν_{CH} from 3035 cm^{-1} in Ia to ν_{CD} at 2295 cm^{-1} (ν_{CH}/ν_{CD} = 1.32, theoretical = 1.36) in Ib.

$\mu,5,6,7,8,9,10\text{-}D_{10}B_{10}H_4(d_5)$. Decaborane(14) with approximately 50% D at each of the bridge and 5,6,7,8,9,10 terminal sites was prepared by a modification of the procedure of Dupont and Hawthorne.[33] Decaborane(14) (39.6 g, 0.324 mol) was dissolved in 600 ml of 5.5 M DCl in dioxane (3.3 mol) and allowed to equilibrate for 2 weeks at ambient temperature. Dioxane and HCl-DCl were removed under vacuum, and the deuterated decaborane was collected by sublimation to 0° cold finger. This crude product was resublimed to yield 38.8 g of $\mu,5,6,7,8,9,10\text{-}D_{10}B_{10}H_4(d_5)$ (94%). The ^{11}B NMR spectrum of the product showed collapse of the doublets assigned to B(6,9) and B(5,7,8,10) to broad singlets due to partial replacement of terminal H by D at those sites. The ir spectrum (Nujol mull) exhibited bands due to both ν_{BH} (2600, 2560 cm^{-1}) and ν_{BD} (1960, 1940 cm^{-1}); in a KBr pellet, the ν_{BDB} band could be observed at 1390 cm^{-1}.

$3,4,5,6,7,11\text{-}D_6\text{-}1,2\text{-}C_2B_{10}H_6(d_3)$. This hexadeuteriocarborane was prepared in 55% yield from $\mu,5,6,7,8,9,10\text{-}D_{10}B_{10}H_4(d_5)$ by the procedure of Todd et al.[38] The product had an ^{11}B NMR spectrum identical with that of $1,2\text{-}C_2B_{10}H_{12}$, but with partial collapse of the B(3,6) and B(4,5,7,11) doublets to singlets due to the partial replacement of H by D at those sites. The ir spectrum (KBr) showed ν_{BD} at 1950 cm^{-1} (m) and ν_{BH} at 2600 cm^{-1} (s).

$1\text{-}PMe_2\text{-}3,4,5,6,7,11\text{-}D_6\text{-}1,2\text{-}C_2B_{10}H_5(d_3)$ (Ic). Ic was prepared as described for Ia but with $3,4,5,6,7,11\text{-}D_6\text{-}1,2\text{-}C_2B_{10}H_6(d_3)$ as the starting carborane.

General Procedure for Preparation of Complexes IIa-c. $Ir(1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{11})_2[1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{10}]HCl$ (IIa). Addition of 920 mg of $1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{11}$ (4.5 mmol) to a yellow-orange suspension of 600 mg of $[Ir(C_8H_{14})_2Cl]_2$ in 25 ml of cyclohexane resulted in an immediate change in color of the suspension to yellow, presumably forming the L_3IrCl complex. The mixture was heated at the reflux temperature for 2 hr and allowed to cool. The off-white powder was then collected by filtration, washed twice with 5 ml of cyclohexane, and dried in vacuo to yield 1.10 g (98%) of $Ir(1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{11})_2[1\text{-}PMe_2\text{-}1,2\text{-}C_2B_{10}H_{10}]HCl$. The product could be recrystallized from $CHCl_3$ to obtain white microcrystals, mp 260-265° dec. The ir spectrum (Nujol mull) exhibited the following bands: 2860 (sh), 2600 (s), 2220 (m), 1298 (m), 1285 (m), 1100 (w), 1175 (m), 1130 (m), 1000 (w), 952 (m), 911 (s), 876 (w), 856 (m), 847 (w), 742 (m), 732 (m), 706 (m). Anal. Calcd for $C_{12}H_{51}B_{30}P_3ClIr$: C, 17.15; H, 6.12; B, 38.59; P, 11.06; Cl, 4.22; Ir, 22.87; mol wt, 840. Found: C, 16.88; H, 5.88; B, 38.03; P, 10.90: Cl, 4.22; Ir, 23.01; mol wt, 829 ± 24.

The complexes IIb and IIc were prepared similarly from $[(Ir(C_8H_{14})_2Cl)]_2$ and the phosphines Ib and Ic, respectively.

$3,6\text{-}D_2\text{-}1,2\text{-}C_2B_{10}H_{10}(d_{1.6})$. A 500-ml flask was charged with 362 mg (2.51 mmol) of $1,2\text{-}C_2B_{10}H_{12}$, 14.5 mg (0.0143 mmol) of $(PPh_3)_3RuHCl\cdot C_6H_5CH_3$, and a magnetic stir bar. The flask was evacuated, filled with D_2 to 645 mm (ca. 21 mmol), and sealed. The 20 ml of benzene was added through a rubber septum. The sealed flask was immersed in a 50° water bath and the solution magnetically stirred for 3 days. The deuterated carborane was isolated from the cooled solution by evaporation of solvent and sublimation under high vacuum. The product was examined by 251-MHz ^{11}B NMR and was determined to be deuterated ca. 80% at B(3,6) and less than 5% elsewhere.

2,3-D_2-1,7-$C_2B_{10}H_{10}$(d_1). A stream of D_2 (ca. 10 cm^3/min) was bubbled through a solution of 1.0 g (7 mmol) of 1,7-$C_2B_{10}H_{12}$ and 350 mg (0.35 mmol) of $(PPh_3)_3RuHCl \cdot C_6H_5CH_3$ in 50 ml of toluene. The solution was magnetically stirred and heated at 100° for 4 hr and then allowed to cool. Carborane was isolated by evaporation of solvent and sublimation under high vacuum. The 80.53-MHz ^{11}B NMR spectrum of the product indicated ca. 50% D at the **B**(2,3) positions and ca. 5% at the **B**(4,6,8,11) positions.

Preparation of *B*-σ-Carboranyl Iridium Complexes III–XI. Table I gives the conditions for and results of selected syntheses of *B*-σ-carboranyl iridium complexes. In general, the reagents were mixed in a Schlenk flask under N_2 and stirred at the reflux temperature for the indicated time. Some of the cyclohexane preparations briefly dissolved to a red solution before the yellow crystalline product began to precipitate. The ethanol and hexane preparations and some of the cyclohexane preparations remained mixtures in which the yellow crystalline product slowly replaced the orange suspension which immediately formed from the reagents. The benzene solutions lightened from red to orange during the reaction period and the products were slowly crystallized from the cooled solutions by addition of the indicated solvent.

Recrystallization of the 1,2-carborane adducts could be accomplished in the atmosphere by dissolution in CH_2Cl_2, addition of an equal volume of ethanol, and slow rotary evaporation to remove the more volatile solvent. The other adducts were recrystallized similarly in the drybox because of the air sensitivity of their solutions. Attempts to recrystallize 3-[$(PPh_3)_2IrHCl$]-1,12-$C_2B_{10}H_{11}$, even in the drybox, failed due to decomposition of the complex.

The analyses given in Table IV were taken on the samples of the complexes for which melting point data are given in Table I.

Reactions of 2-[$(PPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$ (III). Carbon Monoxide. A suspension of 100 mg (0.111 mmol) of 2-[$(PPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$ in 10 ml of warm benzene was treated with a stream of CO for 3 min, during which time the complex dissolved to afford a pale yellow solution. The solution was heated briefly to reflux, cooled, and treated with 10 ml of pentane, whereupon a yellow crystalline product slowly precipitated. After 1 hr, the product was collected by filtration, washed with pentane, and air-dried. The ir spectrum was identical with that of authentic *trans*-$(PPh_3)_2(CO)IrCl$. The yield was 70 mg (80%).

The filtrate was evaporated to dryness and the residue sublimed to a 0° cold finger at 60° in high vacuum. 1,2-$C_2B_{10}H_{12}$ (13.2 mg, 82%) was collected. The ir spectrum was identical with that of authentic 1,2-$C_2B_{10}H_{12}$.

Triphenylphosphine. To 100 mg (0.111 mmol) of 3-[$(PPh_3)_2IrHCl$]-1,2-$C_2B_{10}H_{11}$ suspended in 10 ml of benzene was added 117 mg (0.446 mmol) of PPh_3 and the mixture was heated briefly to the reflux temperature. After cooling, the solvent was evaporated and the residue was dissolved in 10 ml of CH_2Cl_2. Hexane (50 ml) was added and the solution was evaporated to ca. 5 ml. Filtration afforded 69 mg (61%) of a yellow powder which ir analysis showed to be a mixture of $(PPh_3)_3IrCl$ and the ortho metalated derivative. The identity of the latter was confirmed by the chemical shift and distinctive eight line multiplicity of the hydride resonance in the ^1H NMR spectrum, identical with that of the authentic ortho metalated species.[14] Evaporation and sublimation of the filtrate afforded 1,2-$C_2B_{10}H_{12}$.

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