POLYHEDRAL ORGANOIRIDAAZABORANE CHEMISTRY. THE PREPARATION OF THE ELEVEN-VERTEX *nido* COMPOUND [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNHB_9H_{10}$] AND ITS CHARACTERIZATION BY SINGLE-CRYSTAL X-RAY DIFFRACTION ANALYSIS AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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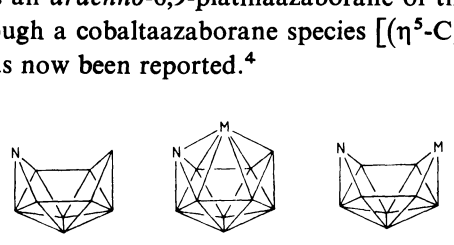
Reaction between *nido*-6-HNB_9H_{11} (from [9-(MeNC)-*arachno*-6-HNB_9H_{11}] and [(η^5-C_5Me_5).$IrCl_2]_2$ in the presence of N,N,N',N'-tetramethylnaphthalene-1,8-diamine) gives [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNHB_9H_{10}$] as a yellow crystalline solid in 40% yield. Crystals are triclinic, space group $P\bar{1}$, $Z = 2$, with $a = 825{\cdot}5(1)$, $b = 986{\cdot}4(2)$, $c = 1\,158{\cdot}7(2)$ pm, $\alpha = 95{\cdot}12(1)$, $\beta = 91{\cdot}00(1)$, $\gamma = 111{\cdot}90(1)°$. The molecular structure is based on an open-faced *nido* $\{IrNB_9\}$ eleven-vertex polyhedron with the iridium and nitrogen atoms in adjacent positions in the open face. Nuclear magnetic single and multiple resonance spectroscopy assigns the cluster ^{11}B and ^1H resonances, and suggests strong electronic similarities to the sulphur-containing analogue [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{10}$].

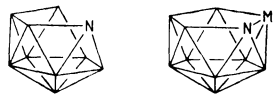
We recently reported[1] that reaction of [*nido*-6-HNB_9H_{11}] (schematic configuration I) with [(η^6-MeC_6H_4-4-^{i}Pr)$RuCl_2]_2$ results in the formation of an eleven-vertex ruthenaazaborane of the *closo*-type configuration II. Prior to this, the only reported metallaazaborane was an *arachno*-6,9-platinaazaborane of the ten-vertex configuration III (refs[2,3]), although a cobaltaazaborane species [(η^5-C_5H_5)CoB_9H_9NH], also of configuration II, has now been reported.[4]



IA II III

We have interests in the investigation of the reactions of [(η^5-(C_5Me_5)$IrCl_2]_2$ with polyhedral boron-containing substrates,[5-9] and in the development of azaborane chemistry,[1-3,10-13] and within these contexts we now report the reaction of [(η^5-

$-C_5Me_5)IrCl_2]_2$ with [*nido*-6-HNB_9H_{11}] to give an eleven-vertex iridaazaborane of *nido* configuration IV. As far as we are aware, this is the first reported example of an eleven-vertex *nido* metallaazaborane compound.



IB IV

RESULTS AND DISCUSSION

Reaction between $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ and [*nido*-6-NHB_9H_{11}] (formed in situ from the dissociation of [9-(CH_3CN)-*arachno*-6-NHB_9H_{11}]) in the presence of the non-nucleophilic base N,N,N′,N′-tetramethylnaphthalene-1,8-diamine (TMND), for 140 min in dichloromethane solution, followed by chromatographic separation of the reaction products, resulted in the formation in a 39% isolated yield of a pale yellow iridaazaborane, identified by single-crystal X-ray crystallography and NMR spectroscopy (described below) as [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNHB_9H_{10}$]. The compound, a crystalline solid, was reasonably air-stable in the solid state (weeks), but was less stable in solution in air. A reasonable stoicheiometry may be written down for its formation (Eq. (*A*)), with the presence of a boron–chlorine bond in the product indicating that the mechanism of formation is somewhat more complex than a displacement of halide from the starting $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ by the incipient $[B_9H_{10}NH]^-$ anion, although of course, such a process (e.g. structures B → V) could be an initial step in the overall mechanism.

$$[(C_5Me_5)IrCl_2]_2 + [HNB_9H_{11}] + \text{base} \rightarrow$$
$$\rightarrow [(C_5Me_5)IrNHB_9H_{10}Cl] + \text{baseH}^+Cl^- \qquad (A)$$

In view of the vast amount of reported carbaborane and metallacarbaborane chemistry, it is surprising that heteroborane and metallaheteroborane chemistry where the heteroatom is an electronegative first-row element other than carbon is sparsely represented in the literature, with only a handful of compounds being known.[1–4,10–18] The ready synthesis in reasonable yield of the open eleven-vertex iridaazaborane now emphasizes that there is a potentially rich chemistry in this area to be investigated.

Crystals suitable for X-ray diffraction experiments were grown from pentane/dichloromethane. A drawing of the molecular structure is given in Fig. 1. Salient interatomic distances and angles between interatomic vectors are given in Tables I and II, respectively. All cluster hydrogen atom positions, except that of the Ir—H—B bridge, were readily apparent on a Fourier difference synthesis although they were

not refined (see Experimental). The presence of the Ir—H—B bridge was strongly suggested by a deep potential minimum using XHYDEX calculations,[19,20] and confirmed by NMR experiments (see later). The position of the Ir—H—B potential minimum is shown with outline bonds in the figure.

TABLE I

Selected interatomic distances (pm) for [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNB_9H_{11}$] with estimated standard deviations (e.s.d.'s) in parentheses

		From the iridium atom	
C(1)—Ir(8)	215·3(5)	C(3)—Ir(8)	221·2(6)
C(2)—Ir(8)	219·6(5)	C(5)—Ir(8)	220·1(6)
C(4)—Ir(8)	221·7(6)		
N(7)—Ir(8)	222·0(5)	B(9)—Ir(8)	224·8(7)
B(3)—Ir(8)	222·6(6)	B(4)—Ir(8)	220·7(6)
		Boron–nitrogen	
B(2)—N(7)	167·5(8)	B(3)—N(7)	167·5(8)
B(11)—N(7)	158·4(8)		
		Boron–boron	
B(9)—B(10)	190·1(8)	B(10)—B(11)	183·3(9)
other B—B	174·2(9)—183·2(9)		
		Others	
B(9)—Cl(9)	181·8(6)	C—C(Me)	149·0(7)—151·3(8)
C—C(cyclic)	141·1(7)—143·8(7)		

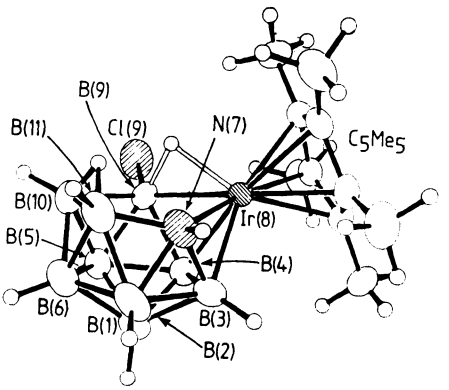


FIG. 1

ORTEP drawing of the crystallographically determined molecular structure of [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNHB_9H_{10}$]

The molecular structure is seen to be based upon an open *nido*-type eleven vertex $\{IrB_9\}$ cluster with the iridium and nitrogen atoms occupying adjacent positions on the open face (schematic structure IV above). There is a chlorine atom bound in an *exo*-terminal position to the open-face boron atom next to the iridium atom, all other boron atoms having *exo*-terminal hydrogen atoms bound to them, as does the nitrogen. The $\{\eta^5\text{-}C_5Me_5\}$ group is bound to the iridium atom in a straightforward manner, and there are bridging hydrogens in the Ir(8)—B(9) and B(10)—B(11) positions on the open face. The compound therefore conforms to the Williams–Wade[21,22] cluster-geometry and electron-counting rules, with a conventionally *nido*-shaped eleven-vertex cluster[21] and a 26-electron (i.e. $2n + 4$) Wadian[22] cluster electron count. In these terms the iridium centre formally contributes three orbitals and two electrons to the cluster bonding scheme, and is thereby formally octahedral iridium(III), and the nitrogen centre three orbitals and four electrons, and is thereby formally tetrahedral nitrogen(V) as it is in the *nido* ten-vertex precursor $[6\text{-}HNB_9H_{11}]$.

Apart from B(8)—B(9) at 190·1(8) pm, the interboron distances of 174·2(9) to 183·3(9) pm all appear to be within normal ranges for Wadian species, as are the iridium–boron[23] distances. The iridium–nitrogen distance is towards the longer end

TABLE II

Selected angles between interatomic vectors (°) for $[9\text{-Cl-}8\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}8,7\text{-}IrNB_9H_{11}]$ with e.s.d.'s in parentheses

	At iridium		
B(3)—Ir(8)—B(4)	48·8(2)	N(7)—Ir(8)—B(9)	84·6(2)
N(7)—Ir(8)—B(3)	44·3(2)	B(9)—Ir(8)—B(4)	48·0(2)
N(7)—Ir(8)—B(4)	79·0(2)	B(9)—Ir(8)—B(3)	85·1(3)
	At nitrogen		
B(2)—N(7)—B(3)	65·2(4)	Ir(8)—N(7)—B(11)	119·1(4)
B(2)—N(7)—Ir(8)	127·3(4)	B(3)—N(7)—Ir(8)	68·1(3)
B(2)—N(7)—B(11)	68·4(4)	B(3)—N(7)—B(11)	119·7(4)
	Others		
Ir(8)—B(9)—B(10)	111·7(4)	N(7)—B(11)—B(10)	112·1(4)
B(9)—B(10)—B(11)	106·8(4)	Cl(9)—B(9)—B(10)	118·3(4)
Cl(9)—B(9)—Ir(8)	122·0(3)	Cl(9)—B(9)—B(5)	116·0(4)
Cl(9)—B(9)—B(4)	123·1(4)		

of the range of 167·7 – 236·0 pm that has been reported so far,[24] and is more typical of a quaternarily bound nitrogen. There are limited comparison data available for the $\{Ir(C_5Me_5)\}$ moiety in metallaborane species,[7,8] but there appears to be a tilt [of 6·5(2)°] of the $\{C_5Me_5\}$ unit away from the nitrogen atom (compare ref.[1]), with the C(1)—Ir(8) distance *trans* to N(7) being significantly shorter, at 215·3(5) pm, than the C(3)—Ir(8) and C(4)—Ir(8) distancess, *cisoid* to N(7), at c. 221·5 pm. The methyl groups of the $\{C_5Me_5\}$ moiety are bent away from the least-squares plane of the C_5 ring by varying mounts [range 1·0(2) – 4·3(2)°], and on the side opposite to the iridium atom. The methyl groups most affected are the two closest to the cluster (and also closest to the chlorine substituent), i.e. *trans* to the heteroatom, suggesting that the bending is attributable, in part, to steric effects. The boron–nitrogen distances fall into two distinct regions, viz. a shorter distance of 158·4(8) pm on the open face and two longer distances of 167·5(8) pm for the linkages off the open face. A similar pattern is observed for the eleven-vertex *closo*-type complex $[(C_6Me_6)RuNHB_9H_9]$ (ref.[1]). Overall, the $\{IrEB_9\}$ cluster dimensions are very similar to those[8] of the previously synthesized sulphur analogue $[9\text{-Cl-8-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}8,7\text{-}IrSB_9H_{10}]$, except for the linkages to the heteroatom, which are longer for sulphur than for nitrogen (Table III).

The measured NMR properties of $[9\text{-Cl-8-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}8,7\text{-}IrNHB_9H_{10}]$ are summarised in Table IV and Fig. 2. These are consistent with the molecular structure, confirming that the crystal selected for single-crystal X-ray diffraction analysis was representative of the bulk sample. The ^{11}B and ^1H resonances are reasonably assigned to their structural positions using $[^{11}B\text{–}^{11}B]$-COSY, $^1H\text{–}\{^{11}B(\text{selective})\}$, and $[^1H\text{–}^1H]$-COSY experiments in a combined procedure as elaborated elsewhere (e.g. refs[25–28]). In the $[^{11}B\text{–}^{11}B]$-COSY experiments correlations between pairs of atoms in the open face, and between pairs of atoms flanking the nitrogen atom,

TABLE III

Comparative interatomic distances (pm) to the heteroatom in $[9\text{-Cl-8-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}8,7\text{-}IrENB_9H_{10}]$, where E = NH (this work) and S (data from ref.[8])

Distance	(a) E = NH	(b) E = S[a]	(b)–(a)
E(7)—Ir(8)	222·0(5)	235·7	14
E(7)—B(2)	167·5(8)	200·8	33
E(7)—B(3)	167·5(8)	208·7	41
E(7)—B(11)	158·4(8)	196·3	38

[a] Mean values of two independent molecules in the unit cell.

TABLE IV

Observed ^{11}B and ^{1}H NMR properties for [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNB_9H_{11}$] in CD_2Cl_2 solution at 194–296 K

Assignment	$\delta(^{11}B)$ ppm	$^{1}J(^{11}B-^{1}H)$	Observed [$^{11}B-^{11}B$]-COSY correlations[a,b]	$\delta(^{1}H)$[c] ppm	Observed [$^{1}H-^{1}H$]-COSY correlations[b,d]
1	−27·8	145	(2/4)m[e] (5)m (6)w	+0·90	[(2)w (3)m (5)w][f]
2	−20·4	c. 145	[(1)m (3)w][e]	+0·21	(1/4)w[f] (6)m (7)w (10)m[f] (11)m[f]
3	−4·9	160	(2/4)w[e]	+2·56	(1/4)m[f] (2)m
4	−20·4	c. 145	[(1)m (5)m (9)s][e]	+0·93	[(3)m (5)m (6)w][f]
5	+6·5	144	(1)m (5)m (9)s (10)w	+4·35	(1/4)m[f] (6)m (10)m μ(8, 9)s μ(10, 11)w
6	−25·0	148	(1)w (5)w (11)m	+2·71	(4/1)m[f] (2)m (3)m (10)m (11)m μ(8, 9)m
7	N	—	—	+3·45 (NH)	(2)w (11)w
8	Ir	—	—	+2·07 (C_5Me_5)	—
9	+4·6	Cl	(4)s (5)s	—	—
10	−24·1	—	(3)m (5)m (9)m	+1·91	(2)m? (5)m (6)m μ(8, 9)s
11	−12·1	—	(6)m	+2·51	(2)m? (7)w μ(8, 9)s
μ(8, 9)	—	—	—	−6·28	(6)m (10)s (11)s μ(10, 11)m
μ(10, 11)	—	—	—	−3·02	(2)m μ(8, 9)m

[a] Measured under conditions of $\{^{1}H$(broad-band noise)$\}$ decoupling. [b] s strong, w weak, m intermediate, ? uncertain. [c] ^{1}H resonances related to directly bound ^{11}B atom positions by $^{1}H\{^{11}B$(selective)$\}$ experiments. [d] Measured with simultaneous $\{^{11}B$(broad-band noise)$\}$ decoupling. [e] Some minor ambiguities arise in the assignment of some correlations because of ^{11}B peak overlap at $\delta(^{11}B)$ −20·4. [f] Some minor ambiguities arise in the assignment of some correlations because of ^{1}H peak overlap of the resonances at $\delta(^{1}H)$ +0·90 and +0·93.

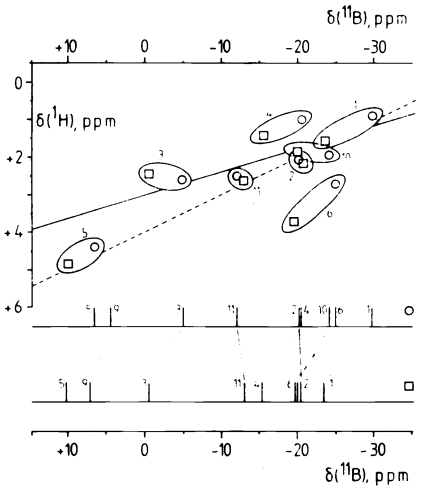
were generally somewhat the weaker (compare refs[8,26,28–30]), and in the [^{1}H–^{1}H]-COSY work it was of interest to see correlations between the NH(7) proton and two of its circumjacent BH protons.

Assigned data for any other related polyhedral nitrogen-containing species are not available for comparison purposes, but one striking comparison is afforded by the ^{11}B and ^{1}H shielding characteristics of the recently synthesised[8] sulphur analogue [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{10}$] mentioned above, for which data are also included in Fig. 2 for comparison. Thus although the sulphur-containing compound exhibits ^{11}B shieldings generally some 2–3 ppm below those of the iridaazaborane (mean $\delta(^{11}B)$ values −10·6 and −12·8 ppm, respectively), possibly due to lower excitation energies associated with the polarizable sulphur atom, this difference is not large in terms of cluster ^{11}B shielding variation,[30,31] and there is a striking parallel in the ^{11}B shielding properties of equivalent sites in the two species. The similarities are also reflected in the geometries discussed above (Table III).

The BH(*exo*) proton shielding behaviour is also similar between the two compounds, the most notable deviations from the expected $\delta(^{11}B) : \delta(^1H)$ correlation (solid line, Fig. 2, uppermost diagram) being for the lower ^{1}H shielding of the BH(6) sites antipodal to the heavy iridium atom, for which there is now precedent in *closo* twelve-vertex chemistry.[9,28,32]. It is not clear whether the BH(5) sites antipodal to the main-group heteroatoms exhibit a similar proton deshielding effect, or whether there is a deviation to higher proton shielding above a steeper correlation gradient (hatched line in Fig. 2) for the BH(3) and BH(4) sites adjacent to the {Ir(C_5Me_5)} moiety.

FIG. 2

NMR data for [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNHB_9H_{10}$] (○) together with those of the sulphur analogue [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{10}$] (□),d ata from ref.[8], for comparison. The uppermost plot is a plot of $\delta(^1H)$ vs $\delta(^{11}B)$ for the BH(*exo*) units, the solid line drawn having slope $\delta(^1H) : \delta(^{11}B)$ 1 : 16, intercept +3·0 in $\delta(^1H)$ (compare, for example, refs[6,26,27,30]), and the hatched line $\delta(^1H) : \delta(^{11}B)$ 1 : 10, intercept +4·0 in $\delta(^1H)$ (compare, for example, refs[28,32]). The bottom two diagrams are stick representations of the ^{11}B chemical shifts of the two species, with lines joining equivalent positions: ——— adjacent (α) to the N/S position, ----- β, and ····· γ (antipodal) to the heteroatom



EXPERIMENTAL

Preparation and isolation of [9-Cl-(η^5-C_5Me_5)-*nido*-8,7-$IrNHB_9H_{10}$]. Solvents were dried and degassed before use, and the reaction was carried out under strictly anhydrous and oxygen-free conditions. A sample each of [9-(CH_3CN)-*arachno*-6-NHB_9H_{12}] (0·25 g, 0·76 mmol; prepared as in refs[11,12]) and TMND (0·16 g; 0·75 mmol) were stirred together in CH_2Cl_2 solution (c. 20 cm^3) for 10 min. To the resulting yellow solution was added a solution of [Ir.

TABLE V

Non-hydrogen and cluster hydrogen atom co-ordinates (.10^4) for [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNB_9H_{11}$] with e.s.d.'s in parentheses

Atom	*x*	*y*	*z*
Ir(8)	3409·6(2)	1516·3(2)	2615·5(1)
Cl(9)	6786(2)	220(2)	2408(2)
C(1)	5203(5)	3277(4)	3756(4)
C(2)	5316(5)	3749(4)	2617(4)
C(3)	3736(5)	3767(4)	2254(4)
C(4)	2608(5)	3350(4)	3202(4)
C(5)	3544(5)	3072(4)	4135(4)
C(6)	6638(5)	3217(5)	4480(4)
C(7)	6902(5)	4207(5)	1947(4)
C(8)	3276(6)	4200(5)	1114(4)
C(9)	851(5)	3326(5)	3223(5)
C(10)	2917(6)	2643(5)	5298(4)
B(1)	1217(5)	−2115(5)	2925(5)
B(2)	−10(6)	−1793(5)	1845(5)
B(3)	1101(5)	−367(5)	2987(5)
B(4)	3106(5)	−535(5)	3376(4)
B(5)	3178(5)	−2002(5)	2388(4)
B(6)	1314(6)	−2719(5)	1424(5)
N(7)	1148(5)	−70(4)	1585(4)
B(9)	4531(5)	−191(5)	2198(4)
B(10)	3308(6)	−1576(5)	937(4)
B(11)	1375(6)	−1236(5)	640(5)
H(1)	560	−2947	3526
H(2)	3544	−366	4250
H(3)	3911	−2600	2610
H(4)	817	−3827	1031
H(5)	−1384	−2241	1737
H(6)	233	11	3479
H(7)	237	231	1383
H(10)	4060	−2066	368
H(11)	761	−1330	−237
H(10, 11)	3017	−605	511

$.(C_5Me_5)Cl_2]_2$ (0·30 g, 0·38 mmol; prepared as in ref.[33]), whereupon an immediate colour change to dark orange occurred. After stirring for a further 130 min, the mixture was filtered through silica (Fluka; type GF 254), washing the silica with additional CH_2Cl_2 (c. 20 cm^3) to give an orange filtrate. This combined solution (c. 40 cm^3) was then reduced to dryness (rotary evaporator, room temperature, water-pump pressure), taken up in hexane–CH_2Cl_2 (20 : 80), and separated by HPLC (column dimensions 16 × 250 mm, Lichrosorb Si60 (Knauer); eluting medium hexane–CH_2Cl_2 (20 : 80); flow rate 10 cm^3 min^{-1}; silica gel (Fluka, type GF 254) in 5 × 60 mm pre-column; detection by UV at 260 nm). Of several fractions observed, the predominant one, with retention time 19·4—22·5 min, was collected, reduced to dryness as above, taken up in hexane–CH_2Cl_2 (50 : 50) and purified by HPLC [eluting medium hexane–CH_2Cl_2 (40 : 60), otherwise as above] to give [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrNHB_9H_{10}$] with retention time 35·5—38·8 min. Recrystallisation by diffusion of pentane into a solution in CH_2Cl_2 gave pale yellow blocks (0·139 g; 0·29 mmol; 38%) which were moderately stable in air (weeks), but decomposed more rapidly in solutions exposed to air.

Nuclear magnetic resonance spectroscopy. NMR spectroscopy was carried out at 2·35 (100 MHz . ^1H) or 9·4 Tesla (400 MHz ^1H) on JEOL FX 100 and Bruker AM 400 instruments respectively, with the techniques of [^{11}B–^{11}B]-COSY (ref.[29]), [^1H–^1H]-COSY (ref.[34]) and ^1H–{^{11}B(selective)} (refs[25,35,36]) spectroscopy, and also the general techniques, being essentially as described in more detail in more recent papers that deal with NMR work from our laboratories[25–28]. Chemical shifts δ are given positive to high frequency (low field) of Ξ 100 ($SiMe_4$) for ^1H (quoted ±0·05 ppm), and Ξ 32·083 971 MHz (nominally $BF_3(OEt_2)$ in $CDCl_3$) for ^{11}B (quoted ±0·5 ppm), Ξ being defined as in ref.[37]; spectra were calibrated in δ by using solvent deuteron or residual proton resonances as internal secondary standards. Values of $^1J(^{11}B$–$^1H)$ are given in Hz and were measured from the resolution-enhanced ^{11}B trace, digital resolution 8 Hz.

Single-crystal X-ray diffraction analysis. All crystallographic data were obtained on a Nicolet P3/F diffractometer operating in the $\omega - 2\Theta$ scan mode using graphite-monochromated MoK_α radiation essentially following a standard procedure described in detail elsewhere.[38] The data set was corrected for absorption empirically once the structure had been determined.[39] The structure was determined via standard heavy-atom methods and was refined by full-matrix least-squares analysis using the SHELX program system.[40] All non-hydrogen atoms were refined with anisotropic thermal parameters. The methyl hydrogen atoms were included in calculated positions (C—H 96 pm) and were assigned an overall isotropic thermal parameter. All the azaborane cluster hydrogen atoms were located on Fourier difference syntheses with the exception of the Ir—H—B bridge atom which was not located. However, these hydrogen atoms proved unstable to free refinement (see also Results and Discussion) and were therefore assigned a fixed isotropic thermal parameter and were fixed in found positions. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used, in which the parameter g was included in the refinement in order to obtain a flat analysis of variance for increasing sine Θ and $[F/F_{max}]^{1/2}$. Final non-hydrogen and cluster hydrogen atomic co-ordinates are given in Table V.

Crystal data for $C_{10}H_{26}B_9ClNIr$. $M = 485·3$, triclinic, $a = 825·5(1)$, $b = 986·4(2)$, $c = 1\,158·7(2)$ pm, $\alpha = 95·12(1)$, $\beta = 91·00(1)$, $\gamma = 11·90(1)°$, $U = 0·8990(3)$ nm^3, $Z = 2$, space group, $P\bar{1}$, $D_c = 1·79$ Mg m^{-3}, $\mu = 72·73$ cm^{-1}, $F(000) = 464$.

Data collection. Scan widths 2·0° + α-doublet splitting, scan speeds 2·0—29·3° min^{-1}, $4·0 < 2\Theta < 50·0°$. Number of data collected 3 249, 3 088 with $I > 2·0\sigma(I)$ considered observed, $T = 290$ K.

Structure refinement. Number of parameters 255, $g = 0·0002$, $R = 0·0250$, $R_w = 0·0270$.

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REFERENCES

1. Baše K., Bown M., Štíbr B., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: J. Chem. Soc., Chem. Commun. *1988*, 1240.
2. Baše K., Petřina A., Štíbr B., Petříček V., Malý K., Linek A., Zakharova I. A.: Chem. Ind. London *1979*, 212.
3. Baše K., Štíbr B., Zakharova I. A.: Synth. React. Inorg. Met.-Org. Chem. *10*, 509 (1980).
4. Little J. L., Kester J. G., Chapman R. W., Huffman J. C., Todd L. J.: *1st Boron U.S.A. Meeting (BUSA-1), Dallas, April 10—13, 1988.* Abstract no. TA34, p. 39; Kester J. G., Chapman R. W., Huffman J. C., Todd L. J.: Inorg. Chem. *27*, 4528 (1988).
5. Nestor K.: Presented at *6th International Meeting of Boron Chemists (IMEBORON VI), Bechyně, June 22—26, 1987*, Abstract no. CA14, p. 53.
6. Bown M., Fowkes H., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Nestor K., MacKinnon P.: J. Chem. Soc., Dalton Trans. *1988*, 2597.
7. Nestor K., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: J. Chem. Soc., Dalton Trans. *1989*, 1465.
8. Nestor K., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: J. Chem. Soc., Dalton Trans. *1991*, in press.
9. Nestor K., Štíbr B., Jelínek T., Heřmánek S., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: J. Chem. Soc., Dalton Trans. *1990*, 681.
10. Baše K., Plešek J., Heřmánek S., Huffman J., Ragatz P., Schaeffer R.: J. Chem. Soc., Chem. Commun. *1975*, 934.
11. Baše K., Hanousek F., Plešek J., Štíbr B., Lyčka A.: J. Chem. Soc., Chem. Commun. *1981*, 1163.
12. Baše K.: Collect. Czech. Chem. Commun. *48*, 2593 (1983).
13. Štíbr B., Kennedy J. D., Jelínek T.: J. Chem. Soc., Chem. Commun. *1990*, 1309.
14. Hertler W. R., Klanberg F., Muetterties E. L.: Inorg. Chem. *6*, 1696 (1967).
15. Arafat A., Huffman J. C., Todd L. J.: Inorg. Chem. *25*, 3757 (1986).
16. Borse R., Kroekert B., Paetzold P.: Chem. Ber. *120*, 1913 (1987).
17. Micciche R. P., Briguglio J. J., Sneddon L. G.: Inorg. Chem. *23*, 3992 (1984).
18. Fontaine X. L. R., Fowkes H., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: J. Chem. Soc., Chem. Commun. *1985*, 1722; J. Chem. Soc., Dalton Trans. *1986*, 2417.
19. Orpen A. G.: *XHYDEX, Program for the Indirect Location of Hydrogen Atoms.* University of Bristol, Bristol 1985.
20. Orpen A. G., Kennedy J. D., Thornton-Pett M.: Unpublished results.
21. Williams R. E.: Inorg. Chem. *10*, 210 (1971); Adv. Inorg. Chem. Radiochem. *18*, 67 (1976).
22. Wade K.: J. Chem. Soc. Chem. Commun. *1971*, 792; Adv. Inorg. Chem. Radiochem. *18*, 1 (1976).
23. Kennedy J. D.: Prog. Inorg. Chem. *34*, 211 (1986) and references cited therein.
24. Cotton F. A., Poli R.: Organometallics *6*, 1743 (1987).
25. Fontaine X. L. R., Kennedy J. D.: J. Chem. Soc., Dalton Trans. *1988*, 1573.
26. Bown M., Fontaine X. L. R., Kennedy J. D.: J. Chem. Soc., Dalton Trans. *1988*, 1467.
27. Beckett M. A., Bown M., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: J. Chem. Soc., Dalton Trans. *1988*, 1962.

28. Ferguson G., Fontaine X. L. R., Kennedy J. D., Faridoon, Spalding T. R.: J. Chem. Soc. Dalton Trans. *1988*, 2555.
29. Venable T. L., Hutton W. C., Grimes R. N.: J. Am. Chem. Soc. *106*, 29 (1984).
30. Kennedy J. D. in: *Multinuclear NMR* (J. Mason, Ed.), Chap. 8, p. 221 and references cited therein. Plenum, London and New York 1987.
31. Heřmánek S., Jelínek T., Plešek J., Štíbr B., Fusek J., Mareš F. in: *Boron Chemistry (IME-BORON 6)* (S. Heřmánek, Ed.), p. 26 and references cited therein. World Scientific, Singapore 1987.
32. Faridoon, Ni Dhubhghaill O., Spalding T. R., Ferguson G., Kaitner B., Fontaine X. L. R., Kennedy J. D., Reed D.: J. Chem. Soc., Dalton Trans. *1986*, 2739.
33. Kang J. W., Mosely K., Maitlis P. M.: J. Am. Chem. Soc. *91*, 5970 (1969).
34. Fontaine X. L. R., Kennedy J. D.: J. Chem. Soc., Chem. Commun. *1986*, 779.
35. Kennedy J. D., Wrackmeyer B.: J. Magn. Reson. *38*, 529 (1980).
36. Kennedy J. D., Greenwood N. N.: Inorg. Chim. Acta *38*, 93 (1980).
37. McFarlane W.: Proc. R. Soc. London, A *306*, 185 (1968).
38. Modinos A., Woodward P.: J. Chem. Soc., Dalton Trans. *1974*, 2065.
39. Walker N., Stuart D.: Acta Crystallogr., A *39*, 158 (1983).
40. Sheldrick G. M.: *SHELX 76, Program System for X-Ray Structure Determination.* University of Cambridge, Cambridge 1976.