

Ten-vertex Metallaborane Chemistry: Synthesis and Characterization of Some *ortho*-Cycloboronated *nido*-5- and -6-Iridadecaboranes; Crystal Structures of [5-H-5-(PPh₃)-5-(PPh₂-*o*-C₆H₄)-*nido*-5-IrB₉H₁₂-2] and [5-H-5,7-(PPh₃)₂-5-(PPh₂-*o*-C₆H₄)-*nido*-5-IrB₉H₁₀-2] *

Jonathan Bould, Janet E. Crook, Norman N. Greenwood, John D. Kennedy, and Mark Thornton-Pett

School of Chemistry, University of Leeds, Leeds LS2 9JT

The *arachno*-anion [B₉H₁₄]⁻ reacts with [IrCl(PPh₃)₃] to give an 80% yield of the known compound [6-H-6,6-(PPh₃)₂-*nido*-6-IrB₉H₁₃] (1), whereas the reaction of *nido*-[B₉H₁₂]⁻ with [IrCl(PPh₃)₃] gives a mixture of products. These have been characterized by a combination of multi-element n.m.r. spectroscopy and single-crystal X-ray diffraction analysis to be [*sym*-6-H-6-(PPh₃)-6-(PPh₂-*o*-C₆H₄)-*nido*-6-IrB₉H₁₂-5] (2) (60% yield), [*asym*-6-H-6-(PPh₃)-6-(PPh₂-*o*-C₆H₄)-*nido*-6-IrB₉H₁₂-5] (3) (20% yield), [5-H-5-(PPh₃)-5-(PPh₂-*o*-C₆H₄)-*nido*-5-IrB₉H₁₂-2] (4) (0.1–20% yield) and [5-H-5,7-(PPh₃)₂-5-(PPh₂-*o*-C₆H₄)-*nido*-5-IrB₉H₁₀-2] (5) (5% yield). Crystals of compound (4) are triclinic, space group *P* $\bar{1}$ with *a* = 1 254.4(3), *b* = 1 524.6(4), *c* = 1 091.7(2) pm, α = 97.69(2), β = 115.09(2), γ = 88.79(2)°, and *Z* = 2. Crystals of the bis(chloroform) solvate of (5) are triclinic, space group *P* $\bar{1}$ with *a* = 1 501.3(3), *b* = 1 571.6(3), and *c* = 1 478.1(3) pm, α = 104.27(2), β = 113.81(2), γ = 97.98(2)°, and *Z* = 2. A further compound was isolated and tentatively identified as a phosphine-substituted *nido*-6-iridadecaborane. A scheme to explain the mixture of products is briefly discussed.

In a previous paper we have reported on the reactions of various low-oxidation-state rhodium and iridium compounds with the *arachno*-[B₉H₁₄]⁻ anion.¹ These resulted in the oxidative addition of the metal to the borane cluster and the formation of *nido*-6-metalladecaboranes. The yields, however, were low (*ca.* 5%) and, as one of the aims of our programme is to generate compounds that can act as 'B-frame' matrices^{2,3} for the stepwise addition of metal centres, investigations were undertaken to improve the yields. This paper reports on some of the compounds produced during these investigations, some preliminary aspects of which [for compound (4)] have been reported previously.³

Results and Discussion

The reaction of [IrCl(PPh₃)₃] with *arachno*-[B₉H₁₄]⁻ in dichloromethane resulted in the almost instantaneous formation (in *ca.* 80% yield) of the bright yellow solid [6-H-6,6-(PPh₃)₂-*nido*-6-IrB₉H₁₃] (1) plus approximately 2% yield of a pale violet *isonido*-iridadecaborane.⁴ This latter compound will be described more fully elsewhere. Compound (1) has already been described in considerable detail¹ though it was previously obtained in only *ca.* 1% yield from the reaction of [Ir(CO)Cl(PPh₃)₂] with *arachno*-[B₉H₁₄]⁻. The much higher yield now obtained with [IrCl(PPh₃)₃] probably reflects the greater lability of the {(PPh₃)₃} *versus* the {(CO)(PPh₃)₂} ligation sphere as discussed below.

Following the high yield of (1) so obtained it became of interest to explore the reaction of the tris(tertiary phosphine)-metal complex with the *nido*-nonaborate anion [B₉H₁₂]⁻. The reaction between [IrCl(PPh₃)₃] and [NEt₄][B₉H₁₂]⁻ in dichloromethane solution gave a number of novel metallaboranes in combined isolated yields approaching 100%. The main products, obtained in yields of 60 and 20% respectively, were the bright yellow solids *sym*-(2) and *asym*-[6-H-6-(PPh₃)-6-(PPh₂-*o*-C₆H₄)-*nido*-6-IrB₉H₁₂-5] (3). These were identified by n.m.r. spectroscopy by comparison with known¹ *nido*-6-metallade-

caboranes. Their measured ¹H, ¹¹B, and ³¹P n.m.r. data (Tables 1 and 2) provide sufficient information for their structures to be deduced. In each case the *ortho*-cycloboronated phenylene ring was indicated by the proton spectrum in the aromatic region, which for each compound exhibits an extended complex pattern that is also observed for the structurally characterized *isonido*-ten-vertex cluster compound [(PPh₃)(PPh₂-C₆H₄)IrC(OH)B₈H₆(OMe)],^{5,6} for the structurally characterized compound (4) described below, and also for other recently characterized compounds.⁷ The main characteristic features are a doublet at δ (¹H) *ca.* +8 and a triplet at *ca.* +6. Illustrations of the proposed structures are in Figure 1.

The symmetric compound (2) smoothly isomerizes in CDCl₃ solution at *ca.* 65 °C to give the unsymmetric (3). Stronger heating produces an *isocloso*-iridadecaborane.^{8,9}

Compounds (2) and (3) accounted for about 80% of the overall yield; the remaining 20% consisted of several other species of which three have been isolated and characterized. The first of these, (4), is a direct structural isomer of (2) and (3), isolated as a bright yellow solid, generally in a low yield that, interestingly, seemed to vary with the age of the starting materials. Freshly prepared [IrCl(PPh₃)₃] and [B₉H₁₂]⁻ gave yields as low as 0.1%, whereas with reactants prepared 2 weeks before use the yield of (4) would rise to 20% though the reactants had been stored under nitrogen and showed no apparent change in their n.m.r. spectra. Compound (4) was identi-

* 2,5-(*o*-Diphenylphosphinophenyl)-5-hydrido-5-triphenylphosphine-5-irida-*nido*-decaborane and 2,5-(*o*-diphenylphosphinophenyl)-5-hydrido-5,7-bis(triphenylphosphine)-5-irida-*nido*-decaborane.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

Throughout this paper, *sym* and *asym* are used as convenient labels to describe the ligand distribution about iridium in compounds (2) and (3) respectively (see Figure 1), even though both compounds are of course in the absolute sense asymmetric.

Table 1. Boron-11 and ¹H n.m.r. data for *sym*- (2) and *asym*-[6-H-6-(PPh₃)-6-(PPh₂C₆H₄)-6-IrB₉H₁₂] (3)^a

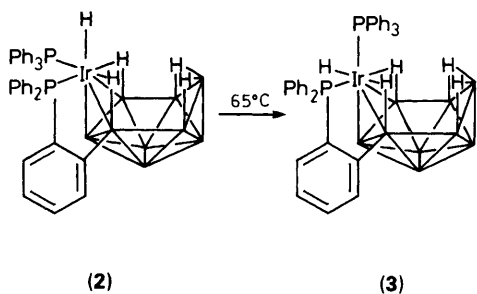
Assignment	Compound (2) ^{b-d}		Compound (3) ^{b-d}	
	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H)
B(5)	+19.5		+25.5	
(1), (3)	+9.7(3)	+4.97(2), +4.65	+13.9	+4.86
(10), (9)	+5.0	+3.62	+9.4	+4.61
(7), (8)	+5 ± 5	+3.30	+4.5 ± 2(3)	+5.36, +3.57
(2), (4)	-0.5	+3.07	-1.6	+3.21, +2.65
H(5,6)	-25.0	+0.38	-26.8	+0.28
H(6,7)	-34.0	+2.15	-31.8	+2.06
H(8,9)		-9.14 ^{g,h}		-5.59 ^g
H(9,10)		-10.66 ^h		-9.47 ^h
H(6)		-2.83		-3.03
		-3.10		-3.98
		-10.98 ^h		-10.75 ^h

^a Terminal proton resonances assigned to corresponding ¹¹B resonances by selective ¹H-¹¹B n.m.r. experiments at 100 MHz. ^b Dilute CDCl₃ solution at +21 °C; δ(¹¹B) in p.p.m. ±0.5 to low field (high frequency) of BF₃·OEt₂, recorded at 128 MHz; δ(¹H) ±0.05 to low field of SiMe₄, recorded at 400 MHz. ^c Figures in parentheses indicate relative intensity of that resonance, all others have intensity one. ^d All peaks apparently decoupled together in ¹H-¹¹B n.m.r. selective experiments. ^e Not possible to assign separate positions. ^f Not possible to assign positively but, by comparison with [H(PPh₃)₂IrB₉H₁₃] (1), low-field resonances probably B(2)H(2) and high-field resonances B(4)H(4). ^g Assigned by apparent selective sharpening on irradiating at δ(¹¹B) +19.5 p.p.m. for (2) and δ(¹¹B) +25.5 p.p.m. for (3). ^h Coupled to other nuclei, see Table 2.

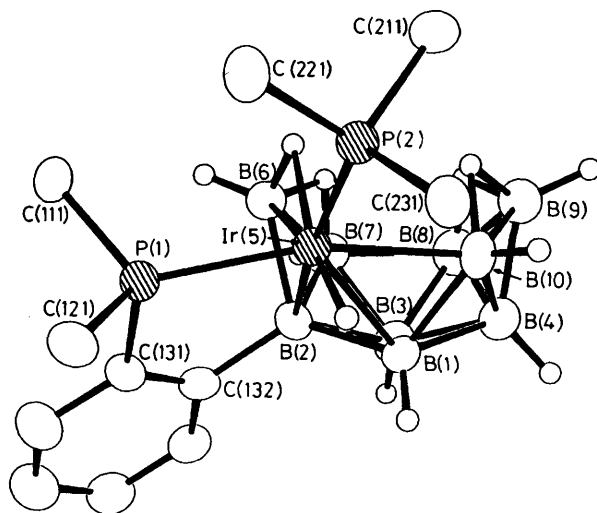
Table 2. Phosphorus-31 and ¹H n.m.r. chemical shift and coupling constant data for compounds (2) and (3)

Parameter	Compound (2) ^a	Compound (3) ^a
δ(³¹ P)/p.p.m. (-47 °C)	+26.7, +14.1	+28.2
δ(³¹ P)/p.p.m.	—	+28.1, +27.1 ^b
² J(³¹ P- ³¹ P) <i>cis</i> /Hz	19 ± 1	19 ± 2
δ[¹ H(6)]	-10.98	-10.75
² J(³¹ P- ¹ H(6)) <i>cis</i> /Hz	20 ± 1, 31 ± 1	14 ± 1, 25 ± 1
² J(¹ H(6)- ¹ H(5,6)) <i>trans</i> /Hz	— ^c	5 ± 1 ^d
δ[¹ H(5,6)]	-9.14	-5.59
δ[¹ H(6,7)]	-10.66	-9.47
² J(³¹ P- ¹ H(5,6)) <i>trans</i> /Hz	65 ± 1	—
² J(³¹ P- ¹ H(6,7)) <i>trans</i> /Hz	64 ± 1	59 ± 1

^a In CDCl₃ solution at +21 °C unless otherwise stated; δ(³¹P) to low field (high frequency) of 85% H₃PO₄. ^b Assigned to P(2) since *w*₄[P(2)] ≫ *w*₄[P(1)]. For detailed discussion see text. ^c No large coupling ²J(¹H-Ir-¹H) observed, indicating mutually *cis* disposition of ¹H(6) and ¹H(5,6). ^d Confirmed by ¹H-¹¹B(broad-band), ¹H(selective) triple-resonance experiments.

**Figure 1.** Suggested structures for compounds (2) and (3); these are essentially similar except for the arrangement of the *exo*-polyhedral ligands about the iridium atom. Compound (2) smoothly converts into (3) at *ca.* 65 °C in CHCl₃ solution

fied as [5-H-5-(PPh₃)-5-(PPh₂-*o*-C₆H₄)-*nido*-5-IrB₉H₁₂-2] by its n.m.r. properties and from a single-crystal X-ray structural study. Although comparison of the ¹H, ¹¹B, and ³¹P n.m.r. data for (4) (Table 3) with those of the known clusters [5-(η⁵-C₅H₅)-*nido*-5-CoB₉H₁₃]¹⁰ and [5-(η⁵-C₅H₅)-*nido*-5,9,10-CoC₂B₇H₁₁]¹¹ {and with others such as [5-(η⁶-C₆Me₆)-*nido*-

**Figure 2.** ORTEP drawing of the molecular structure of [5-H-5-(PPh₃)-5-(PPh₂-*o*-C₆H₄)-*nido*-5-IrB₉H₁₂-2] (4). The hydrogen-atom positions, which were located directly from X-ray data, are in agreement with ¹H-¹¹B n.m.r. spectroscopic data. For clarity, all phenyl carbon atoms have been omitted except for the *ipso* ones and the *ortho*-cycloborated ring

5-RuB₉H₁₁-7-(PR₃)¹², established (4) as a *nido*-5-metalladecaborane having the same number of boron, hydrogen, and phosphorus atoms as (2) and (3), and an *ortho*-cycloborated phenyl ring, it did not permit the unambiguous assignment of the position of the *ortho*-phenylene substituent. As this was needed to assess possible mechanisms of formation (see below), a single-crystal X-ray diffraction analysis of (4) was undertaken.

A drawing of the molecular structure is in Figure 2, and selected interatomic distances and angles are in Tables 4 and 5 respectively. It is clear that the *nido*-5-iridadecaborane cluster is substituted by the *ortho*-phenylene group at the apical B(2) position. Hydrogen atoms were located in the X-ray analysis and their positions, also consistent with results using the Orpen HYDEX potential-well method,^{13,14} are in accord with the n.m.r. data, confirming that the crystal was representative of the bulk material.

Table 3. Boron-11, ¹H (and ³¹P)^a n.m.r. data for [5-H-5-(PPh₃)₂-5-(PPh₂C₆H₄)₂-5-IrB₉H₁₂] (4), compared with those for [5-(η⁵-C₅H₅)₂-5-CoB₉H₁₃]¹⁰ and [5-(η⁵-C₅H₅)₂-5,8,9-CoC₂B₇H₁₁]¹¹

Assignment [for (4) only]	Compound (4)		[(C ₅ H ₅)CoB ₉ H ₁₃]		[(C ₅ H ₅)CoC ₂ B ₇ H ₁₁] ^b δ(¹¹ B)
	δ(¹¹ B)	δ(¹ H) ^c	δ(¹¹ B)	δ(¹ H)	
(6)	+27.0	+5.02	+30.2	<i>d</i>	+26.3
<i>e</i>	+23.2	+5.68	+25.1	<i>d</i>	+11.1
<i>e</i>	+8.8	+3.08	+12.3	<i>d</i>	
<i>e</i>	+8.0	+3.34	+8.0(2)	<i>d</i>	+9.1
<i>e</i>	+1.3	+4.90	+2.2	<i>d</i>	+1.0
<i>e</i>	+0.6	+2.39	-2.9	<i>d</i>	-5.1
(7), (8), or (10) ^f	-8.4	+1.97	-16.0	<i>d</i>	-14.2
(2)	-8.4	<i>g</i>			
(4)	-37.9	+0.85	-36.4	<i>d</i>	-32.8
(5,6)	—	-8.49 ^h	—	-19.2	
(6,7), (8,9)	—	-3.31 ⁱ	—	-2.5(3)	
(9,10)	—	-1.52	—		
(5)	—	-2.27	—		
		-14.65 ^j			

^a Observed for compound (4) at -50 °C in CDCl₃ solution: δ(³¹P) +32.4 and +21.4 p.p.m.; ²J(³¹P-³¹P)*cis* 17.0 ± 0.1 Hz. ^b In CD₂Cl₂ solution at ambient temperature. Resonances are unassigned and are related to those of the other compounds merely by chemical shift. ^c Terminal proton resonances assigned to corresponding ¹¹B resonance by selective ¹H-¹¹B experiments at 360 MHz. ^d Not reported. ^e B(1), B(3), B(7), B(8), or B(9). ^f Probably B(10). ^g Site of *ortho*-phenylene link. ^h ²J[¹H(5)-¹H(5,6)]*trans* 8 ± 2 Hz. ⁱ ¹H-¹¹B. ^j Selective irradiation of resonance at δ(¹¹B) -8.4 p.p.m. causes decoupling of this resonance. ^k Doublet of doublet of doublets, ²J[³¹P(1)-¹H(5)]*cis* 17.1 ± 0.5, ²J[³¹P(2)-¹H(5)]*cis* 17.0 ± 0.5 and ²J[¹H(5,6)-¹H(5)]*trans* 8 ± 2 Hz.

Table 4. Selected interatomic distances (pm) for [5-H-5-(PPh₃)₂-5-(PPh₂C₆H₄)₂-5-IrB₉H₁₂] (4) with estimated standard deviations (e.s.d.s) in parentheses

<i>(i) From the iridium atom</i>			
Ir(5)-P(1)	231.6(3)	Ir(5)-P(2)	230.8(3)
Ir(5)-B(1)	220.8(6)	Ir(5)-B(2)	222.6(6)
Ir(5)-B(6)	222.5(6)	Ir(5)-B(10)	232.6(6)
Ir(5)-H(5)	149(5)	Ir(5)-H(5,6)	194(7)
<i>(ii) Interboron</i>			
B(1)-B(2)	180.5(8)	B(2)-B(3)	177.1(8)
B(1)-B(3)	178.1(8)	—	—
B(1)-B(4)	179.8(8)	B(3)-B(4)	176.8(9)
B(1)-B(10)	180.8(8)	B(3)-B(8)	173.2(9)
B(2)-B(6)	178.3(8)	B(4)-B(9)	171.8(9)
B(3)-B(7)	174.5(9)	—	—
B(4)-B(8)	177.7(9)	B(4)-B(10)	179.2(9)
B(6)-B(7)	178.2(8)	—	—
B(7)-B(8)	196.5(10)	—	—
B(9)-B(10)	180.5(9)	B(8)-B(9)	179.2(10)
<i>(iii) Boron-hydrogen</i>			
B(1)-H(1)	99(4)	B(3)-H(3)	120(4)
—	—	B(4)-H(4)	109(4)
B(7)-H(7)	109(4)	—	—
B(10)-H(10)	110(4)	B(8)-H(8)	112(5)
—	—	B(9)-H(9)	111(4)
B(6)-H(5,6)	120(7)	B(6)-H(6,7)	126(4)
—	—	B(7)-H(6,7)	121(4)
B(8)-H(8,9)	125(5)	B(10)-H(9,10)	137(4)
B(9)-H(8,9)	119(5)	B(9)-H(9,10)	131(4)
<i>(iv) Others</i>			
B(2)-C(132)	162.9(7)	—	—
P(1)-C(131)	182.5(4)	P(2)-C(211)	183.6(4)
P(1)-C(132)	182.9(4)	P(2)-C(221)	183.4(4)
P(1)-C(133)	181.1(4)	P(2)-C(231)	182.2(4)

The Ir-B interatomic distances are similar to those in the 6-iridadecaborane (1),¹ except for Ir(5)-B(10) which is

Table 5. Selected angles between interatomic vectors (°) for compound (4) with e.s.d.s in parentheses

<i>(i) About the iridium atom</i>			
P(1)-Ir(5)-P(2)	105.6(1)	P(2)-Ir(5)-B(1)	127.9(2)
P(1)-Ir(5)-B(1)	117.6(2)	P(2)-Ir(5)-B(2)	170.7(1)
P(1)-Ir(5)-B(2)	82.8(2)	P(2)-Ir(5)-B(6)	128.9(2)
P(1)-Ir(5)-B(6)	81.8(2)	P(2)-Ir(5)-B(10)	87.6(2)
P(1)-Ir(5)-B(10)	164.5(1)	B(2)-Ir(5)-B(6)	47.2(2)
B(1)-Ir(5)-B(2)	48.0(2)	B(2)-Ir(5)-B(10)	84.7(3)
B(1)-Ir(5)-B(6)	86.7(3)	B(6)-Ir(5)-B(10)	96.3(3)
B(1)-Ir(5)-B(10)	46.9(2)		
<i>(ii) Iridium-boron-boron</i>			
Ir(5)-B(1)-B(2)	66.5(5)	Ir(5)-B(2)-B(1)	65.4(3)
Ir(5)-B(1)-B(3)	116.1(4)	Ir(5)-B(2)-B(3)	115.6(4)
Ir(5)-B(1)-B(4)	122.1(4)	Ir(5)-B(2)-B(6)	66.3(3)
Ir(5)-B(1)-B(10)	70.0(3)	Ir(5)-B(2)-B(7)	113.8(4)
Ir(5)-B(6)-B(2)	66.4(3)	Ir(5)-B(10)-B(4)	116.5(4)
Ir(5)-B(6)-B(7)	113.9(4)	Ir(5)-B(10)-B(9)	123.5(4)
Ir(5)-B(10)-B(1)	63.1(3)		
<i>(iii) Others</i>			
B(6)-B(7)-B(8)	119.4(4)	B(7)-B(8)-B(9)	117.5(5)
B(8)-B(9)-B(10)	105.7(4)	—	—
Ir(5)-H(5,6)-B(6)	87(4)	B(6)-H(6,7)-B(7)	92(3)
B(8)-H(8,9)-B(9)	95(3)	B(9)-H(9,10)-B(10)	85(3)
C(131)-C(132)-B(2)	117.3(3)	C(133)-C(132)-B(2)	122.7(3)
B(1)-B(2)-C(132)	128.4(4)	B(3)-B(2)-C(132)	124.6(4)
Ir(5)-B(2)-C(132)	113.1(3)	B(7)-B(2)-C(132)	120.3(4)
B(6)-B(2)-C(132)	111.3(4)		

significantly longer than the others (see Table 4), presumably reflecting the weaker (5)-(10) bonding that is a characteristic of *nido*-decaborane clusters. This is also apparent in the B(7)-B(8) distance of 197(1) pm [*cf.* 197.3(5) pm in B₁₀H₁₄ itself], which is more than 14 pm longer than the other B-B distances in (4).

Among the remaining 10-15% of products there was a 5% yield of a phosphine-substituted *nido*-5-iridadecaborane, [5-H-5,7-(PPh₃)₂-5-(PPh₂-*o*-C₆H₄)₂-*nido*-5-IrB₉H₁₀-2] (5). This formulation was again established by n.m.r. spectroscopy, and

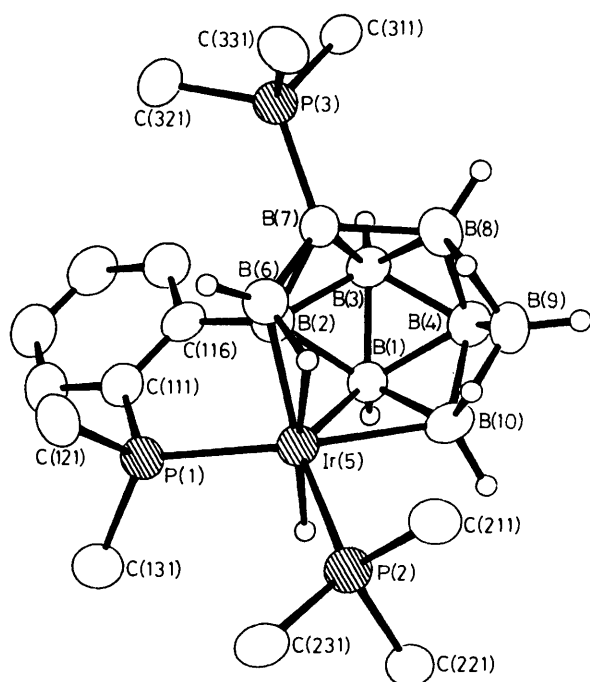


Figure 3. ORTEP drawing of the molecular structure of [5-H-5,7-(PPh₃)₂-5-(PPh₂-*o*-C₆H₄)-nido-5-IrB₉H₁₀-2] (5). The hydrogen positions were located from X-ray data and are in agreement with n.m.r. spectroscopic data; they include a terminal metal hydride on the iridium atom *trans* to one bridging M-H-B hydrogen atom and two B-H-B bridging hydrogen atoms. For clarity, all carbon atoms other than the *ipso* ones and the *ortho*-cycloboronated ring have been omitted

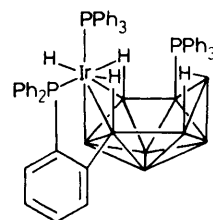
Table 6. Boron-11 and ¹H n.m.r. data for [5-H-5,7-(PPh₃)₂-5-(PPh₂-C₆H₄)-5-IrB₉H₁₀-2] (5)

Assignment ^a	δ(¹¹ B) ^{b-d} /p.p.m.	δ(¹ H) ^{d,e}
(6)	+57.7	+6.64
(2)	+8.4	<i>f</i>
(3), (10)	+6.8	+3.76
(1)	-3 ± 1(4) ^g	+2.76, +2.56, +1.49
(7), (8)		
(9)	-18.0	+1.25
(4)	-40.7	-0.14
(5,6)	—	-9.86 ^h
(8,9)	—	-2.85
(9,10)	—	
(5)	—	-16.45 ^h

^a Based upon ¹H-¹¹B selective experiments. ^b Figures in parentheses indicate relative intensity, all others have intensity one. ^c In CDCl₃ solution, +21 °C. ^d See footnote *b* to Table 1. ^e In CD₂Cl₂ solution, +21 °C. ^f Absent due to *o*-phenylene link. ^g One unresolved doublet due to phosphine substituent; see footnote *d* to Table 7. ^h Complex multiplet from coupling to other nuclei (see Table 7); irradiation at ν(¹H) corresponding to δ(¹H) -9.86 results in collapse to an approximate 1:2:1 triplet with splitting *ca.* 27 Hz.

by single-crystal X-ray diffraction analysis (of the CHCl₃ disolvate). The ¹H, ¹¹B, and ³¹P n.m.r. data are in Tables 6 and 7, the interatomic distances and angles for (5)·2CHCl₃ in Tables 8 and 9, and a diagram of the cluster structure in Figure 3.

Again the hydrogen-atom positions were located directly from the X-ray data and also supported by potential-well calculations.^{13,14} They are entirely in accord with the n.m.r. data, also confirming that the crystal was representative of the bulk material. The majority of the interatomic distances and



(6)

Figure 4. A possible structure for compound (6). The phosphine P(3) is shown attached to B(8) but might instead be on B(9) or B(10) (see text). Each boron vertex has a terminal hydrogen atom attached, except for B(8)

angles in compound (5) (Tables 8 and 9) are within 3 pm and 3° of the equivalent values in (4). The main differences arise from the effect of the phosphine ligand on B(7) which is associated with a significant reduction in the B(6)-B(7) and B(7)-B(8) distances of 12(3) and 17(3) pm respectively compared with those in (4); this is due to the phosphine acting as a two-electron donor, equivalent to an H⁻ ligand, thus eliminating the need for the bridging hydrogen atom which thereby increases the two-centre contribution to the B(6)-B(7) bonding vector. It presumably has a similar shortening effect on the B(7)-B(8) distance which is an especially 'long' distance in *nido*-decaborane itself.¹⁵ These interatomic distances can also usefully be compared with those in the *nido*-[B₁₀H₁₃]⁻ anion¹⁶ in which a bridging proton has been removed from the parent B₁₀H₁₄ structure: B(6)-B(7) 164.8(4) pm [*cf.* 166(2) pm (5)], and B(7)-B(8) 184.5(4) pm [*cf.* 180(2) pm in (5)]. Thus (5) may be regarded as equivalent to a *nido*-cluster having the 3630 *styx* topology¹⁷ of [B₁₀H₁₃]⁻ rather than the 4620 topology of B₁₀H₁₄ and compounds (1)-(4).

One final significant point concerning the structure of compound (5) is that, whereas the phosphine ligands on Ir(5) and B(7) are in essentially geometrically equivalent positions with regard to B(2), it is a phenyl ring on the Ir-bonded, rather than the B-bonded, ligand that is *ortho*-cycloboronated. This suggests, as might be expected, that the metal atom plays a significant part in the cyclization reaction. Indeed, as far as we are aware, all reported cycloboronation reactions involve metal-attached phosphine ligands.^{7,18-21}

The third minor product, isolated from the reaction in *ca.* 10% yield, is a light yellow solid tentatively identified as [*x*-(PPh₃)-6-H-6-(PPh₃)-6-(PPh₂-*o*-C₆H₄)-nido-6-IrB₉H₁₀-5] (6), where *x* = 8, 9, or 10. Figure 4 illustrates the proposed structure and Tables 10 and 11 summarize the measured ¹H, ¹¹B, and ³¹P n.m.r. data.

These data indicate a B-phosphine-substituted *ortho*-cycloboronated *nido*-6-metalladecaborane with a metal environment analogous to the arrangement found in (1) and (2) as discussed above, and with the phenylene substituent cyclized to B(5) or B(7), rather than to B(2) as it is in (5). The position of the boron-bound phosphine ligand is more difficult to place with certainty. In the few^{12,19} characterized examples of *nido*-type boranes that have (on boron) a two-electron donor that notionally replaces a terminal and a bridging hydrogen atom, such as in [7-(PMe₂Ph)-7-PtB₁₆H₁₈-9'-(PMe₂Ph)],²² [5-(η⁵-C₅Me₅)-7-(PMe₂Ph)-*nido*-5-RhB₉H₁₁],²³ compound (5) above, and [7,7,9-(PPh₃)₃-*isonido*-7-IrB₉H₁₀],⁴ the ligand is generally adjacent to the site of the bridging hydrogen atom it notionally replaces. If this is also so in (6) the phosphine ligand would be placed at B(7), B(8), B(9), or B(10). Selective ¹H-¹¹B n.m.r. experiments on the resonance at δ(¹¹B) -10.2 p.p.m. cause the simultaneous decoupling of the terminal proton

Table 7. Phosphorus-31 n.m.r. chemical shift and coupling constant data for compound (5)

Parameter	Chemical shift ^a / p.p.m.	Coupling constant/Hz
P(1)	+17.5 ^b	—
P(2)	+34.9 ^c	—
P(3)	+22 (broad) ^d	—
² J[³¹ P(1)– ³¹ P(2)] _{cis}	—	ca. 17 ^a
⁴ J[³¹ P(1 and 2)– ³¹ P(3)]	—	ca. 17 ^a
² J[³¹ P(1 and 2)–H(5)] _{cis}	—	ca. 27.0
² J[¹ H(5,6)– ¹ H(5)] _{trans} ^e	—	14.7 ± 0.2 ^e

^a Recorded in CDCl₃ solution at –40 °C; all other data at +21 °C.
^b Triplet due to coupling to P(2) and P(3), assigned by ¹H-³¹P selective experiments. ^c Doublet due to coupling to P(1); see footnote *b* for assignment. ^d Broadness due to partially collapsed coupling ¹J(³¹P–¹¹B) to the B(7) position. ^e Confirmed by ¹H-¹¹B (broad-band), ¹H(selective) triplet-resonance experiments.

Table 8. Selected interatomic distances (pm) for [5-H-5,7-(PPh₃)₂-5-(PPh₂C₆H₄)-5-IrB₉H₁₀-2] (5) with e.s.d.s in parentheses

<i>(i) From the iridium atom</i>			
Ir(5)–P(1)	229.8(5)	Ir(5)–P(2)	232.9(5)
Ir(5)–B(1)	224.7(13)	Ir(5)–B(2)	226.1(12)
Ir(5)–B(6)	222.9(11)	Ir(5)–B(10)	231.7(14)
Ir(5)–H(5)	162(3)	Ir(5)–H(5,6)	166(3)
<i>(ii) Interboron</i>			
B(1)–B(2)	179.8(13)	B(2)–B(3)	177.7(18)
B(1)–B(3)	178.1(17)	—	—
B(1)–B(4)	181.5(19)	B(3)–B(4)	180.5(16)
B(1)–B(10)	183.6(18)	B(3)–B(8)	183.5(17)
B(2)–B(6)	186.8(13)	B(4)–B(9)	165.8(18)
B(3)–B(7)	174.5(12)	—	—
B(4)–B(8)	179.2(14)	B(4)–B(10)	178.8(20)
B(6)–B(7)	166.0(18)	—	—
B(7)–B(8)	179.5(17)	—	—
B(9)–B(10)	176.0(19)	B(8)–B(9)	179.9(17)
<i>(iii) Boron–hydrogen</i>			
B(1)–H(1)	110(3)	B(3)–H(3)	122(4)
—	—	B(4)–H(4)	121(3)
B(10)–H(10)	122(3)	B(8)–H(8)	136(4)
—	—	B(9)–H(9)	82(4)
B(6)–H(5,6)	143(4)	—	—
B(8)–H(8,9)	131(4)	B(10)–H(9,10)	126(3)
B(9)–H(8,9)	130(3)	B(9)–H(9,10)	118(4)
<i>(iv) Others</i>			
B(7)–P(3)	192.9(11)	B(2)–C(116)	158.8(13)
P(1)–C(111)	182.2(7)	P(2)–C(211)	183.1(8)
P(1)–C(121)	183.3(6)	P(2)–C(221)	183.3(6)
P(1)–C(131)	183.3(8)	P(2)–C(231)	184.8(8)
P(3)–C(311)	180.2(8)	P(3)–C(321)	180.6(7)
P(3)–C(331)	181.6(6)	—	—

resonance at δ(¹H) +3.74 and the ¹H(6,7) resonance, thereby ascribing this ¹¹B resonance to B(7) and showing that it has no substituent. Position B(9) can also be excluded, at least tentatively, since there is no two-bond coupling, ²J(³¹P–B–¹H), to the remaining bridging hydrogen atom [though it should be mentioned that there are no examples of similar systems in the literature with which to compare it, and it is known that values of cisoid geminal coupling constants ²J(³¹P–X–¹H) are able to pass through zero^{24,25}]. The presence of a coupling J(³¹P–³¹P) between the iridium-bound phosphine and the phosphine on the boron cluster, as also observed in (4) [17 ± 1 in (4) vs.

Table 9. Selected angles between interatomic vectors (°) for compound (5) with e.s.d.s in parentheses

<i>(i) About the iridium atom</i>			
P(1)–Ir(5)–P(2)	107.6(2)	P(2)–Ir(5)–B(1)	129.9(3)
P(1)–Ir(5)–B(1)	115.5(4)	P(2)–Ir(5)–B(2)	81.1(4)
P(1)–Ir(5)–B(2)	81.1(4)	P(2)–Ir(5)–B(6)	125.4(3)
P(1)–Ir(5)–B(6)	83.9(4)	P(2)–Ir(5)–B(10)	86.0(4)
P(1)–Ir(5)–B(10)	162.3(3)	B(2)–Ir(5)–B(6)	49.2(3)
B(1)–Ir(5)–B(2)	47.0(3)	B(2)–Ir(5)–B(10)	86.5(5)
B(1)–Ir(5)–B(6)	85.9(4)	B(6)–Ir(5)–B(10)	97.5(5)
B(1)–Ir(5)–B(10)	47.4(4)	—	—
<i>(ii) Iridium–boron–boron</i>			
Ir(5)–B(1)–B(2)	66.9(6)	Ir(5)–B(2)–B(1)	66.1(6)
Ir(5)–B(1)–B(3)	115.0(5)	Ir(5)–B(2)–B(3)	114.5(6)
Ir(5)–B(1)–B(4)	116.8(7)	Ir(5)–B(2)–B(6)	64.5(5)
Ir(5)–B(1)–B(10)	68.3(6)	Ir(5)–B(2)–B(7)	106.1(6)
Ir(5)–B(6)–B(2)	66.3(5)	Ir(5)–B(10)–B(4)	64.3(6)
Ir(5)–B(6)–B(7)	113.5(5)	Ir(5)–B(10)–B(9)	118.9(6)
Ir(5)–B(10)–B(1)	64.3(6)	—	—
<i>(iii) Others</i>			
P(3)–B(7)–B(2)	129.1(7)	P(3)–B(7)–B(3)	120.7(8)
P(3)–B(7)–B(6)	116.2(6)	P(3)–B(7)–B(8)	112.6(8)
B(6)–B(7)–B(8)	116.1(9)	B(7)–B(8)–B(9)	124.8(10)
B(8)–B(9)–B(10)	105.9(9)	—	—
Ir(5)–H(5,6)–B(6)	92(2)	—	—
B(8)–H(8,9)–B(9)	88(2)	B(10)–H(9,10)–B(9)	93(2)
C(111)–C(116)–B(2)	116.8(6)	C(115)–C(116)–B(2)	123.2(7)
B(1)–B(2)–C(116)	125.2(7)	B(3)–B(2)–C(116)	125.4(8)
Ir(5)–B(2)–C(116)	114.6(7)	B(7)–B(2)–C(116)	125.5(7)
B(6)–B(2)–C(116)	115.7(7)	—	—

Table 10. Boron-11, ¹H, and ³¹P n.m.r. data for [x-(PPh₃)₆-H-6-(PPh₃)₆-(PPh₂-C₆H₄)-6-IrB₉H₁₀] (6)

Assignment ^a	δ(¹¹ B) ^b /p.p.m.	δ(¹ H) ^b
(5)	+35.2 ^c	<i>d</i>
(1), (3)	+24.7	+4.36
(9) or (8)	+6.45(2)	+3.95(2)
(9) or (10)	–0.6	+3.89
(7)	–10.2	+3.74
(8), (9), or (10)	–10.2 ^e	—
(2)	–17.5	+2.64
(4)	–23.5	+0.54
(5,6)	—	–8.89 ^f
(6,7)	—	–6.46 ^f
(10,9)	—	–3.70
(6)	—	–13.10 ^f

^a Based upon ¹H-¹¹B selective experiments (see text, also footnote *c*), and upon general similarities to compounds (1)–(3) (e.g. Tables 1 and 2). ^b Figures in parentheses indicate relative intensity, all others unit intensity. ^c Broad; no fine structure discernible. Sharpens only δ(¹H) at –8.89 in ¹H-¹¹B(selective) experiments. ^d Absent due to *o*-phenylene link. ^e Unresolved doublet due to phosphine substituent. ^f Coupled to other nuclei; see Table 11.

4.4 ± 0.2 Hz in (6)] suggests a related ⁴J pathway, and that the phosphine-substituted site is at B(8) or B(10) in (6). The lower ⁴J value in (6) may arise because the ⁴J path traverses the 'weak' *nido*-decaboranyl B(7)–B(8) [or B(5)–B(10)] linkages. Furthermore, the products from the reaction of [6-(η⁵-C₅Me₅)-*nido*-6-RhB₉H₁₃] and PMe₂Ph have been rationalized²³ in terms of an initial attack of the phosphine on B(8) [or B(10)] and, since the probable source of the phosphine in (5) is the free phosphine liberated from [IrCl(PPh₃)₃] during the formation

Table 11. Phosphorus-31 n.m.r. chemical shift and coupling constant data for compound (6)

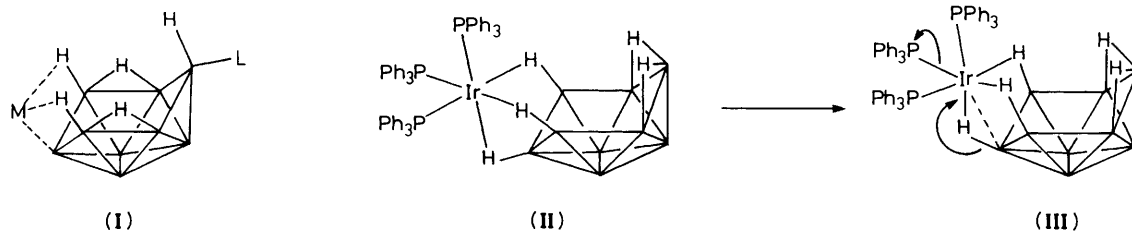
Parameter ^a	Chemical shift/p.p.m.	Coupling constant/Hz
$\delta(^{31}\text{P})^b$	+31.0 ^c +17.2 ^c +16.3 ^d	
$^2J[^{31}\text{P}(1)-^{31}\text{P}(2)]_{cis}$		17.0 ± 0.2
$^4J[^{31}\text{P}(1,2)-^{31}\text{P}(3)]$		4.4 ± 0.2
$\delta(^1\text{H}(6))$	-13.10	
$^2J[^1\text{H}(6)-^{31}\text{P}(1/2)]_{cis/trans}$		16.0 ± 0.3
$^2J[^1\text{H}(6)-^{31}\text{P}(2/1)]_{trans/cis}$		12.7 ± 0.3
$\delta(^1\text{H}(5,6))$	-8.89	
$^2J[^1\text{H}(6)-^1\text{H}(5,6)]_{trans}$		5.0 ± 0.3
$\delta(^1\text{H}(6,7))$	-6.46	
$^2J[^{31}\text{P}(2)-^1\text{H}(6,7)]_{trans}$		70.0 ± 1.0
$^2J[^1\text{H}(6,7)-^1\text{H}(6)]_{cis}$		1 ± 0.5

^a The *trans* and *cis* assignments are based on relative magnitudes of J , and upon comparison with compounds (1)–(3). ^b Recorded at -40 °C, all other data at +21 °C. ^c Assigned to P(1) or P(2). ^d Very broad, due to boron coupling; assigned to P(3).

of compounds (2)–(4), it is likely that it then attacks the cluster in a similar way. The slight steric crowding between the *ortho*-cycloboronated phenyl ring and the phosphine might possibly favour B(8) rather than B(10) as the substituent site. Despite this slight residual uncertainty concerning the precise position of the ligand on the borane cluster, (5) is clearly a *nido*-6-iridadecaborane.

Increasingly smaller amounts of other products were present in the reaction mixture but they were not isolated: in some cases their n.m.r. spectroscopic properties indicated interesting metallaborane structures but the quantities available were insufficient for detailed investigation.

The above structural variations in the products (1)–(5) from the reactions of $[\text{IrCl}(\text{PPh}_3)_3]$ with either *arachno*- $[\text{B}_9\text{H}_{14}]^-$ or *nido*- $[\text{B}_9\text{H}_{12}]^-$ merit some comment. The overall process can be regarded as an oxidative addition to the square-planar iridium(I) complex to give an octahedral iridium(III) product in which the $\{\text{IrH}(\text{PPh}_3)_2\}$ moiety notionally subrogates a $\{\text{BH}\}$ vertex of a *nido*-decaborane, thereby contributing three orbitals and two electrons to the cluster-bonding scheme in a straightforward Wadlan²⁶ manner. In the reaction with $[\text{B}_9\text{H}_{14}]^-$ the initial halide displacement may yield an iridium(I) intermediate in which the metal is bound to the cluster either (a) *via* two Ir–H–B bonds similar to those proposed for $[(\text{PPh}_3)_2\text{Cu}-\text{B}_9\text{H}_{13}\text{L}]$ ²⁷ [structure (I); L = H, NCS, NCSe, or NCBPh₃] or (b) by the addition of the metal to the three *endo*-terminal bridging hydrogen atoms in the B(6,7,8) face of $[\text{B}_9\text{H}_{14}]^-$ to form an *arachno*-type intermediate with a metal–borane linkage similar to those found in $[(\text{CO})_3\text{MnB}_8\text{H}_{13}]$ ²⁸ and $[(\text{CO})_3\text{MnB}_3\text{H}_8]$ ²⁹ [structure (II)]. In either case this would be followed by the elimination of a ligand and rearrangement of the bridging hydrogen atoms to form the product Ir–B(2) bond and a terminal metal hydride with concomitant loss of one phosphine [structure (III)]. The higher yield obtained by use of

**Table 12.** Crystallographic data for compounds (4) and (5)*

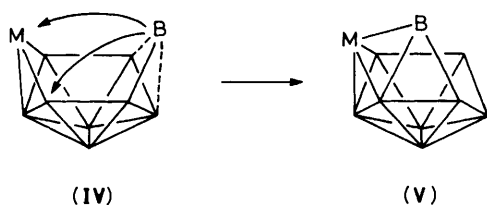
Compound	(4)	(5)
Formula	$\text{C}_{36}\text{H}_{42}\text{B}_9\text{IrP}_2$	$\text{C}_{54}\text{H}_{55}\text{B}_9\text{IrP}_3 \cdot 2\text{CHCl}_3$
M	826.20	1 299.19 (includes solvent)
a/pm	1 254.4(3)	1 501.3(3)
b/pm	1 524.6(4)	1 571.6(3)
c/pm	1 091.7(2)	1 478.1(3)
$\alpha/^\circ$	97.69(2)	104.27(2)
$\beta/^\circ$	115.09(2)	113.81(2)
$\gamma/^\circ$	88.79(2)	97.98(2)
U/nm^3	1.8723(7)	2.979(1)
$D_e/\text{g cm}^{-3}$	1.47	1.45
$F(000)$	822	1 324
μ/cm^{-1}	36.60	25.02
No. of data collected	4 845	7 992
No. observed [$I > 2\sigma(I)$]	4 638	7 060
R	0.0214	0.0486
R'	0.0243	0.0520
Weighting factor g	0.0008	0.0004
No. of variables	414	579

* Details common to both compounds: scan width $2.0^\circ + \alpha$ -doublet splitting; scan speed 2.0 – $29.3^\circ \text{ min}^{-1}$; $4.0 < 2\theta < 45.0^\circ$; crystal system, triclinic; space group $P\bar{1}$; $Z = 2$.

$[\text{IrCl}(\text{PPh}_3)_3]$ rather than $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ may reasonably be explained in terms of the greater lability of PPh_3 over CO in this ligation sphere.

The reaction with *nido*- $[\text{B}_9\text{H}_{12}]^-$ must necessarily be more complex since (a) it involves the breaking of a B–B bond in the more closed *nido* structure,^{30–34} and (b) there is an *ortho*-cycloboronation at some stage. The greater variety of products also suggest a greater complexity, and we hope to deal with this more fully in a later paper on some closely related reactions, though some arguments³⁵ have been summarized in a general review.¹⁹ Relevant here, however, is a brief discussion on the formation of the *nido*-5-iridadecaboranyl cluster observed in (4) and (5).

The *nido*-5-iridadecaborane (4) can be conceptually generated from the *nido*-6-iridadecaborane (2) or (3) *via* an isomerization of the 10-vertex cluster. Thus, if the B(9) vertex is moved to connect across the 6, 7, 8 positions (or the enantiomeric 6, 5, 10 positions), then this will effect the isomerization [structures (IV) and (V)]. With no substituents on the cluster the two product molecules would be essentially the same, although enantiomers. However, in this system the *ortho*-cycloboronated phenyl ring in the 5 position acts both as an anchor to hold the 5 and 6 vertices together, and as a marker which gives information on the course of the proposed isomerization. Thus, a clockwise movement [in the sense of diagram (VI)] of B(9) to bond to Ir(6)B(5)B(10) would result in a *nido*-5-iridadecaborane isomer with the phenylene ring at B(2) [structures (VI) and (VII)], whereas an anticlockwise movement to bond to Ir(6)B(7)B(8) [structure (VIII)] would result in a *nido*-5-iridadecaborane isomer with the phenylene ring at B(10) [structures (IX)]. A similar move of the iridium vertex Ir(6) would be restricted by the necessity of the (initially numbered) 5 and 6 vertices to



remain adjacent, so that a move of Ir(6) to join up with B(5)B(10)B(9) would be the only possibility. This would result in the opposite enantiomer to the starting molecule.

An analogous base-initiated isomerization during the reaction of $[6,6,6-(\text{CO})_3-2(\text{thf})\text{-}n\text{-ido-6-MnB}_9\text{H}_{13}]$ (thf = tetrahydrofuran) with NEt_3 has been postulated.³⁶ In this latter process the metal vertex rather than a boron one is believed to shift in such a way as to cause the 2-substituted vertex to become the 8 vertex in the rearranged cluster [structures (X)—(XII) s = thf or NEt_3].

Further evidence for vertex swings comes from the reaction between (3) and $\text{trans-[PtCl}_2(\text{PMe}_2)_2]$ after treatment with KH .³ The nature of the platinumiridadecaborane species produced can be rationalized in terms of an isomerization of (3) [structure (XIII)] followed by oxidative addition to platinum [structure (XIV)], similar to that shown in (VI) above. The base-catalysed enantiomerization of the $n\text{-ido-[5,6-C}_2\text{B}_8\text{H}_{11}]^-$

anion probably also proceeds *via* a vertex-swing mechanism.³⁷

A straightforward vertex-swing approach seems, however, too simplistic to account for compounds (4) and (5), because we think it probably would not in fact occur spontaneously and rapidly from *preformed* *nido*-6-iridadecaboranes under the conditions used. Simple geometric considerations suggest that the vertex swings would however involve *isonido*-structured intermediates or transition states,³⁵ and we discuss elsewhere⁹ evidence that the initial reaction of $[\text{IrCl}(\text{PPh}_3)_3]$ and $n\text{-ido-[B}_9\text{H}_{12}]^-$ probably forms a less-stable *isonido*-type precursor⁴ which may then rearrange to produce the observed mixture of isomers.³⁵

Finally, it seems reasonable to assume that the phosphine-substituted compound (6) arises from reaction of (3) with free phosphine ligand in solution. Consistent with this, the products of the reaction of $[6-(\eta^5\text{-C}_5\text{Me}_5)\text{-}n\text{-ido-6-RhB}_9\text{H}_{13}]$ with PMe_2Ph in dichloromethane²³ appear to be produced *via* attack of the phosphine at B(10), producing a structural analogue of (6), followed by a vertex swing of B(9) to give a 7-substituted-*nido*-5-metalladecaborane as one of the products.

The role of cycloboronation is also noteworthy. Thus, whereas *arachno*- $[\text{B}_9\text{H}_{14}]^-$ has exactly the right number of hydrogen atoms to form the stable *nido*-decaborane-like product, $n\text{-ido-[B}_9\text{H}_{12}]^-$ has two hydrogen atoms (and therefore two electrons) less. It appears, therefore, that these missing electrons are supplied *via* an *ortho*-cycloboronation reaction which effectively contributes two electrons to the

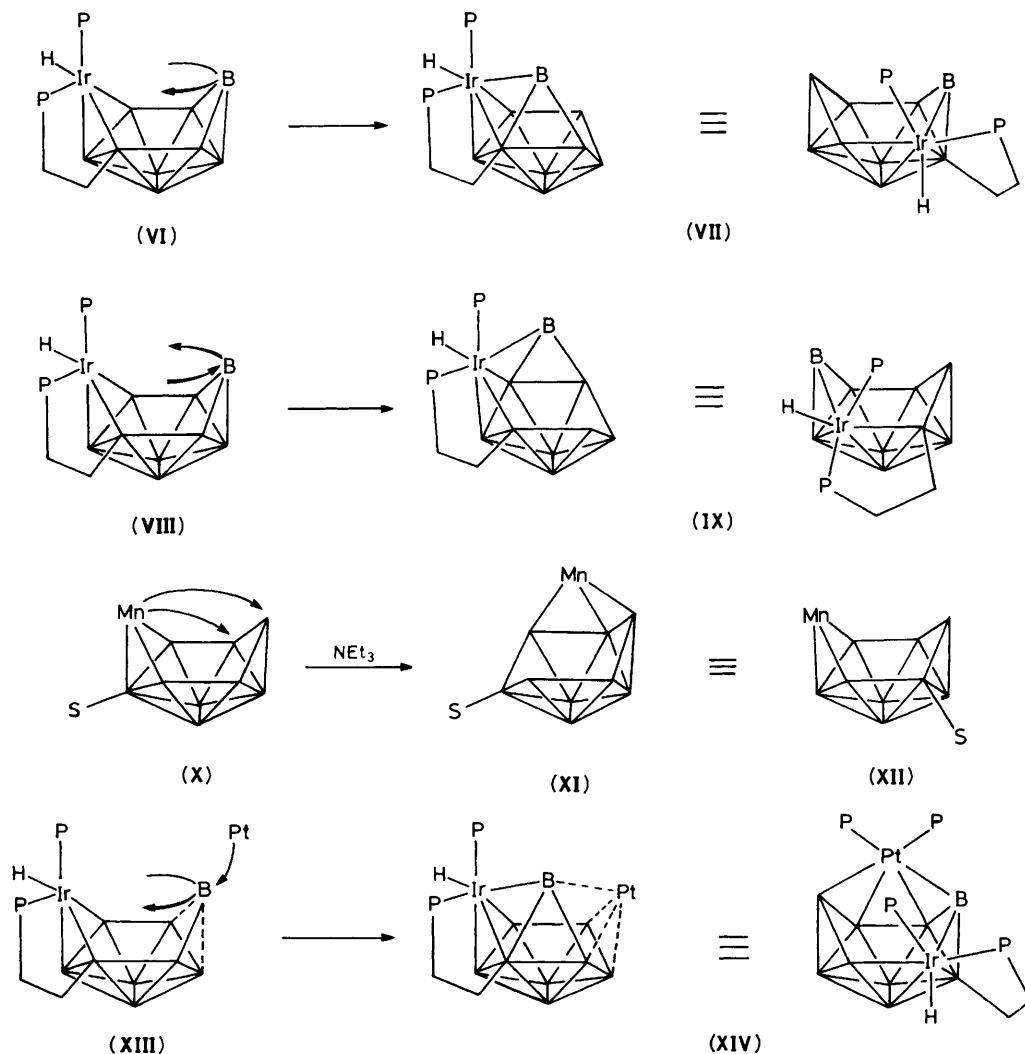


Table 13. Fractional atom co-ordinates ($\times 10^4$) for compound (4)

Atom	x	y	z	Atom	x	y	z
Ir(5)	-3 974.6(1)	-2 441.4(1)	-506.5(1)	C(131)	-5 587(1)	-2 592(2)	-3 799(2)
P(1)	-4 034.1(8)	-2 452.0(6)	-2 658.1(9)	C(132)	-6 359(1)	-2 865(2)	-3 292(2)
P(2)	-2 088.7(8)	-1 948.5(6)	1 013(1)	C(133)	-7 559(1)	-2 989(2)	-4 144(2)
B(1)	-5 628(4)	-2 196(3)	-281(4)	C(134)	-7 989(1)	-2 842(2)	-5 502(2)
B(2)	-5 794(4)	-3 028(3)	-1 699(4)	C(135)	-7 217(1)	-2 570(2)	-6 009(2)
B(3)	-6 618(4)	-3 130(3)	-746(5)	C(136)	-6 017(1)	-2 445(2)	-5 157(2)
B(4)	-5 932(4)	-2 645(3)	984(5)	C(211)	-1 530(2)	-2 686(1)	2 331(2)
B(6)	-4 678(4)	-3 824(3)	-1 366(5)	C(212)	-1 469(2)	-3 587(1)	1 932(2)
B(7)	-6 013(4)	-4 072(3)	-1 254(5)	C(213)	-1 114(2)	-4 172(1)	2 900(2)
B(8)	-6 097(5)	-3 814(4)	515(6)	C(214)	-821(2)	-3 855(1)	4 268(2)
B(9)	-4 827(5)	-3 287(4)	1 934(5)	C(215)	-881(2)	-2 954(1)	4 667(2)
B(10)	-4 446(4)	-2 339(3)	1 350(5)	C(216)	-1 236(2)	-2 370(1)	3 698(2)
C(111)	-3 307(2)	-3 344(1)	-3 260(3)	C(221)	-923(2)	-1 891(2)	430(3)
C(112)	-3 916(2)	-3 989(1)	-4 370(3)	C(222)	-988(2)	-1 220(2)	-5 150(3)
C(113)	-3 322(2)	-4 701(1)	-4 692(3)	C(223)	-155(2)	-1 152(2)	-869(3)
C(114)	-2 119(2)	-4 769(1)	-3 904(3)	C(224)	743(2)	-1 753(2)	-609(3)
C(115)	-1 509(2)	-4 125(1)	-2 794(3)	C(225)	808(2)	-2 424(2)	171(3)
C(116)	-2 104(2)	-3 412(1)	-2 472(3)	C(226)	-25(2)	-2 492(2)	690(3)
C(121)	-3 604(3)	-1 459(1)	-3 140(3)	C(231)	-1 880(2)	-843(1)	1 970(2)
C(122)	-3 833(3)	-629(1)	-2 613(3)	C(232)	-2 825(2)	-330(1)	1 933(2)
C(123)	-3 605(3)	132(1)	-3 057(3)	C(233)	-2 617(2)	514(1)	2 682(2)
C(124)	-3 148(3)	63(1)	-4 028(3)	C(234)	-1 465(2)	847(1)	3 467(2)
C(125)	-2 919(3)	-767(1)	-4 555(3)	C(235)	-520(2)	334(1)	3 504(2)
C(126)	-3 147(3)	-1 528(1)	-4 111(3)	C(236)	-727(2)	-510(1)	2 755(2)

Table 14. Fractional atom co-ordinates ($\times 10^4$) for compound (5)

Atom	x	y	z	Atom	x	y	z
Ir(5)	1 470.1(2)	2 474.6(2)	2 250.4(2)	C(214)	-60(4)	5 544(3)	2 924(4)
P(1)	3 003(2)	2 272(1)	2 398(2)	C(215)	933(4)	5 482(3)	3 374(4)
P(2)	978(2)	3 356(1)	1 172(2)	C(216)	1 239(4)	4 833(3)	2 819(4)
P(3)	2 537(2)	2 681(1)	6 029(2)	C(221)	-51(3)	2 802(3)	-164(3)
B(1)	508(7)	1 362(6)	2 429(7)	C(222)	-485(3)	1 863(3)	-539(3)
B(2)	1 796(7)	1 737(5)	3 435(7)	C(223)	-1 253(3)	1 443(3)	-1 564(3)
B(3)	794(7)	1 456(6)	3 748(7)	C(224)	-1 588(3)	1 960(3)	-2 213(3)
B(4)	-355(7)	1 687(7)	2 941(8)	C(225)	-1 154(3)	2 899(3)	-1 838(3)
B(6)	2 283(7)	3 007(6)	3 998(7)	C(226)	-385(3)	3 320(3)	-813(3)
B(7)	1 736(7)	2 473(6)	4 556(7)	C(231)	1 883(3)	4 011(3)	875(3)
B(8)	451(7)	2 491(7)	4 227(8)	C(232)	2 173(3)	4 961(3)	1 218(3)
B(9)	-365(7)	2 770(7)	3 125(8)	C(233)	2 840(3)	5 415(3)	944(3)
B(10)	-162(8)	2 211(7)	2 066(7)	C(234)	3 217(3)	4 919(3)	328(3)
C(111)	3 182(3)	1 364(2)	2 964(3)	C(235)	2 926(3)	3 968(3)	-15(3)
C(112)	3 916(3)	907(2)	2 970(3)	C(236)	2 259(3)	3 514(3)	258(3)
C(113)	4 093(3)	281(2)	3 505(3)	C(311)	1 835(3)	2 109(3)	6 550(3)
C(114)	3 536(3)	114(2)	4 033(3)	C(312)	1 497(3)	2 585(3)	7 221(3)
C(115)	2 802(3)	571(2)	4 027(3)	C(313)	888(3)	2 110(3)	7 539(3)
C(116)	2 625(3)	1 196(2)	3 492(3)	C(314)	617(3)	1 160(3)	7 187(3)
C(121)	4 163(3)	3 198(3)	3 257(4)	C(315)	956(3)	684(3)	6 517(3)
C(122)	5 020(3)	3 070(3)	4 003(4)	C(316)	1 565(3)	1 159(3)	6 198(3)
C(123)	5 896(3)	3 789(3)	4 606(4)	C(321)	3 723(3)	2 381(3)	6 452(4)
C(124)	5 915(3)	4 636(3)	4 465(4)	C(322)	4 036(3)	2 026(3)	7 271(4)
C(125)	5 058(3)	4 763(3)	3 719(4)	C(323)	4 976(3)	1 838(3)	7 632(4)
C(126)	4 182(3)	4 044(3)	3 115(4)	C(324)	5 602(3)	2 006(3)	7 174(4)
C(131)	3 106(4)	1 827(3)	1 185(3)	C(325)	5 288(3)	2 361(3)	6 354(4)
C(132)	3 917(4)	2 214(3)	1 049(3)	C(326)	4 349(3)	2 549(3)	5 993(4)
C(133)	3 945(4)	1 873(3)	98(3)	C(331)	2 901(4)	3 891(3)	6 757(4)
C(134)	3 161(4)	1 144(3)	-716(3)	C(332)	3 798(4)	4 280(3)	7 690(4)
C(135)	2 350(4)	757(3)	-580(3)	C(333)	4 063(4)	5 207(3)	8 251(4)
C(136)	2 323(4)	1 099(3)	371(3)	(C334)	3 432(4)	5 745(3)	7 879(4)
C(211)	552(4)	4 247(3)	1 813(4)	C(335)	2 535(4)	5 356(3)	6 945(4)
C(212)	-441(4)	4 309(3)	1 363(4)	C(336)	2 270(4)	4 428(3)	6 384(4)
C(213)	-747(4)	4 958(3)	1 918(4)				

cluster bonding by inclusion of the otherwise skeletally non-active electron pair in the C(phenyl)-H bond; this results in the formation of an *exo*-terminal C(phenyl)-B bond and permits the concomitant incorporation of the phenyl hydrogen atom into the cluster.

Experimental

General.—The metal complex $[\text{IrCl}(\text{PPh}_3)_3]$ was prepared by the standard method³⁸ and the salt $[\text{NEt}_4][\text{B}_9\text{H}_{14}]$ using the method described previously for $[\text{NMe}_4][\text{B}_9\text{H}_{14}]$.³⁹ Reactions were carried out, and solids and solutions kept,

under an atmosphere of dry nitrogen, although manipulations and separatory procedures were carried out in air. Preparative thin-layer chromatography was performed using silica gel G (Fluka type GF254) as the stationary phase and CH_2Cl_2 -pentane as the mobile phase.

N.M.R. Spectroscopy.—Boron-11, phosphorus-31, and proton spectra at ca. 32, ca. 40, and ca. 100 MHz respectively were obtained at 2.34 T on a JEOL FX-100 instrument in these laboratories, with the multiple resonance $^1\text{H}\{-^{11}\text{B}\}$ and $^1\text{H}\{-^{11}\text{B}, ^1\text{H}\}$ experiments being carried out as described elsewhere.^{1,39-43} Boron-11 spectra at ca. 115.5 and ca. 128 MHz respectively were recorded using Bruker WH-360 and WH-400 instruments (S.E.R.C. Service, Universities of Edinburgh and Sheffield). There was often advantage in recording the ^{31}P spectra at lower temperatures (see Tables) to maximize the 'thermal decoupling' of ^{10}B and ^{11}B from the phosphine ligand resonances.⁴⁴ Chemical shifts $\delta(^1\text{H})$, $\delta(^{31}\text{P})$, and $\delta(^{11}\text{B})$ are given in p.p.m. to high frequency (low field) of Ξ 100, Ξ 40.480 730 (nominally 85% H_3PO_4), and Ξ 32.083 971 MHz (nominally $\text{F}_3\text{B}\cdot\text{OEt}_2$ in CDCl_3)⁴⁵ respectively, Ξ being defined as in ref. 46.

Reaction of $[\text{IrCl}(\text{PPh}_3)_3]$ with $[\text{NEt}_4][\text{B}_9\text{H}_{14}]$.—The compound $[\text{IrCl}(\text{PPh}_3)_3]$ (0.205 g, 0.2 mmol) was stirred in CH_2Cl_2 with the $[\text{B}_9\text{H}_{14}]^-$ salt (0.072 g, 0.2 mmol) for 45 min (the reaction is almost instantaneous: shorter times may be used), the resultant mixture reduced in volume on a rotary evaporator and then separated using preparative t.l.c. with CH_2Cl_2 -pentane (1:1) as mobile phase. Two main bands were apparent. The first, a bright yellow band, R_f 0.5, after removal from the plate gave *nido*- $[\text{H}(\text{PPh}_3)_2\text{IrB}_9\text{H}_{13}]$ (0.127 g, 81% yield). The second, a pale violet band at R_f 0.2, was an *isonido*-iridadecaborane.^{4,19,35}

Reaction of $[\text{IrCl}(\text{PPh}_3)_3]$ and $[\text{NEt}_4][\text{B}_9\text{H}_{12}]$.—In a typical procedure the compound $[\text{IrCl}(\text{PPh}_3)_3]$ (0.15 g, 0.15 mmol) and the $[\text{B}_9\text{H}_{12}]^-$ salt (0.04 g, 0.1 mmol) were stirred in CH_2Cl_2 solution. The mixture was chromatographically separated as above giving a number of bands. Compound (4) (R_f 0.85) appeared as a yellow band at the top of the t.l.c. plate, and was isolated in yields of 0.1–20% depending on the freshness of the starting materials. Compounds (2) and (3) (R_f 0.8 and 0.75 respectively) were the major components [typical yields: (2), 0.077 g, 63%; and (3), 0.026 g, 21%]. Compound (2) was found to isomerize smoothly to (3) at ca. 65 °C and so the work-up conditions affect the relative amounts isolated, with the yields stated being the highest (2):(3) ratio found. Compounds (5) and (6) (R_f 0.65 and 0.65) required further separation by h.p.l.c. They gave yields of 0.006 (5%) and 0.012 g (10%), again depending on the freshness of starting materials. Finally a pale violet band, R_f 0.2, of the *isonido*-iridadecaborane mentioned in the preceding reaction was isolated (2–3 mg, 2% yield).

Single-crystal X-Ray Diffraction Analysis.—The crystallographic measurements for both structures were made on a Syntex P2₁ diffractometer operating in the ω -2 θ scan mode using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 71.069$ pm) following a standard procedure described elsewhere.⁴⁷ Both data sets were corrected for absorption empirically.⁴⁸

Both structures were solved *via* standard heavy-atom methods and were refined by full-matrix least squares using the SHELX system.⁴⁹ Refinement for both compounds was essentially the same with all non-hydrogen atoms being assigned anisotropic thermal parameters apart from two chloroform molecules in (5) (one of which was slightly disordered) which were refined with isotropic parameters. All phenyl groups were treated as rigid bodies and were refined with

idealized hexagonal symmetry (C–C 139.5 pm). All phenyl hydrogen atoms were included in calculated positions and were assigned an overall isotropic thermal parameter. The remaining hydrogen atoms were located in Fourier difference maps and were freely refined with individual isotropic thermal parameters. The weighting scheme $w^{-1} = \sigma^2(F_o) + g(F_o)^2$ was used for both compounds with the parameter g included in refinement to give satisfactory agreement analyses.

Relevant crystal data, data collection, and structure refinement values are given in Table 12. Atomic co-ordinates for compounds (4) and (5) are given in Tables 13 and 14 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining interatomic distances and angles.

Acknowledgements

We thank the S.E.R.C. for financial support and for a maintenance grant (to J. B.).

References

- S. K. Boocock, J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1982, 713.
- J. Bould, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1983, 951.
- J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1983, 949.
- J. Bould and W. S. McDonald, unpublished work, see N. N. Greenwood and J. D. Kennedy in 'Metal Interactions, with Boron Clusters,' R. N. Grimes (ed.), Plenum, New York, 1982 and also refs. 19 and 35 below.
- J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1983, 83.
- J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1981, 933.
- M. Eltrington, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 2277.
- J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 465.
- J. Bould, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, following paper.
- J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, 1977, **16**, 3251; G. J. Zimmerman, L. W. Hall, and L. G. Sneddon, *ibid.*, 1980, **19**, 3642.
- C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1972, **94**, 8391.
- M. Bown, X. L. R. Fontaine, N. N. Greenwood, and J. D. Kennedy, *J. Organomet. Chem.*, 1987, **325**, 233.
- A. G. Orpen, HYDEX, *J. Chem. Soc., Dalton Trans.*, 1980, 2509; XHYDEX, University of Bristol, 1986, personal communication.
- M. Thornton-Pett, J. D. Kennedy, and A. G. Orpen, unpublished work.
- A. Tippe and W. C. Hamilton, *Inorg. Chem.*, 1969, **8**, 464.
- L. G. Sneddon, J. C. Huffman, R. O. Schaeffer, and W. E. Streib, *J. Chem. Soc., Chem. Commun.*, 1972, 474.
- W. N. Lipscomb, 'Boron Hydrides,' W. A. Benjamin, New York, 1963.
- J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 517 and refs. therein.
- J. D. Kennedy, *Prog. Inorg. Chem.*, 1986, **34**, 211 and refs. therein.
- K. Baše, B. Štíbr, A. Kukina, and I. A. Zakharova, Proc. 8th Conf. Coord. Chem., Smolenice, Czechoslovakia, 1980, p. 17.
- Faridooon, G. Ferguson, and T. R. Spalding, *Acta Crystallogr., Sect. C*, 1988, **44**, 1371.
- M. A. Beckett, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 552.
- X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 1431.
- See, for example, J. D. Kennedy, W. McFarlane, and D. S. Rycroft, *Inorg. Chem.*, 1973, **12**, 2742 and refs. therein.
- J. L. Bookham, X. L. R. Fontaine, J. D. Kennedy and W. McFarlane, *Inorg. Chem.*, 1987, **28**, 1111.
- K. Wade, *Chem. Commun.*, 1971, 792; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
- D. G. Meina and J. H. Morris, *J. Chem. Soc., Dalton Trans.*, 1985, 1903.

- 28 J. C. Calabrese, M. B. Fischer, D. F. Gaines, and J. W. Lott, *J. Am. Chem. Soc.*, 1974, **96**, 6318.
- 29 S. J. Hildebrandt, D. F. Gaines, and J. C. Calabrese, *Inorg. Chem.*, 1978, **17**, 790.
- 30 A. R. Siedle, G. M. Bodner, A. R. Garber, and L. J. Todd, *Inorg. Chem.*, 1974, **13**, 1756.
- 31 J. Bould, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1984, 2477.
- 32 G. B. Jacobsen, D. G. Meina, J. H. Morris, C. Thompson, S. J. Andrews, D. Reed, A. J. Welch, and D. F. Gaines, *J. Chem. Soc., Dalton Trans.*, 1985, 1645.
- 33 M. A. Beckett, M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 1969.
- 34 S. Heřmánek, J. Fusek, B. Štíbr, J. Plešek, and T. Jelínek, *Polyhedron*, 1986, **5**, 1873.
- 35 J. Bould, Ph.D. Thesis, University of Leeds, 1983.
- 36 D. F. Gaines, J. W. Lott, and J. C. Calabrese, *Inorg. Chem.*, 1974, **13**, 2419.
- 37 B. Štíbr, J. Plešek, and A. Zobáčová, *Polyhedron*, 1982, **1**, 826; see also N. N. Greenwood, *Pure Appl. Chem.*, 1983, **55**, 1415 and refs. therein.
- 38 J. L. Herde, J. C. Lambert, and C. V. Senoff, *Inorg. Synth.*, 1974, **15**, 18.
- 39 S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1981, 1415.
- 40 J. D. Kennedy and B. Wrackmeyer, *J. Magn. Reson.*, 1980, **38**, 529.
- 41 J. D. Kennedy and N. N. Greenwood, *Inorg. Chim. Acta*, 1980, **38**, 93.
- 42 T. C. Gibb and J. D. Kennedy, *J. Chem. Soc., Faraday Trans. 2*, 1982, 525.
- 43 J. D. Kennedy, unpublished work.
- 44 J. D. Kennedy and J. Staves, *Z. Naturforsch.*, 1979, **34b**, 808.
- 45 J. D. Kennedy, in 'Multinuclear NMR,' ed. J. Mason, Plenum, 1987, ch. 8.
- 46 W. McFarlane, *Proc. R. Soc. London, Ser. A*, 1968, **306**, 185.
- 47 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.
- 48 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
- 49 G. M. Sheldrick, SHELX 76, Program System for X-Ray Structure Determination, University of Cambridge, 1976.

Received 7th June 1989; Paper 9/02410G