

## Comparative Metallaborane Chemistry: Preparation and Nuclear Magnetic Resonance Studies of Some *nido*-5-Metalladecaboranes of Rhodium, Iridium, Ruthenium, and Osmium

Mark Bown, Hayat Fowkes, Xavier L. R. Fontaine, Norman N. Greenwood, John D. Kennedy, Peter MacKinnon, and Karl Nestor  
School of Chemistry, University of Leeds, Leeds LS2 9JT

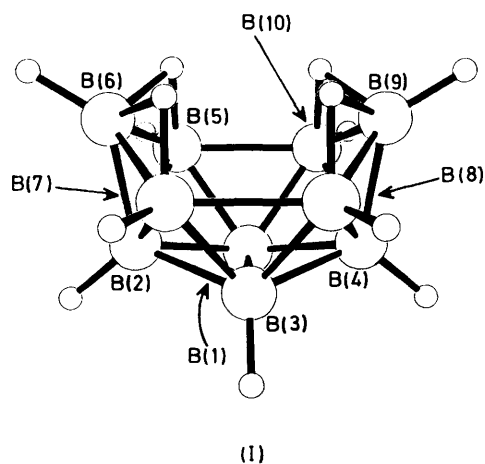
The isolation, and characterisation by n.m.r. spectroscopy, of the new ten-vertex *nido*-metalladecaboranes [5-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-5-RhB<sub>9</sub>H<sub>13</sub>], [5-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-5-IrB<sub>9</sub>H<sub>13</sub>], [6-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-6-IrB<sub>9</sub>H<sub>13</sub>], [5-( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)-*nido*-5-RuB<sub>9</sub>H<sub>13</sub>], and [5-( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)-*nido*-5-OsB<sub>9</sub>H<sub>13</sub>] are described. The n.m.r. data of the *nido*-5-metalladecaboranes, together with those of the previously reported first-row transition element compounds [5-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-5-CoB<sub>9</sub>H<sub>13</sub>] and [5-( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>-1,3,5)-*nido*-FeB<sub>9</sub>H<sub>13</sub>] permit an examination of n.m.r. shielding trends for this compound type across two columns and down three rows of the Periodic Table. Similarities within the periods are more marked than those within the groups. [6-(OH)-5-( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)-*nido*-5-OsB<sub>9</sub>H<sub>12</sub>] was also tentatively identified during this work.

The establishment of the systematics of the n.m.r. behaviour of polyhedral boron-containing compounds is a matter of current interest,<sup>1</sup> and we have recently reported systematic <sup>11</sup>B and <sup>1</sup>H shielding trends in mutually related series of unsubstituted *nido*-6-metalladecaboranes.<sup>2-4</sup> Here we report the preparation and n.m.r. investigation of a new series of unsubstituted *nido*-5-metalladecaboranes [MB<sub>9</sub>H<sub>13</sub>] in which the metal centres M are Ru( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>) (1), Rh( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) (2), Os( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>) (3), and Ir( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) (5). The *nido* ten-vertex numbering system is given in structure (1), which represents the structure of *nido*-B<sub>10</sub>H<sub>14</sub>. The *nido*-metalladecaboranes described in this work derive from this by the replacement of a BH vertex by an isolobal and isoelectronic metal one.

### Results and Discussion

The ruthenium, rhodium, and osmium species (1)–(3) were all prepared by the same general method, *viz.* the reaction between [ $\{\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)\}_2$ ], [ $\{\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)\}_2$ ], or [ $\{\text{OsCl}_2(\eta^6\text{-C}_6\text{Me}_6)\}_2$ ] and the *nido*-[B<sub>10</sub>H<sub>13</sub>]<sup>-</sup> anion in dichloromethane solution, and isolated by chromatography as yellow crystalline air-stable solids. These reactions were accompanied by the formation of other coloured metallaborane products. In the rhodium reaction the two major ones have been identified as [9-(OH)-5-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-5-RhB<sub>9</sub>H<sub>12</sub>] and [9,9'-(5-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-5-RhB<sub>9</sub>H<sub>12</sub>)<sub>2</sub>O] as described elsewhere.<sup>5</sup> In the ruthenium and osmium reactions the yield of by-products was much lower; on the scale of the reactions (*ca.* 100  $\mu$ mol) the only one obtained in yields viable for examination was tentatively identified as [6-(OH)-5-( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)-*nido*-5-OsB<sub>9</sub>H<sub>12</sub>] (4) by n.m.r. spectroscopy (see Experimental section). The formation of such nine-boron ten-vertex metallaboranes from ten-boron starting substrates is dealt with elsewhere.<sup>5</sup>

The iridium species [5-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-5-IrB<sub>9</sub>H<sub>13</sub>] (5) was prepared *via* its isomer [6-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-6-IrB<sub>9</sub>H<sub>13</sub>] (6), which isomerizes to give the 5-metalla species (5) in solution in the presence of air. In an analogous route to the high-yield preparation of the rhodium analogue, *viz.* [6-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-6-RhB<sub>9</sub>H<sub>13</sub>],<sup>6</sup> reaction between [ $\{\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)\}_2$ ] and *arachno*-[B<sub>9</sub>H<sub>14</sub>]<sup>-</sup>, followed by h.p.l.c. separation on silica under reasonably anaerobic conditions, resulted in the isolation of the 6-isomer (6) as an orange crystalline solid in a yield of



55%. It was readily identified by n.m.r. spectroscopy and comparison<sup>6</sup> with the rhodium analogue. By contrast, separation of the reaction mixture entirely by t.l.c. on silica in air resulted in the isolation of the 5-isomer (5) as a yellow crystalline solid, in 40% yield. Passage of dioxygen through a solution of (6) in dichloromethane resulted in complete conversion to (5) over 75 min with some decomposition, as monitored by n.m.r. spectroscopy.

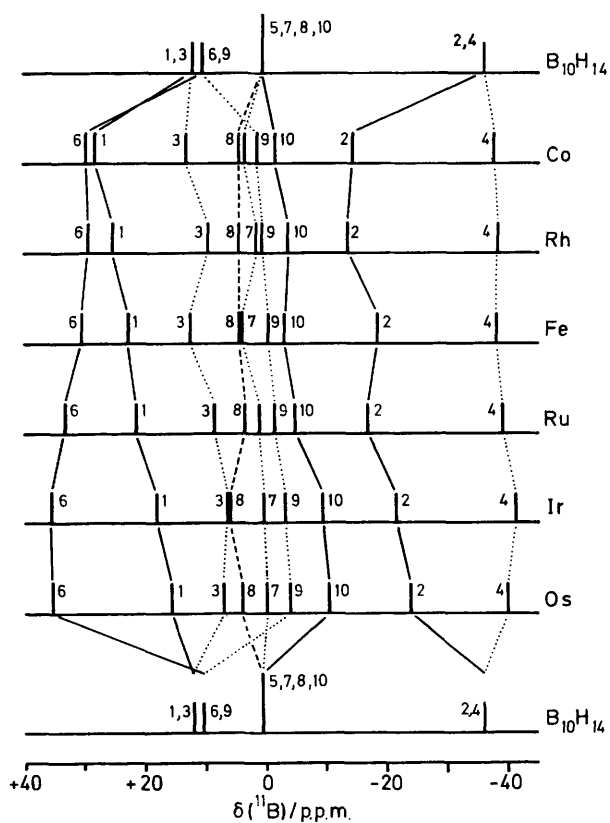
The characterisation of the *nido*-5-metalladecaboranes (1)–(3) and (5) as the 5-isomers readily followed from n.m.r. spectroscopy. The basic <sup>11</sup>B n.m.r. shielding patterns were very closely similar to, and incidence and relative intensities of the observed [<sup>11</sup>B–<sup>11</sup>B]-COSY cross-correlations were essentially identical to, those previously reported<sup>7</sup> for the cobalt analogue [5-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*nido*-5-CoB<sub>9</sub>H<sub>13</sub>]. Selective <sup>1</sup>H–{<sup>11</sup>B} spectroscopy then related the resonances in the <sup>1</sup>H spectra to their directly bound boron atom positions, and the observed [<sup>1</sup>H–<sup>1</sup>H]-COSY correlations (in experiments carried out with simultaneous {<sup>11</sup>B} decoupling) for compounds (1), (3), and (5) closely resembled those previously reported elsewhere in another context for the rhodium compound (2).<sup>8</sup> Implicit in this n.m.r. identification is an assignment of the <sup>11</sup>B and <sup>1</sup>H n.m.r. spectra, the results being summarized in the Table.

Figure 1 represents the relative intensities and chemical shifts

**Table.** Measured  $^{11}\text{B}$  and  $^1\text{H}$  n.m.r. parameters for [5-( $\eta^6\text{-C}_6\text{Me}_6$ )-*nido*-5-RuB $_9$ H $_{13}$ ] (1), [5-( $\eta^5\text{-C}_5\text{Me}_5$ )-*nido*-5-RhB $_9$ H $_{13}$ ] (2), [5-( $\eta^6\text{-C}_6\text{Me}_6$ )-*nido*-5-OsB $_9$ H $_{13}$ ] (3), and [5-( $\eta^5\text{-C}_5\text{Me}_5$ )-*nido*-5-IrB $_9$ H $_{13}$ ] (5) at 293–294 K

Assignment	(1) (CD $_2$ Cl $_2$ )		(2) (CD $_2$ Cl $_2$ )		(3) (CDCl $_3$ )		(5) (CDCl $_3$ )	
	$\delta(^{11}\text{B})/\text{p.p.m.}^a$ [ $^1J(^{11}\text{B}-^1\text{H})/\text{Hz}$ ] <sup>b</sup>	$\delta(^1\text{H})/\text{p.p.m.}^c$	$\delta(^{11}\text{B})/\text{p.p.m.}^a$ [ $^1J(^{11}\text{B}-^1\text{H})/\text{Hz}$ ] <sup>b</sup>	$\delta(^1\text{H})/\text{p.p.m.}^c$	$\delta(^{11}\text{B})/\text{p.p.m.}^a$ [ $^1J(^{11}\text{B}-^1\text{H})/\text{Hz}$ ] <sup>b</sup>	$\delta(^1\text{H})/\text{p.p.m.}^c$	$\delta(^{11}\text{B})/\text{p.p.m.}^a$ [ $^1J(^{11}\text{B}-^1\text{H})/\text{Hz}$ ] <sup>b</sup>	$\delta(^1\text{H})/\text{p.p.m.}^c$
(1)	+21.2 [135]	+3.48	+25.3 [136]	+3.87	+15.3 [135]	+4.01	+17.8 [139]	+4.14
(2)	-16.9 [140]	+0.40	-13.5 [145]	+0.70	-23.6 [141]	+0.53	-21.7 [153]	+0.40
(3)	+8.5 [137]	+2.61	+9.5 [138]	+2.77	+7.0 [139]	+2.36	+6.4 [140]	+2.41
(4)	-39.2 [146]	+0.17	-38.3 [147]	+0.27	-40.1 [145]	+0.64	-41.1 [147]	+0.59
(5)	Ru [-]	[+2.19] <sup>d</sup>	Rh [-]	[+1.94] <sup>d</sup>	Os [-]	[+2.22] <sup>d</sup>	Ir [-]	[+2.03] <sup>d</sup>
(6)	+33.1 [152]	+4.72	+28.7 [158]	+4.55	+35.2 [155]	+5.74	+35.2 [154]	+5.86
(7)	+1.1 [149]	+3.50	+1.6 [150]	+3.63	-0.1 [150.44]	+4.89	+0.2 [151.46]	+5.03
(8)	+3.5 [152]	+2.86	+4.5 [139]	+3.02	+4.0 [145]	+3.03	+6.4 [140]	+3.31
(9)	-1.5 [158]	+2.91	+0.6 [148]	+3.15	-4.0 [149.37]	+2.85	-3.3 [159]	+3.00
(10)	-5.3 [144]	+2.32	-4.0 [148]	+2.33	-10.5 [139]	+2.48	-9.4 [144]	+2.38
(5,6)		-15.63		-12.50 <sup>e</sup>		-16.87		-16.90
(6,7)		-2.83		-2.42		-2.73		-2.26 <sup>f</sup>
(8,9)		-3.10		-2.75		-3.11		-2.88 <sup>f</sup>
(9,10)		-2.13		-1.85		-2.58		-2.23 <sup>f</sup>

<sup>a</sup>  $\pm 0.5$  p.p.m. to high frequency of BF $_3(\text{OEt})_2$ . <sup>b</sup>  $\pm 8$  Hz; measured from  $^{11}\text{B}$  spectrum with resolution enhancement. <sup>c</sup>  $\pm 0.05$  p.p.m. to high frequency of SiMe $_4$ ; <sup>d</sup>  $^1\text{H}$  resonances related to directly-bound B positions in  $^1\text{H}\{-^{11}\text{B}\}$  selective experiments. <sup>e</sup> Refers to  $\delta(^1\text{H})$  in  $\eta^6\text{-C}_n\text{Me}_n$  groupings. <sup>f</sup> Doublet,  $^1J(^{103}\text{Rh}-^1\text{H}) = 33$  Hz. <sup>g</sup> Precise assignment of these three resonances for compound (5) among the (6,7), (8,9), and (9,10) positions not certain.

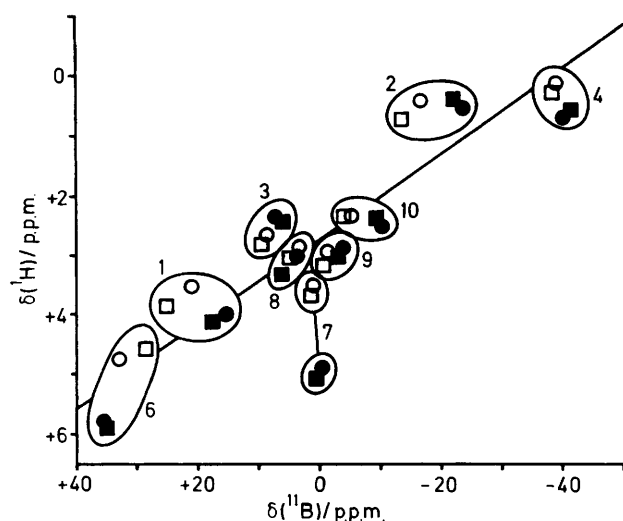


**Figure 1.** Stick representations of the relative intensities and chemical shifts in the  $^{11}\text{B}$  n.m.r. spectra of B $_{10}$ H $_{14}$ , (3) (Os), (5) (Ir), (1) (Ru), [5-( $\eta^6\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5}$ )-*nido*-5-FeB $_9$ H $_{13}$ ] (Fe, data from ref. 10), (2) (Rh), [5-( $\eta^5\text{-C}_5\text{Me}_5$ )-*nido*-5-CoB $_9$ H $_{13}$ ] (Co, data from ref. 7), and, again, B $_{10}$ H $_{14}$ . For numbering see structure (I). The lines connect resonance positions for equivalent sites in the different molecules: (—) adjacent ( $\alpha$ ) to metal atom, (····)  $\beta$  to metal atom, and (---)  $\gamma$  (which in this case is also antipodal) to metal atom

in the  $^{11}\text{B}$  spectra of the *nido*-5-metalladecaboranes (1)–(3) and (5), together with data for B $_{10}$ H $_{14}$ ,<sup>9</sup> [5-( $\eta^5\text{-C}_5\text{Me}_5$ )-*nido*-5-CoB $_9$ H $_{13}$ ],<sup>7</sup> and [5-( $\eta^6\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5}$ )-*nido*-5-FeB $_9$ H $_{13}$ ]<sup>10</sup> for comparison. The resonances for the cobalt compound are assigned, but their precise positioning in the figure may be somewhat inexact as their values had to be estimated from a scale on a diagram in the reference cited.<sup>7</sup> Those for the iron compound are more accurate; they were unassigned in the reference cited,<sup>10</sup> but can be reasonably assigned as labelled in Figure 1 on the basis of comparison with the other compounds.

It is apparent from Figure 1 that many of the basic shielding elements of *nido*-B $_{10}$ H $_{14}$  are retained, as was also observed with the *nido*-6-metallaborane analogues reported previously.<sup>4</sup> The principal change in these latter 6-metalla species was a substantial deshielding of the  $^{11}\text{B}$  nuclei at positions adjacent to the metal atom. In the 5-metalla species reported here this occurs consistently only for two of the four sites adjacent ( $\alpha$ ) to the metal atom. Of these the open-face  $^{11}\text{B}$ (6) site is deshielded by some 20 p.p.m., the effect being somewhat greater for the heavier *versus* the lighter metal atoms, and the  $^{11}\text{B}$ (2) site by some 10–20 p.p.m., the effect now being somewhat greater for the lighter metal atoms. By contrast, the effect at the other two adjacent sites is variable. At  $^{11}\text{B}$ (10) the shielding is little changed for the lighter metal atoms, but there are shielding *increases* of up to *ca.* 10 p.p.m. for the heavier ones, whereas at  $^{11}\text{B}$ (1) there is little change for the heavier metal atoms, but now there are shielding *decreases* of up to 15 p.p.m. or so for the lighter metal atoms. There is no significant antipodal ( $\gamma$ ) effect at  $^{11}\text{B}$ (8), but, interestingly, the  $^{11}\text{B}$ (9) site  $\beta$  to the metal is substantially shifted upfield in all compounds, by some 10–14 p.p.m.

Figure 2 summarizes the *exo*-terminal proton shielding data for compounds (1)–(3) and (5) (those for the iron<sup>10</sup> and cobalt<sup>7</sup> species not being available), presented as a plot of  $\delta(^1\text{H})$  against  $\delta(^{11}\text{B})$  for directly attached BH groupings (the proton data being measured using solvents that do not exhibit significant anisotropic shielding effects upon their solutes). There is a general parallel between  $\delta(^1\text{H})$  and  $\delta(^{11}\text{B})$ , the general correlation line drawn [ $\delta(^{11}\text{B})$ : $\delta(^1\text{H})$  14:1] being of slope similar to but somewhat less steep than the 16:1 correlation<sup>4</sup>



**Figure 2.** Plot of  $\delta(^1\text{H})$  (*exo*) versus  $\delta(^{11}\text{B})$  for directly bound atoms in compounds (1) (○), (2) (□), (3) (●), and (5) (■). Cartouches enclose data for equivalent sites in the different molecules. The line drawn has slope  $\delta(^{11}\text{B}):\delta(^1\text{H})$  14:1, intercept  $\delta(^1\text{H}) + 2.75$  p.p.m. Note the grouping of the Os/Ir (●, ■) and Ru/Rh (○, □) pairs and the low proton shieldings for  $^{11}\text{B}^1\text{H}(7)$  in the Os/Ir pair

for the *nido*-6-metallaborane analogues, the positioning of the data for the BH(2) and BH(4) sites somewhat to either side of the line also mirroring the behaviour of the 6-metalla species. There is no antipodal variation at the BH(8) positions, the only marked deviation from the 14:1 trend being at BH(7) for the heavier metal compounds (3) and (5) which exhibit  $\delta(^1\text{H})$  values some 1.5 p.p.m. less shielded than the corresponding positions in the ruthenium and rhodium species (1) and (2). This interesting transannular 'three-bond' proton deshielding effect that is induced by third-row transition elements when they are cluster constituents has also been observed in *nido* five-vertex clusters.<sup>11,12</sup> A similar effect has been observed in *closo* twelve-vertex clusters for a 'four-bond' antipodal disposition,<sup>13,14</sup> and it also appears to be present for the antipodal BH(4) position in  $[6-(\eta^5\text{-C}_5\text{Me}_5)\text{-nido-6-IrB}_9\text{H}_{13}]$  (6) (see summarized data in the Experimental section) and  $[6-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-6-OsB}_9\text{H}_{13}]$ ,<sup>4</sup> although the effect is not so marked in *nido*-6-metalladecaboranes that have phosphine-type ligands.<sup>2,3</sup>

A final interesting effect apparent from Figure 2 is that the third-row transition element compounds (filled symbols in the Figure) are much more similar to each other in their shielding behaviour and thence electronic structure than they are to their second-row congeners (open symbols). Figure 1 also illustrates this, and additionally shows that this distinction does not hold so readily when the second-row and first-row analogues are compared, the iron and ruthenium compounds being somewhat more similar to each other than either iron to cobalt or ruthenium to rhodium.

## Experimental

**General.**—Reactions were carried out in dry solvents under dry nitrogen but subsequent manipulatory and separatory procedures were carried out in air. The compounds  $[\{\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ ,<sup>15</sup>  $[\{\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)\}_2]$ ,<sup>15</sup>  $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)\}_2]$ ,<sup>16</sup> and  $[\{\text{OsCl}_2(\eta^6\text{-C}_6\text{Me}_6)\}_2]$ <sup>4</sup> were prepared according to literature methods. Preparative thin-layer chromatography (t.l.c.) was carried out using 0.75-mm layers of silica gel G (Fluka, type GF254) made from water slurries on glass plates of dimensions 20 × 20 cm<sup>2</sup>, followed by drying in

air at 100 °C for >2 d. Preparative high-pressure liquid chromatography (h.p.l.c.) was carried out using a Lichrosorb Si60 (7 μm) column (Knauer) of dimensions 25 cm × 16 mm diameter, CH<sub>2</sub>Cl<sub>2</sub>-hexane (2:3) as liquid phase, retention times  $R_f$  being given for a flow rate of 10 cm<sup>3</sup> min<sup>-1</sup>, detection by ultraviolet absorption at 254 nm. Compounds (1)–(5) all exhibited *m/e* (max.) corresponding to their calculated formula molecular ions in their 70-eV electron-impact mass spectra (AEI/Kratos MS30 instrument, solid-sample introduction probe).

**Nuclear Magnetic Resonance Spectroscopy.**—N.m.r. spectroscopy was performed at 9.4 T using Bruker AM400 instrumentation, the techniques of  $[^{11}\text{B}\text{-}^{11}\text{B}]$ -COSY,<sup>7</sup>  $[^1\text{H}\text{-}^{11}\text{B}]$ -COSY,<sup>8</sup> and  $^1\text{H}\text{-}\{^{11}\text{B}\}$ <sup>17</sup> spectroscopy being essentially as described and illustrated in other recent papers from our laboratories.<sup>18–21</sup> For the *nido*-5-metalladecaboranes (1)–(4) the incidence and relative intensities of the  $[^{11}\text{B}\text{-}^{11}\text{B}]$ -COSY and  $[^1\text{H}\text{-}^{11}\text{B}]$ -COSY correlations were essentially as described elsewhere for  $[5-(\eta^5\text{-C}_5\text{Me}_5)\text{-nido-5-CoB}_9\text{H}_{13}]$ <sup>7</sup> and compound (2)<sup>8</sup> respectively, with those for compound (5) similarly mirroring those reported previously<sup>6</sup> for  $[6-(\eta^5\text{-C}_5\text{Me}_5)\text{-nido-6-RhB}_9\text{H}_{13}]$ . Chemical shifts ( $\delta$ ) are given in p.p.m. positive to high frequency (low field) of  $\approx 100$  (SiMe<sub>4</sub>) for  $^1\text{H}$  and  $\approx 31.083\,971$  MHz [nominally BF<sub>3</sub>·OEt<sub>2</sub> in CDCl<sub>3</sub>]<sup>9</sup> for  $^{11}\text{B}$ ,  $\approx$  being defined as in ref. 22.

**Preparation of  $[5-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-5-RuB}_9\text{H}_{13}]$  (1).**—A sample of *N,N,N',N'*-tetramethylnaphthalene-7,8-diamine (tmnd) (12.9 mg, 600 μmol) was added to a degassed solution of B<sub>10</sub>H<sub>14</sub> (73 mg, 600 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (ca. 40 cm<sup>3</sup>) and stirred for 15 min at room temperature to generate a yellow solution of [Htmnd][B<sub>10</sub>H<sub>13</sub>].  $[\{\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)\}_2]$  (100 mg, 150 μmol) was then added and the solution stirred for 4.5 h during which time the initially red solution turned yellow. The solution was reduced to ca. 5 cm<sup>3</sup> (rotary evaporator, 40 °C bath, water pump) and the product purified by repeated preparative t.l.c., development with *n*-hexane-CH<sub>2</sub>Cl<sub>2</sub> (80:20) giving  $[5-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-5-RuB}_9\text{H}_{13}]$  (1) as a yellow crystalline solid ( $R_f$  0.61, 21 mg, 18.7%) (Found: C, 39.8; H, 7.7. C<sub>12</sub>H<sub>31</sub>B<sub>9</sub>Ru requires C, 38.6; H, 8.4%). Other coloured products were apparent from t.l.c., but these were present in quantities insufficient for reasonable characterisation. Colourless components present contained B<sub>10</sub>H<sub>14</sub> and  $[\text{B}_9\text{H}_{14}]^-$  (identified as such by n.m.r.).

**Preparation of  $[5-(\eta^5\text{-C}_5\text{Me}_5)\text{-nido-5-RhB}_9\text{H}_{13}]$  (2).**—A sample of B<sub>10</sub>H<sub>14</sub> (40 mg, 320 μmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 cm<sup>3</sup>), and then tmnd (140 mg, 520 μmol) was added. The solution was stirred for 10 min at room temperature to generate yellow [Htmnd][B<sub>10</sub>H<sub>13</sub>], then  $[\{\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)\}_2]$  (100 mg, 160 μmol) was added, and stirring continued for a further 30 min, during which time the colour changed from red to bright yellow. The more volatile components were removed (rotary evaporator, 40 °C, water pump), the solid residue redissolved in CH<sub>2</sub>Cl<sub>2</sub> (ca. 5 cm<sup>3</sup>) and the products separated and purified by repeated preparative t.l.c., development with light petroleum (b.p. 60–80 °C)-CH<sub>2</sub>Cl<sub>2</sub> (20:80) giving  $[5-(\eta^5\text{-C}_5\text{Me}_5)\text{-nido-5-RhB}_9\text{H}_{13}]$  (2) as a yellow crystalline solid ( $R_f$  0.78, 23 mg, 20.7%), and compounds identified as  $[9,9'\text{-}\{5-(\eta^5\text{-C}_5\text{Me}_5)\text{-nido-5-RhB}_9\text{H}_{12}\}_2\text{O}]$  ( $R_f$  0.54, 32 mg, 27%) and  $[9\text{-OH-}5-(\eta^5\text{-C}_5\text{Me}_5)\text{-nido-5-RhB}_9\text{H}_{12}]$  ( $R_f$  0.18, 47 mg, 40%) as described elsewhere.<sup>5</sup>

**Preparation of  $[5-(\eta^6\text{-C}_6\text{Me}_6)\text{-nido-5-OsB}_9\text{H}_{13}]$  (3).**—A sample of tmnd (47 mg, 220 μmol) was added to a degassed solution of B<sub>10</sub>H<sub>14</sub> (27 mg, 220 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (ca. 50 cm<sup>3</sup>) and stirred for 15 min at room temperature to generate a yellow

solution of [Htmnd][B<sub>10</sub>H<sub>13</sub>]. To this was added [ $\{\text{OsCl}_2(\eta^6\text{-C}_6\text{Me}_6)_2\}$ ] (62 mg, 73  $\mu\text{mol}$ ) and the solution stirred for a further 18 h. It was then filtered over SiO<sub>2</sub> with CH<sub>2</sub>Cl<sub>2</sub> to remove chromatographically immobile components. The solution was reduced to ca. 5 cm<sup>3</sup> (rotary evaporator, 40 °C, water pump), and the mixture applied to preparative t.l.c. plates. Development with CH<sub>2</sub>Cl<sub>2</sub> revealed two main components that were purified by repeated t.l.c. to yield [5-( $\eta^6\text{-C}_6\text{Me}_6$ )-*nido*-5-OsB<sub>9</sub>H<sub>13</sub>] (3) as a yellow air-stable crystalline solid (*R<sub>f</sub>* 0.85, 15 mg, 22%) and a compound identified<sup>23</sup> as [6-(OH)-5-( $\eta^6\text{-C}_6\text{Me}_6$ )-*nido*-5-OsB<sub>9</sub>H<sub>12</sub>] (4) (*R<sub>f</sub>* 0.47, 4 mg, 5.7%), also a yellow air-stable crystalline solid. Measured n.m.r. parameters in CD<sub>2</sub>Cl<sub>2</sub> at 294 K {(position)  $\delta(^{11}\text{B})/\text{p.p.m.}$  [ $^1J(^{11}\text{B}-^1\text{H})/\text{Hz}$ ],  $\delta(^1\text{H})/\text{p.p.m.}$ } as follows: (1) +19.8 [135], +3.32; (2) -22.7 [139], +1.10; (3) -2.3 [138], +2.04; (4) -44.8 [145], -0.06; (5) Os [-], C<sub>6</sub>Me<sub>6</sub> at +2.25; (6) +49.8 [-], OH at +5.04; (7) -17.7 [138, 62], +2.86; (8) +8.2 [135], +3.20; (9) -8.9 [173] +2.90, (10) -7.5 [144] +2.38; in addition bridging atoms  $\delta(^1\text{H})/\text{p.p.m.}$  as follows: (5,6) -17.25, (6,7) -0.97, (8,9) -2.50 (9,10) -2.04. Assignments by [ $^{11}\text{B}-^{11}\text{B}$ ]-COSY, [ $^1\text{H}-^1\text{H}$ ]-COSY, and  $^1\text{H}-\{^{11}\text{B}(\text{selective})\}$  spectroscopy {cf. [6-(OMe)-5-( $\eta^6\text{-C}_6\text{Me}_6$ )-*nido*-5-RuB<sub>9</sub>H<sub>12</sub>] in ref. 24}. T.l.c. also revealed coloured minor products but these were not present in amounts sufficient to permit characterisation.

*Preparation of [5-( $\eta^5\text{-C}_5\text{Me}_5$ )-*nido*-5-IrB<sub>9</sub>H<sub>13</sub>] (5) and [6-( $\eta^5\text{-C}_5\text{Me}_5$ )-*nido*-6-IrB<sub>9</sub>H<sub>13</sub>] (6).*—A solution of [NBu<sup>n</sup>]<sub>4</sub>[B<sub>9</sub>H<sub>14</sub>] (440 mg, 1.25 mmol) and [ $\{\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)_2\}$ ] (0.50 g, 0.63 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (ca. 45 cm<sup>3</sup>) was stirred for 1 h, during which time a slight deepening of the initial orange colour was observed. The mixture was then filtered through silica and the filtrate evaporated to dryness (rotary evaporator, ambient temperature bath, water pump pressure). The solid residue was then dissolved in CH<sub>2</sub>Cl<sub>2</sub>-hexane (1:1; ca. 5 cm<sup>3</sup>), the resulting solution then being injected batchwise into the h.p.l.c. apparatus. Two principal fractions, with retention times *R<sub>t</sub>* = 3.1 and 6.7 min, were obtained for each injection. Slow reduction in volume of each combined fraction (rotary evaporator, ambient temperature bath) resulted in the precipitation of yellow and orange solids respectively. The yellow solid was found to be [5-( $\eta^5\text{-C}_5\text{Me}_5$ )-*nido*-5-IrB<sub>9</sub>H<sub>13</sub>] (5) (30 mg, 6%) (Found: C, 27.0; H, 6.25. Calc.: C, 27.4; H, 6.45%), and the orange one [6-( $\eta^5\text{-C}_5\text{Me}_5$ )-*nido*-6-IrB<sub>9</sub>H<sub>13</sub>] (6) (300 mg, 55%) (Found: C, 27.4; H, 6.35. Calc.: C, 27.4; H, 6.45%). Measured n.m.r. parameters in CDCl<sub>3</sub> at 294 K {(position)  $\delta(^{11}\text{B})/\text{p.p.m.}$  [ $^1J(^{11}\text{B}-^1\text{H})/\text{Hz}$ ],  $\delta(^1\text{H})/\text{p.p.m.}$ } as follows: (1) (3) +11.0 [138], +4.46; (2) -24.7 [144], -0.12; (4) -29.8 [150], +2.52; (5) (7) +20.8 [149], +5.03; (6) Ir [-], C<sub>5</sub>Me<sub>5</sub> at +2.12; (8) (10) -2.9 [154], +2.84; (9) +7.5 [165], +3.56; in addition bridging atoms  $\delta(^1\text{H})/\text{p.p.m.}$  as follows: (5,6) (6,7), -10.81; (8,9) (9,10), -3.45. If instead of h.p.l.c. repetitive t.l.c. was used for product purification, then only one major component was isolated; this was identified as compound (5) [*R<sub>f</sub>* 0.4 using CH<sub>2</sub>Cl<sub>2</sub>-hexane (3:2) as liquid phase] (220 mg, 40%). The chromatographic experiments also revealed trace quantities of other coloured products, but these were not investigated.

## Acknowledgements

We thank the S.E.R.C. for support and for maintenance grants (to M. B. and K. N.), Mr. A. Hedley and his staff for microanalyses, and Mr. Darshan Singh for mass spectrometry.

## References

- S. Heřmánek, T. Jelínek, J. Plešek, B. Štíbr, J. Fusek, and E. Mareš, Session Lectures of the Sixth International Meeting of Boron Chemistry, IMEBORON VI, Bechyně, Czechoslovakia, 1987, in 'Boron Chemistry,' ed. S. Heřmánek, World Scientific, Singapore, 1987, pp. 26-73.
- M. A. Beckett, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 795.
- N. N. Greenwood, J. D. Kennedy, I. Macpherson, and M. Thornton-Pett, *Z. Anorg. Allg. Chem.*, 1986, **540/541**, 45.
- M. Bown, X. L. R. Fontaine, N. N. Greenwood, and J. D. Kennedy, *J. Organomet. Chem.*, 1987, **325**, 233.
- X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, P. MacKinnon, and M. Thornton-Pett, unpublished work.
- X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 547.
- T. L. Venable, W. C. Hutton, and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, **106**, 29.
- X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1986, 779.
- See, for example, J. D. Kennedy, 'Boron,' ch. 8, in 'Multinuclear NMR,' ed. J. Mason, Plenum, London and New York, 1987, pp. 221-258 and refs. therein.
- R. P. Micciche, J. J. Briguglio, and L. G. Sneddon, *Inorg. Chem.*, 1984, **23**, 3992.
- J. Bould, N. N. Greenwood, and J. D. Kennedy, *J. Organomet. Chem.*, 1983, **249**, 11.
- N. N. Greenwood, J. D. Kennedy, J. D. Woolins, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1985, 2397.
- S. R. Bunkhall, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, unpublished work.
- G. Ferguson, X. L. R. Fontaine, J. D. Kennedy, Faridoun, and T. R. Spalding, *J. Chem. Soc., Dalton Trans.*, in the press.
- J. W. Kong, K. Mosely, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.
- M. A. Bennett, T. N. Huang, T. W. Matheson, and A. K. Smith, *Inorg. Synth.*, 1982, **21**, 75.
- J. D. Kennedy and N. N. Greenwood, *Inorg. Chim. Acta*, 1980, **38**, 529.
- X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1987, 1573.
- X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 2417.
- 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.
- X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and P. MacKinnon, *J. Chem. Soc., Dalton Trans.*, 1988, 1785.
- W. McFarlane, *Proc. R. Soc. London, Ser. A*, 1986, **306**, 185.
- M. Bown, Ph.D. Thesis, University of Leeds, 1987; M. Bown and X. L. R. Fontaine, unpublished work.
- M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 925.

Received 21st January 1988; Paper 8/00225H