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Eleven-vertex polyhedral metalladicarbaborane chemistry. Reactions of neutral *nido*-5,6-$C_2B_8H_{12}$ and the [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ anion to give formally *closo* isomeric 1-(arene) and 1-(cyclopentadiene)-1,2,4- and 1,2,3-metalladicarbaundecaboranes, and some substituent chemistry. Chiral separations, and crystal and molecular structures of [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] and [2-Me-1-(η^5-C_5Me_5)-1,2,3-$RhC_2B_8H_9$]

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It is a pleasure and a privilege for the authors to be able to contribute this paper to the Sheldon Shore 70th Birthday Special Edition of the Journal of Organometallic Chemistry, in recognition of Professor Shore's astute contributions to the area of polyhedral boron-containing cluster chemistry that have been, and will continue to be, an omnipresent inspiration and example for successive generations of boron cluster chemists.

Abstract

Reactions between *nido*-5,6-$C_2B_8H_{12}$ (**1**) and the organometallic halides [{$MLCl_2$}$_2$] (**2**) [where {ML} = {Ru(η^6-C_6Me_6)} (**2a**), {Ru(η^6-*p*-$MeC_6H_4^{i}Pr$)} (**2b**), {Rh(η^5-C_5Me_5)} (**2c**), and {Os(η^6-*p*-$MeC_6H_4^{i}Pr$)} (**2d**)] in the presence of *N*,*N*,*N′*,*N′*-tetramethylnaphthalene-1,8-diamine (tmnda) in dichloromethane or chloroform have generated a series of the corresponding metalladicarbaboranes [1-L-1,2,4-$MC_2B_8H_{10}$] (**3**, *closo* 11-vertex numbering system) [where {ML} = {Ru(η^6-C_6Me_6)} (**3a**), {Ru(η^6-*p*-$MeC_6H_4^{i}Pr$)} (**3b**), {Rh(η^5-C_5Me_5)} (**3c**), and {Os(η^6-*p*-$MeC_6H_4^{i}Pr$)} (**3d**)] in yields of 48–94%. The substituted species, [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**5-Br-3a**) and [**7-Br-1**-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**7-Br-3a**) have been obtained from a similar reaction involving [7-Br-*nido*-5,6-$C_2B_8H_{11}$] (**7-Br-1**) (combined yield 75%, separated by preparative HPLC). Each of the compounds **5-Br-3a** and **7-Br-3a** has been resolved into its enantiomers by use of chiral HPLC separation techniques. Analogous reactions between [{$MLCl_2$}$_2$] (**2**) and the [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ anion (species **4**$^{2-}$) have produced a series of the isomeric symmetrical complexes [1-L-*closo*-1,2,3-$MC_2B_8H_{10}$] (**5**) [where {ML} = {Ru(η^6-C_6Me_6)} (**5a**), {Ru(η^6-*p*-$MeC_6H_4^{i}Pr$)} (**5b**), {Rh(η^5-C_5Me_5)} (**5c**) and {Os(η^6-*p*-$MeC_6H_4^{i}Pr$)} (**5d**)]; the 2-methyl substituted compound [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (**2-Me-5c**) has been prepared similarly using the [6-Me-*nido*-$C_2B_8H_9$]$^{2-}$ anion (species **2-Me-4**$^{2-}$) as the starting dicarbaborane. All these compounds are characterised by mass spectrometry and ^{11}B- and ^{1}H-NMR spectroscopy. Single-crystal X-ray diffraction studies have been carried out on compounds **5-Br-3a** and **2-Me-5c** as two representative examples of the compounds in series **3** and in series **5**. The {MC_2B_8} clusters of compounds **3** have four-membered open faces, generating an '*isonido*' geometry, whereas those of compounds **5** approximate more to the classical *closo* cluster geometry. Thermolyses of the {1,2,4-MC_2B_8} compounds **3a**–**3d** cleanly generate their corresponding {1,2,3-MC_2B_8} isomers **5a**–**5d**. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metalladicarbaborane; Eleven-vertex polyhedral; Isonido geometry; Optical resolution of boron cluster

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1. Introduction

Our two laboratories have a continuing and developing interest in the synthesis, NMR properties, structural characterisation, and reactions of the related pair of ten-vertex dicarbaboranes consisting of neutral 5,6-*nido*-$C_2B_8H_{12}$ (**1**) [1–4] and the [*nido*-6,9-$C_2B_8H_{10}]^{2-}$ anion (species $\mathbf{4}^{2-}$), and their derivatives [5,6]. Here we report on reactions resulting in metalladicarbaborane formation.

In the field of metallacarbaborane chemistry, the neutral species **1** and its anion [*nido*-5,6-$C_2B_8H_{11}]^-$ (species $\mathbf{1a}^-$) have been previously used in the synthesis of a variety of eleven-vertex metalladicarbaborane cluster compounds. These include a set of compounds that were initially formulated as closed cluster species [1-L_n-*closo*-1,2,4-$MC_2B_8H_{10}$] [7–10] but which in fact have quadrilateral {M(1)C(2)C(4)B(7)} open faces (see structure **3** in Scheme 1; also Fig. 3 below) and therefore can be regarded as of *isonido* geometry [9]. These have been recognised for $\{ML_n\} = \{Ru(C_6H_6)\}$ [8], $\{IrH(PMe_2Ph)_2\}$ [7], $\{IrH(PPh_3)_2\}$ [9], $\{IrH(PMe_3)_2\}$ [10], and $\{IrH(AsMe_2Ph)_2\}$ [7]. In this reaction category also, it has been reported that the 5,6-dimethyl derivative of compound **1**, viz. [5,6-Me_2-*nido*-5,6-$C_2B_{10}H_{10}$] (**5,6-Me$_2$-1**) affords [2,4-Me_2-1-L-1,2,4-$MC_2B_8H_8$], where $\{ML\} = \{Ru(\eta^6\text{-}C_6Me_6)\}$, $\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$, $\{Rh(\eta^5\text{-}C_5Me_5)\}$, and $\{Os(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$ [11,12], which also adopt the *isonido* cage geometry as in structure **3**. It should be noted here that alternative routes exist for the formation of this type of compound, for example the cobaltadicarbaborane [1-(η^5-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$] [13,14] has been prepared by the elimination of one {BH}vertex from 12-vertex [1-(η^5-C_5Me_5)-*closo*-3,1,2-$CoC_2B_9H_{11}$]. Also, it may be noted that a series of compounds of more conventional [15–19] *nido* eleven-vertex geometry has also been prepared from compound **1**. These include [9-H-9,9-$(PEt_3)_2$-*nido*-9,7,8-$PtC_2B_8H_{11}$] [20,21], [9-(η^5-C_5H_5)-*nido*-9,7,8-$NiC_2B_8H_{11}$] [22], [9,9,9-L_3-10,11-μH-*nido*-9,7,8-$RhC_2B_8H_9$] (where L = PEt_3 and PPh_3) [7], and [9,9,9-L_3-10,11-μH-*nido*-9,7,8-$RhC_2B_8H_9$] [where $PR_3 = PEt_3$, PPh_3, and P(p-tolyl)$_3$] [7]. It may also be noted here that the bridged *nido* ten-vertex complex [μ-6,9-$\{Al(OEt_2)Et\}$-*nido*-6,9-$C_2B_8H_{10}$] [23] (approximate geometry as in schematic **5**) and its double-cluster anionic analogue [μ-6,9-Al-(*nido*-$C_2B_8H_{10})_2]^-$ [24] are also formed from anion $\mathbf{1}^-$, though this now involves a cluster rearrangement. Prepared from anion $\mathbf{1}^-$ there is also another series of compounds [25], formulated as *arachno* eleven-vertex $\{MC_2B_8\}$ species, of general formulation [$M(PPh_3)_n$(5,6-$C_2B_8H_{11}$)], where $\{M(PPh_3)_n\} = \{Au\ (PPh_3)\}$, $\{Cu\ (PPh_3)\}$, and $\{Ag(PPh_3)_2\}$, which also include the structurally characterised dimeric compound $[(PPh_3)Ag(C_2B_8H_{11})]_2$.

The symmetrical anion [*nido*-6,9-$C_2B_8H_{10}]^{2-}$ (species $\mathbf{4}^{2-}$) [5,6] has similarly been used, now to synthesise a series of eleven-vertex dimetallacarbaboranes **5**, of which the geometries now approximate more closely to the classical eleven-vertex *closo*-type as in schematic **5** in Scheme 1 (See also Fig. 2 below). These include species [1-L_n-*closo*-1,2,3-$MC_2B_8H_{10}$], where $\{ML_n\} = \{Co(\eta^5\text{-}C_5H_5)\}$ [26],[1] $\{Pt(PPh_3)_2\}$, $\{Pt(SMe_2)_2\}$, {Ni(*cis*-1,2-dimethylaminocyclohexane)} [6], $\{Pt(PMe_2Ph)_2\}$ [27,28], $\{Pt[P(OMe)_3]_2\}$ [29] and naked Sn [30]. The eleven-vertex formal C_{2v} geometry can accommodate at least five categories of electronic structure [28,31]. Within the set of metalladicarbaboranes just listed, three categories are distinguished. The compounds with $\{ML_n\} = \{Pt(PPh_3)_2\}$, $\{Pt(SMe_2)_2\}$ and {Ni(*cis*-1,2-dimethylaminocyclohexane)} were originally formulated [6] as bridged *nido* ten-vertex species [μ-6,9-(ML_n)-*nido*-6,9-$C_2B_8H_{10}$]. This simple bridged *nido* structure (the first category) has been confirmed for $\{ML_n\} = \{SnMe_2\}$ [29] and $\{Al(OEt_2)Et\}$ [23]. However, the $\{Pt(PPh_3)_2\}$, $\{Pt(SMe_2)_2\}$ and $\{Pt[P(OMe)_3]_2\}$derivatives, together with the nickel species and the naked Sn compound, are thought to approximate more to true *closo* (the second category) [28]. By contrast, the $\{Pt(PMe_2Ph)_2\}$ species is in a third category, with a closed cluster structure that is now more compact than in the two other categories just mentioned, and with what may now be a *nido* electron count [28,31]. Interestingly, the $\{Pt[P(OMe)_3]_2\}$ species can also be induced to adopt this third type of configuration by the utilisation of the steric effect of a C(2)-phenyl substituent [28]. Again, alternative routes exist for the formation of compounds of this general {1,2,3-MC_2B_8} type of configuration, with (a) [1-(η^5-C_5H_5)-1,2,3-$CoC_2B_8H_{10}$] and the structurally analogous double-cluster anion [1,1′-Co(2,3-$CoC_2B_8H_{10})_2]^-$ being obtained from polyhedral-expansion reactions from the neutral [*closo*-1,6-$C_2B_8H_{10}$] [32,33], with (b) the aluminium compounds, as mentioned in the previous paragraph, being obtained from neutral [*nido*-5,6-$C_2B_8H_{12}$] via cluster rearrangement [23,24], and (c) with [1-(η^5-C_5H_5)-1,2,3-$CoC_2B_8H_{10}$] obtainable by thermal rearrangement from its 1,2,4 isomer [33].

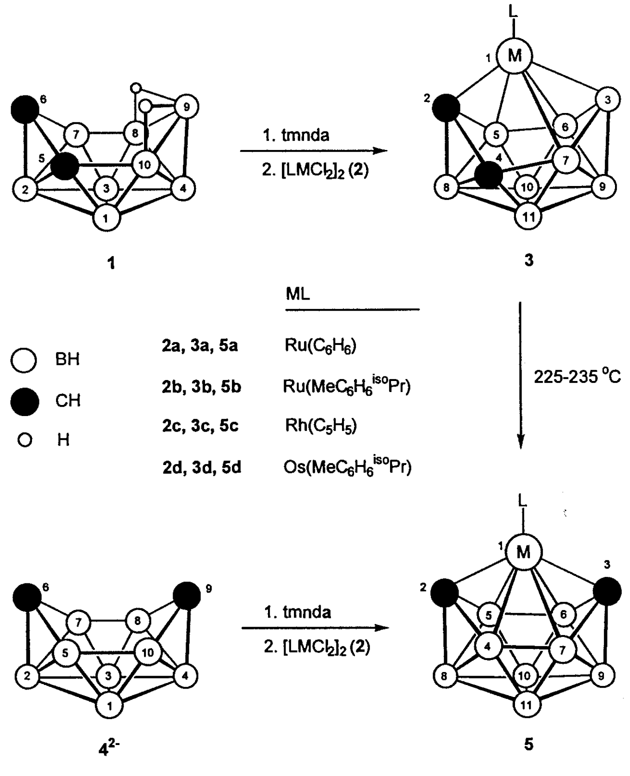
The aim of the work reported in this present paper is to further develop a coherent systematic metalladicarbaborane chemistry based on the neutral dicarbaborane 5,6-*nido*-$C_2B_8H_{12}$ (**1**) and the [*nido*-6,9-$C_2B_8H_{10}]^{2-}$ anion (species $\mathbf{4}^{2-}$), by the preparation of a more extended series of compounds of basic structural types **3** and **5** using ruthenium, rhodium and osmium as the basis of the metal centres. Here, we concentrate on the synthesis of basic parent (i.e. cage-unsubstituted) compounds, although some simple extensions to substitution chemistry are also reported. Extensive substituent modification is known to induce modifications in structure, arising from both electronic and steric effects

[28,29,31], which we currently investigate further and hope to report on in due course. The general structures and numbering schemes of compounds discussed in this work are in Scheme 1 below.

2. Experimental

2.1. General

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques [34], although some subsequent operations, e.g. analytical thin layer chromatography (TLC) and preparative TLC, were carried out in air. The starting neutral carbaboranes [*nido*-5,6-$C_2B_8H_{12}$] (**1**) and [7-Br-*nido*-5,6-$C_2B_8H_{11}$] (**7-Br-1**) [2], together with the sodium salts of the anions [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ (species **4**$^{2-}$) [5] and [6-Me-*nido*-6,9-$C_2B_8H_9$]$^{2-}$ (species **6-Me-4**$^{2-}$) [28], were prepared by literature methods. Hexane and dichloromethane were distilled from calcium hydride, and chloroform from phosphorus pentoxide, prior to use. Other compounds were of reagent or analytical grade and were used as purchased from commercial sources. All evaporations of solvents were carried out using standard rotary evaporation techniques and vacuum filtrations were performed using a standard Schlenk apparatus.



Scheme 1.

2.2. Chromatography

Preparative thin-layer chromatography (TLC) was carried out using silica gel (Fluka, type GF 254) as the stationary phase on plates of dimensions 200 × 200 × 1 mm, made on glass formers from aqueous slurries followed by drying in air at 80°C. The purity of individual chromatographic fractions was checked by analytical TLC on Silufol (Kavalier, silica gel G on aluminium foil; detection by diiodine vapour followed by 2% aqueous $AgNO_3$ spray). For compounds **5-Br-3a** and **7-Br-3a** preparative high-pressure liquid chromatography (HPLC) separations were performed using a stainless-steel column [250 × 25 mm internal diameter; Separon SGX (7 μm, Tessek Ltd., Prague); mobile phase 78:22 hexanes–CH_2Cl_2; flow rate 30 $cm^3\ min^{-1}$; detection by UV at 254 nm]. Chiral HPLC [35,36] was performed on a directly-bonded β-cyclodextrin column (250 × 8 mm internal diameter; mobile phase 68:32 MeOH–H_2O; flow rate 0.8 $cm^3\ min^{-1}$; detection by UV at 270 nm) used essentially as detailed in recent papers on this technique from our laboratories [37–44]. Components were collected from the start to the top of the detector response peak for the initially eluted enantiomer, and from the top of the second peak to the end for the second enantiomer. The HPLC capacity factor k' was defined as in Ref. [45], with HPLC selectivity factor α and resolution R_s defined as in Ref. [36].

2.3. Physical measurements and spectroscopy

Melting points were measured in sealed capillaries under nitrogen and are uncorrected. Low-resolution mass spectra were obtained using JEOL HP-5985 or VG Autospec instruments (E.I. ionisation at 70 eV). ^1H- and ^{11}B-NMR spectroscopy was performed at 2.35, 9.4, and 11.75 T on JEOL FX100, Bruker AM 400, and Varian XL-500 instruments, respectively. The [^{11}B–^{11}B]-COSY and ^1H-{^{11}B(selective)} NMR experiments were essentially as described in other recent papers from our laboratories [46,47]. Chemical shifts δ are given in ppm to high frequency (low field) of $\Xi = 32.083971$ MHz (nominally $F_3B.OEt_2$ in $CDCl_3$) for ^{11}B (quoted ± 0.5 ppm) and $\Xi = 100$ MHz ($SiMe_4$) for ^1H (quoted ± 0.05 ppm), Ξ being defined as in Ref. [48]. Solvent resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B–^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution 8 Hz and are given in hertz. Circular dichroism (CD) spectra were measured for solutions in MeOH on an Auto Dichrograph V instrument (Jobin Yvon) using quartz cells with optical path-lengths of 1 cm.

Table 1
Properties of the products from reactions between *nido*-5,6-$C_2B_8H_{12}$ (compound **1**) and organometallic complexes $[LMCl_2]_2$ (compounds **2a**–**2d**)

Reaction conditions			Products			
Starting complex	Time (h)	Product (s)	Yield (%)	M.p. (°C)	R_F	m/z_{max}
2a	18	**3a**	94	ca. 200 [a]	0.16 [b], 0.43 [c]	386
2a [d]	1	**5-Br-3a**	60		0.50 [e]	466
		7-Br-3a	15			466
2b	1.5	**3b**	89	ca. 190 [a]	0.18 [b], 0.40 [c]	358
2c	1	**3c**	30	ca. 170 [a]	0.67 [b]	360
2d	24	**3d**	48	153	0.30 [b]	446

[a] Approximate transition temperature (to give compounds of type **5**) without melting.

[b] 50% hexane in CH_2Cl_2.

[c] 100% $CHCl_3$.

[d] The substituted compound **7-Br-1** used as the starting carbaborane; products **5-Br-3a** and **7-Br-3a** separated by preparative HPLC.

[e] 50% hexane in $CHCl_3$.

*2.4. General preparation of 1-(η^6-Arene) and 1-η^5-cyclopentadiene)-closo-1,2,4-metalladicarbaundecaboranes (**3**)*

Typically, *N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine (tmnda) (214 mg, 1 mmol) was added to a solution of [*nido*-5,6-$C_2B_8H_{12}$] (**1**) (61 mg, 0.5 mmol) in $CHCl_3$ or CH_2Cl_2 (50 cm^3) and the solution was stirred for ca. 10 min. The appropriate organometallic halide $[MCl_2L]_2$ (**2a**, **2b**, **2c** or **2d**; 0.25 mmol) was then added, and the mixture was stirred at room temperature (r.t.) for between one and 24 h. (see Table 1), whereupon a dark orange colour developed. The mixture was then filtered through a short column of silica gel (TLC grade, ca. 2.5 × 5 cm) and the filtrate evaporated to dryness. The residue was washed with hexane (ca. 50 cm^3) and the remaining orange solid subjected to column or preparative TLC chromatography, using the solvent mixtures as in Table 1 as the liquid phases. The main dark orange band was isolated by evaporation (column chromatography) or by extraction with CH_2Cl_2 followed by evaporation (TLC separation). The crude products were then crystallised from a concentrated CH_2Cl_2 solution that was over-layered by a ca. twofold amount of hexane, to obtain dark yellow or dark orange crystals (yields 48–94%, see Table 1), which were identified as the appropriate compounds **3a**, **3b**, **3c** or **3d** by mass spectrometry and NMR spectroscopy (see Tables 1 and 5).

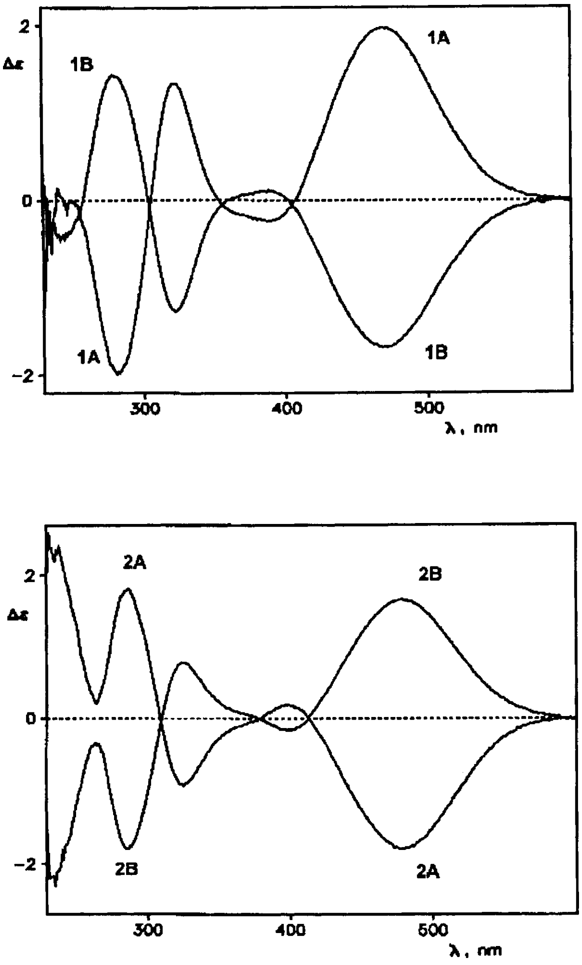


Fig. 1. CD spectra in methanol solution. Upper diagram: the first-eluted enantiomer (1A) (260μM) and the second-eluted enantiomer (1B) (300 μM) of [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**5-Br-3a**). Lower diagram: the first-eluted enantiomer (2A) (220 μM) and the second-eluted enantiomer (2B) (260 μM) of [**7-Br-1**-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**7-Br-3a**). It is of interest that the first-eluted enantiomers 1A and 2A of the two isomeric components **5-Br-3a** and **7-Br-3a** exhibit opposite orientations of their Cotton curves.

*2.5. Preparation of 5-bromo-1-(η^6-hexamethylbenzene)-closo-1,2,4-metalladicarbaundecaborane (**5-Br-3a**) and 7-bromo-1-(η^6-hexamethylbenzene)-closo-1,2,4-metalladicarbaundecaborane (**7-Br-3a**), and their chiral resolution*

The mixture of compounds **5-Br-3a** and **7-Br-3a** (consisting of ca. 80 mol% of **5-Br-3a** and 20 mol% of **7-Br-3a**, as assessed by integrated ^{11}B-NMR spectro-

Table 2
Products from reactions between [*nido*-6,9-$C_2B_8H_{10}$]Na_2 (Na^+ salt of compound **4^{2-}**) and organometallic complexes [$LMCl_2$]$_2$ (**2a**–**2d**)

Reaction conditions		Products			
Starting complex	Time/h	Product(s)	Yield/%	R_F [a]	m/z_{max} [b]
2a	12	**5a**	45	0.11	386
2b	18	**5b**	39	0.13	358
2c	4	**5c**	68	0.18	360
2c	4	**2-Me-5c** [c]	64	0.20	374
2d	74	**5d**	54	0.20	446

[a] 50% hexane in CH_2Cl_2.

[b] EI mode, 70 eV.

[c] The substituted anion **6-Me-4^{2-}** used as the starting carborane.

scopy) was prepared as in the preceding experiment (combined yield 75%), using [7-Br-*nido*-5,6-$C_2B_8H_{11}$] (**7-Br-1**) as the starting carbaborane in place of unsubstituted compound 1. A sample of this mixture (ca. 200 mg) was separated into the two individual compounds **5-Br-3a** and **7-Br-3a** (pure yields 150 and 35 mg, respectively) by preparative HPLC (k' values 10.8 and 11.9, respectively; under the same conditions k' was 1.6 for nitrobenzene as external standard). A small sample of each of the pure compounds **5-Br-3a** and **7-Br-3a** thus separated was resolved into its enantiomers by repeated chiral HPLC (concentration 0.25 mg cm^{-3}; injection volume 80 μl). For the two enantiomers of compound **5-Br-3a**, the capacity factors k'_A and k'_B for the first and second eluted isomers A and B were 4.27 and 4.70 respectively, with selectivity $\alpha = 1.09$ and resolution $R_s = 0.85$. For the two enantiomers of compound **7-Br-3a** the values were $k'_A = 3.66$, $k'_B = 4.11$, $\alpha = 1.12$ and $R_s = 1.0$. For each of these chiral separations, the eluents from 15 injections were collected together and evaporated to dryness. The integrity of the components of the individual enantiomeric pairs was assessed by analytical HPLC on the same column, and also by their equal and opposite CD spectra (concentration ca. 0.1 mM in methanol, see Fig. 1). For each of compounds **5-Br-3a** and **7-Br-3a** the later eluting enantiomer B was assessed as being ca. 10% less enantiomerically pure than the initially eluted isomer A.

*2.6. Thermal rearrangement of 1-(η^6-arene and η^5-cyclopentadiene)-closo-1,2,4-metalladicarbaundecaboranes (**3a**, **3b**, **3c**, and **3d**) to give their corresponding 1,2,3-isomers (**5a**, **5b**, **5c** and **5d**)*

Each of the individual compounds **3a**, **3b**, **3c**, and **3d** (50 μmol) was sealed into a thick-wall glass capillary (internal diameter ca. 2 mm) and heated at 225–235°C for 10 min. The tube was then opened and the contents subjected to preparative TLC using 50:50 hexane–CH_2Cl_2 as the liquid phase. In each case one predominant yellow product was obtained. These individual yellow TLC bands were isolated by extraction with CH_2Cl_2 and crystallised from concentrated CH_2Cl_2 solutions that were over-layered by ca. twofold amounts of hexane to obtain orange crystals of the *closo*-1,2,3-metalladicarbaundecaboranes **5a**–**5d** in yields of 78, 80, 75 and 79% respectively, identified by mass spectrometry and NMR spectroscopy (see Tables 2 and 6).

*2.7. General preparation of the 1-(η^6-arene) and the 1-(η^5-cyclopentadiene)-closo-1,2,3-metalladicarbaundecaboranes (**5a-5d**) from the [nido-6,9-$C_2B_8H_{10}$]$^{2-}$ anion (species **4^{2-}**)*

Typically, the appropriate starting organometallic complex [MCl_2L]$_2$ (**2a**, **2b**, **2c** or **2d**) (250 μmol), was added to a stirred suspension of the sodium salt of the anion [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ (species **4^{2-}**) (84 mg, 500 μmol) in CH_2Cl_2 (30 cm^3), and the resulting mixture stirred at room temperature (r.t.) for between one and 12 h. (see Table 2), whereupon a yellow colour developed. The mixture was then filtered through a short column of silica gel (TLC grade; ca. 2.5 × 5 cm) and the filtrate was evaporated to dryness. The residue was washed with hexane (ca. 25 cm^3) and the remaining orange solid subjected to preparative TLC using 50:50 hexane–CH_2Cl_2 as the liquid phase. In each case the main yellow component was isolated by extraction with CH_2Cl_2 and the crude product crystallised from a concentrated CH_2Cl_2 solution that was over-layered by a ca. twofold amount of hexane, to obtain yellow crystals which were identified as the appropriate compound **5a**, **5b**, **5c** or **5d** by mass spectrometry and NMR spectroscopy (yields 39–68%, see Tables 2 and 6). The C-methyl substituted starting dicarbaborane anion [6-Me-*nido*-6,9-$C_2B_8H_9$]$^{2-}$(species **6-Me-4^{2-}**) was similarly employed in place of the unsubstituted anion **4^{2-}** to prepare the methylated metalladicarbaborane derivative [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (**2-Me-5c**).

2.8. X-ray crystallography

Crystals of [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**5-Br-3a**) and [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (**2-Me-5c**) suitable for single crystal X-ray diffraction studies were grown from CH_2Cl_2–hexane mixtures as described in the preceding paragraphs. For the β-bromo-substituted compound **5-Br-3a** all crystallographic measurements were made at ambient temperature on a Nicolet P3/F diffractometer operating in the ω–θ scan mode using graphite-monochromated Mo–K_α radiation. The structure was determined using standard heavy-atom techniques and was refined by full-matrix least-squares using SHELX-97 [49]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The methyl hydrogen atoms were placed in calculated positions (C–H = 96 pm) and refined with an overall isotropic displacement parameter, whereas the metalladicarbaborane cluster hydrogen atoms were located on a Fourier difference map and were freely refined. The weighting scheme $w = [\sigma^2(F_o) + 0.0008(F_o)^2]^{-1/2}$ was used. Full details of crystal data, data collection, and structure solution and refinement, are given in Table 3, and are deposited with the CCDC, deposition no. 14316. For the C-methyl substituted compound **2-Me-5c**, the experimental details of the X-ray work have previously been presented in a preliminary communication (CCDC reference acronym JEZPAF # ADATE 19910704) [50], but crystallographic parameters are also included here in Table 3 for convenience of reference. The original data were processed via SHELX-76; they have been reprocessed using SHELX-97 for this present presentation in order to facilitate comparison; CCDC deposition no. 144317.

Table 3
Crystal data and structure solution parameters for [5-Br-1-(η^6-C_6Me_6)-*closo*-1,2,4-Ru $C_2B_8H_9$] (compound **5-Br-3a**) and [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (compound **2-Me-5c**)

Compound	**5-Br-3a**	**2-Me-5c**
CCDC deposition number	144316	144317
Formula	$C_{14}H_{27}B_8BrRu$	$C_{13}H_{27}B_8Rh$
Size (mm)	$0.8 \times 0.5 \times 0.4$	$0.55 \times 0.45 \times 0.3$
Molecular weight	462.83	372.75
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (pm)	890.6(1)	878.7(2)
b (pm)	1559.3(2)	1500.3(3)
c (pm)	1453.6(2)	1366.1(3)
β (°)	105.48(1)	91.85(2)
V (nm^3)	1.9453(4)	1.7999(6)
D_{calc} (g cm^{-3})	1.58	1.38
Z	4	4
μ (cm^{-1})	28.52	Empirical (DIFABS)
Number of data collected	3598	3382
Number observed	2893	2861
Number of parameters	260	242
Weighting parameter g	0.0008	0.00025
R	0.0447	0.0235
R_w	0.1168	0.0591
$\Delta\rho$ (max., min.) (e $Å^{-3}$)	+1.396, −1.134	+0.321, −0.385

3. Results and discussion

3.1. Syntheses

We have found that the parent (i.e. unsubstituted) metalladicarbaboranes of the general asymmetrical cluster constitution [1-L-1,2,4-$MC_2B_8H_{10}$] (**3**, *closo* eleven-vertex numbering system) [where {ML} = {Ru(η^6-C_6Me_6)} (**3a**), {Ru(η^6-*p*-$MeC_6H_4^i$Pr)} (**3b**), {Rh(η^5-C_5Me_5)} (**3c**), and {Os(η^6-*p*-$MeC_6H_4^i$Pr)} (**3d**)] can be prepared in the same manner as their 2,4-C,C-dimethylated analogues [11,12] when the parent *nido*-5,6-$C_2B_8H_{12}$ dicarbaborane **1** is used as the starting carbaborane material (see Scheme 1), rather than the 5,6-dimethyl-substituted analogue [5,6-Me_2-*nido*-5,6-$C_2B_8H_{10}$]. This is as expected. Thus, reactions between compound **1** and the organometallic complexes [{MCl_2L}$_2$] (**2**) in chloroform or dichloromethane at ambient temperature for between one and 24 h. gave yields of between 45 and 94% (Table 1) according to the stoichiometry as in Eq. (1):

$$2C_2B_8H_{12}\ (\mathbf{1}) + [\{MLCl_2\}_2]\ (\mathbf{2}) + 4\text{tmnda} \rightarrow 2[LMC_2B_8H_{10}]\ (\mathbf{3}) + 4[\text{tmndaH}]\text{Cl} \qquad (1)$$

The 7-brominated derivative of compound **1**, [7-Br-*nido*-5,6-$C_2B_8H_{11}$] (**7-Br-1**), and [$RuCl_2$(η^6-C_6Me_6)]$_2$ (**2a**) reacted similarly, but yielded a mixture of two monobromo derivatives in ca. 4:1 ratio (as assessed by integrated ^{11}B-NMR spectroscopy). These are formulated as [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**5-Br-3a**) and [**7-Br-1**-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**7-Br-3a**) (combined yield 75%). These two components could be individually separated by preparative HPLC (Separon SGX silica gel support, 22:78 hexane–CH_2Cl_2). Both compounds are chiral[2] and each of them was further resolved, now into its individual enantiomer components (σ)-**5-Br-3a** and (ρ)-**5-Br-3a** (curves 1A and 1B in the upper part of Fig. 1), and (σ)-**7-Br-3a** and (ρ)-**7-Br-3a** (curves 2A and 2B in the bottom part of Fig. 1) by accumulation of evaporates following repeated chiral HPLC [34,35] on an analytical scale (β-cyclodextrin, 32% H_2O in MeOH). The individual mirror-image

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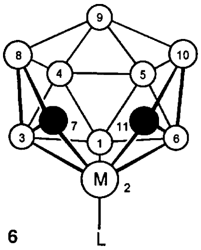
[2] In formal IUPAC nomenclature, the two enantiomers of compound **5-Br-3a** are described as [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] and [4-Br-1-(η^6-C_6Me_6)-1,2,5-$RuC_2B_8H_9$], and those of compound **7-Br-3a** are [7-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] and [6-Br-1-(η^6-C_6Me_6)-1,2,5-$RuC_2B_8H_9$]. Here we use the σ/ρ form of differentiation as in Refs. [51,52].

equal-and-opposite CD spectra obtained for these enantiomeric pairs indicated reasonably clean separation (Fig. 1). Interestingly, both compounds exhibited multiple Cotton effects. As in other cases so far reported of enantiomeric separations of chiral boron-containing cluster compounds using chiral HPLC [35,36], neither the interpretation of individual Cotton effects nor the absolute configuration (i.e. the assignment of structure and CD spectra to individual σ- and ρ-configurations) [51–53] has been determined. Such work will clearly be of interest, and further work in our laboratories is aimed at the isolation of larger quantities of pure enantiomers of these and other suitable species in order to determine absolute configurations [44] and specific rotations, to permit mechanistic and stereochemical studies, and to open up the general area of potential applications of these stereochemically asymmetric species in which the chirality arises from the general asymmetry rather than from discrete chiral centres [35,36].

All the unsubstituted metalladicarbaboranes of the asymmetrical [1-L-1,2,4-$MC_2B_8H_{10}$] cluster type **3** were found to undergo a clean cluster rearrangement when heated at 225–235°C for 10 min. The products were the members of the corresponding series of isomeric symmetrical metalladicarbaboranes [1-L-*closo*-1,2,3-$MC_2B_8H_{10}$] (**5**), where $\{ML\} = \{Ru(\eta^6\text{-}C_6Me_6)$ (**5a**), $\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$ (**5b**), $\{Rh(\eta^5\text{-}C_5Me_5)\}$ (**5c**), and $\{Os(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$ (**5d**)] (see Scheme 1). The same cage rearrangement has also been reported previously with cobalt and ruthenium species, specifically neutral [1-(η^5-C_5H_5)-1,2,4-$CoC_2B_8H_{10}$], the [1,1′-Co(2,4-$CoC_2B_8H_{10})_2]^-$ anion [33,54] and neutral [2,4-Me_2-1-(η^6-*p*-$MeC_6H_4^iPr$)-1,2,4-$RuC_2B_8H_{10}$] (**2,4-Me$_2$-3b**) [11,12]. Aspects of the relative stability of the closed $\{1,2,3\text{-}MC_2B_8\}$ system of compounds **5** versus the less stable asymmetric open $\{1,2,4\text{-}MC_2B_8\}$ system of compounds **3** are briefly discussed below.

These reactions of compounds **3** to give compounds **5** contrast to the thermolyses of the C,C-dimethyl substituted rhodium and osmium analogues [2,4-Me_2-1-(η^5-C_5Me_5)-1,2,4-$RhC_2B_8H_8$] (**2,4-Me$_2$-3c**) and [2,4-Me_2-1-(η^6-*p*-$MeC_6H_4^iPr$)-1,2,4-$OsC_2B_8H_8$] (**2,4-Me$_2$-3d**), which have been reported in a preliminary note [55] to give the structurally different isomers [8,10-Me_2-2-L-2,8,10-$MC_2B_8H_8$], where $\{ML\} = \{Rh(\eta^5\text{-}C_5Me_5)\}$ and $\{Os(\eta^6\text{-}C_6Me_6)\}$ (**6c** and **6d**, respectively, *nido* eleven-vertex numbering system). Even though they have formal *closo* electron counts, the cluster geometries of compounds **6c** and **6d** in fact better approximate to classical [15–17] *nido* eleven-vertex, albeit with an interesting quasi-*arachno* geometrical feature, in that there is a long interboron vector in the open face, viz. B(7)-B(11) at 2.084(9) Å in the osmium compound **6d** [55], i.e. a structural tendency towards eleven-vertex arachno [schematic structure **6**]. It is not clear whether this interesting isomerism is controlled by the steric or the electronic influence of the C-methyl substituents, or to what extent a higher metal oxidation state might be involved [28,31,55,56].



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An alternative route to the more symmetrical complexes [1-L-*closo*-1,2,3-$MC_2B_8H_{10}$] of type **5**, where $\{ML\} = \{Ru(\eta^6\text{-}C_6Me_6)\}$ (**5a**), $\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$ (**5b**), $\{Rh(\eta^5\text{-}C_5Me_5)\}$ (**5c**), and $\{Os(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$ (**5d**), is the reaction between the organometallic halides **2a**–**2d** and the disodium salt of the dianion [*nido*-6,9-$C_2B_8H_{10}]^{2-}$ (species $\mathbf{4}^{2-}$) [5,6] (see again Scheme 1):

$$2[C_2B_8H_{10}]^{2-}\ (\mathbf{4}^{2-}) + [\{MLCl_2\}_2] \rightarrow 2[LMC_2B_8H_{10}]\ (\mathbf{5}) + 4Cl^- \tag{2}$$

This reaction is carried out in dichloromethane or chloroform solution at ambient temperature for between 4 h and 3 days, with yields of compounds **5** ranging from 45 to 68% (Table 2). Yields were variable, but the highest yields (Table 2) were found with samples of anion $\mathbf{4}^{2-}$ that had been freshly prepared. The C-methyl substituted dianion [6-Me-*nido*-6,9-$C_2B_8H_9]^{2-}$ (**6-Me-4^{2-}**) [28] reacted in a similar manner to give [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (**2-Me-5c**) (64%). Interestingly, compound **2-Me-5c** has also been isolated as one of the predominant products from the complex reaction between MeNC and [6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}] in which the cluster carbon atom must derive from the MeNC residue [50].

As seen from Scheme 1, the formation of compounds of type **3** and **5** as in the stoichiometric reactions of Eq. (1) and Eq. (2) looks at first sight to be consistent with a straightforward insertion of the metal centre into the open hexagonal face of the dicarbaborane cages of types **1** and $\mathbf{4}^{2-}$. However, this would predict the formation exclusively of the 5-bromo derivative **5-Br-3a** from the reaction of [7-Br-*nido*-5,6-$C_2B_8H_{11}$] (**7-Br-1**), whereas the concomitant formation of the 7-bromo isomer **7-Br-3a** shows that a cage rearrangement has occurred. That such a rearrangement may be occurring generally in the reactions of the simple unsubstituted species $\mathbf{1}^-$ and $\mathbf{4}^{2-}$ therefore cannot be excluded (for rearrangements in unmetallated ten-vertex carbaborane series see, for example, Refs. [57–60]). The **3** → **5** and **3** → **6** thermal rearrangements mentioned above emphasise the general propensity for cluster rearrangement in this type of eleven-vertex system. Thermodynamically

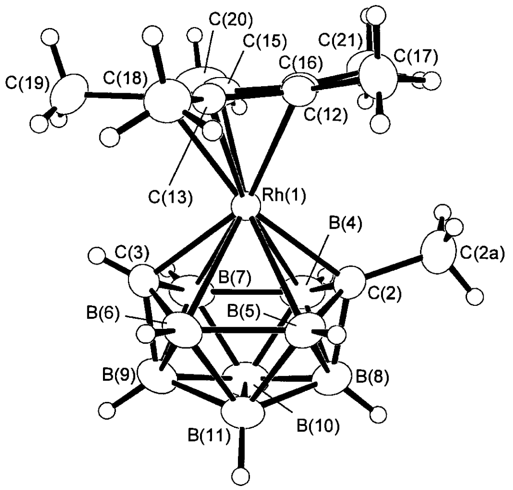

Fig. 2. ORTEP representation of the crystallographically determined molecular structure of [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (**2-Me-5c**). Although in solution there is free rotation of the {C_5Me_5} group relative to the {$RhC_2B_8H_9Me$} unit to give a time-average C_s symmetry, in the crystal the relative orientation of the {C_5Me_5} and the {$RhC_2B_8H_9Me$} residues generates chirality, and in the solid state the compound crystallises as the racemate, containing both enantiomers in the unit cell.

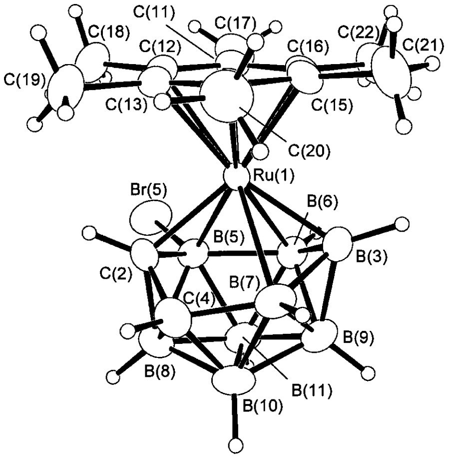

Fig. 3. ORTEP representation of the crystallographically determined molecular structure of [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**5-Br-3a**). Although of *isonido* configuration with a four-membered open face (see text), the structure is numbered according to the eleven-vertex *closo* convention. The compound crystallises as the racemate, containing both enantiomers in the unit cell.

favoured migrations of carbon atoms in carbaborane clusters to carbons-apart configurations, and also to give configurations in which the carbon atoms occupy sites of lower cluster connectivity, have long been recognised [61]. In this general context it is of interest to note a recent renaissance of interest [62–66] in the long recognised [67,68] isomerisations of the corresponding twelve vertex {MC_2B_9} system.

The constitutions of all the compounds of type **3** and **5** have been determined unambiguously by ^{11}B and ^{1}H spectroscopy and by mass spectrometry, with the general structural types **3** and **5** confirmed by single crystal X-ray diffraction analyses of the two substituted species [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**5-Br-3a**) and [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (**2-Me-5c**).

3.2. X-ray diffraction studies

The solid-state molecular structures of the substituted compounds [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (**2-Me-5c**) and [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**5-Br-3a**) were determined by single-crystal X-ray diffraction analyses and are depicted in Figs. 2 and 3, respectively. Crystal data and structure solution parameters are in Table 3, details of structure refinement are in Section 2, and selected interatomic distances and angles are given in Table 4.

Fig. 2 shows the molecular structure of the 2-methyl-substituted derivative of compound **5c**, viz. [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (**2-Me-5c**). The observed structure is at first sight in agreement with a regular eleven-vertex 24-electron *closo* geometry [15–17], approximating to an idealised C_{2v} {MC_2B_8} cluster as conventionally expected [15–17,69,70], and as also previously found for other structurally determined members of this series such as [1-(η^5-C_5H_5)-*closo*-1,2,3-$CoC_2B_8H_{10}$] [32,33], the [*closo*-1,1′-Co-(2,3-$CoC_2B_8H_{10})_2$]$^-$ anion [32,33], and [2,3-Me_2-1-(η^6-*p*-$MeC_6H_4^i$Pr)-*closo*-1,2,3-$RuC_2B_8H_8$] [12]. The cluster carbon atoms reside at the low-connectivity 2- and 3-positions and, in contrast to compounds **3** above, all mutually adjacent cluster atoms are within bonding distances. However, within this symmetrical *closo*-type {MC_2B_8} unit of configuration **5** the metal centre is incorporated significantly more compactly into the cluster than it is in [1,1-{$P(OMe)_3$}$_2$-1,2,3-$PtC_2B_8H_{10}$] [29] and [1,1-$(PPh_3)_2$-1,2,3-$PtC_2B_8H_{10}$] [6,28], which are thought to be more conventionally *closo* [28]. Further, it is incorporated very much more compactly than in the 6,9-bridged *nido* ten-vertex species [1-Et-1-(OEt_2)-1,2,3-$AlC_2B_8H_{10}$] [23]. The dimensions within the metal-to-cluster bonding-sphere are much more comparable to those of the more compact species [2-Me-1,1-$(PMe_2Ph)_2$-1,2,3-$PtC_2B_8H_9$], in which the compactness has been proposed [28] to arise from a platinum(IV) four-electron four-orbital contribution to the cluster which would thereby have a 26-electron *nido* electron count whilst still retaining the closed C_{2v}-based configuration [28,31]. The true 24-electron *closo* eleven-vertex cluster structure itself is recognised to be fragile (see next paragraph) [31], and so, like [2-Me-1,1-$(PMe_2Ph)_2$-1,2,3-$PtC_2B_8H_9$] just mentioned, the structure of compound **2-Me-5c** (and the other species **5** reported here) may similarly gain stability from contributions from a similar enhanced orbital involvement of the metal centre. Such an involvement is not available to a boron atom in this position. In this regard the NMR properties of compounds of type **5a**, **5b**, **5c**, **5d** and **2-Me-5c** (see below) also may suggest an electronic structure that differs from the conventional eleven-vertex C_{2v} 24-electron *closo* as exhibited by neutral [2,3-$C_2B_9H_{11}$], or by the $[CB_{10}H_{11}]^-$ monoanion and the $[B_{11}H_{11}]^{2-}$ dianion.

Table 4
Selected interatomic distances (pm) and angles (°) for [5-Br-1-(η^6-C_6Me_6)-*closo*-1,2,4-$RuC_2B_8H_9$] (compound **5-Br-3a**) and [2-Me-1-(η^5-C_5Me_5)-*closo*-1,2,3-$RhC_2B_8H_9$] (compound **2-Me-5c**)

Compound **5-Br-3a**			
Distances			
C(2)–Ru(1)	209.8(7)	C(2)–C(4)	147.5(10)
C(2)–B(5)	159.1(11)	C(2)–B(8)	169.5(12)
B(3)–Ru(1)	206.8(9)	B(3)–B(6)	172.1(12)
B(3)–B(7)	172.6(11)	B(3)–B(9)	174.2(12)
C(4)–Ru(1)	265.8(9)	C(4)–B(7)	172.3(11)
C(4)–B(8)	170.8(13)	C(4)–B(10)	163.6(13)
B(5)–Ru(1)	226.5(8)	B(5)–Br(5)	197.4(8)
B(5)–B(6)	180.7(10)	B(5)–B(8)	182.5(11)
B(5)–B(11)	179.4(12)	B(6)–B(9)	MTP?
B(6)–Ru(1)	227.8(9)	B(6)–B(11)	181.2(11)
B(7)–Ru(1)	236.7(9)	B(7)–B(9)	188.8(12)
B(7)–B(10)	183.3(12)	B(8)–B(10)	173.1(13)
B(8)–B(11)	171.2(12)	B(9)–B(10)	173.9(12)
B(9)–B(11)	173.8(11)	B(10)–B(11)	180.2(13)
C(ring)–Ru(1) mean	225.6(5)		
Angles			
C(2)–Ru(1)–B(3)	105.9(4)	C(4)–Ru(1)–C(2)	33.6(2)
C(4)–Ru(1)–B(3)	80.5(3)	C(4)–Ru(1)–B(5)	61.3(3)
B(6)–Ru(1)–C(2)	83.0(3)	B(6)–Ru(1)–B(3)	46.3(3)
B(6)–Ru(1)–C(4)	80.3(3)	B(6)–Ru(1)–B(5)	46.9(2)
B(6)–Ru(1)–B(7)	70.0(3)	B(7)–Ru(1)–C(2)	72.2(3)
B(7)–Ru(1)–B(3)	45.2(2)		
Compound **2–Me-5c** [a]			
Distances			
C(2)–Rh(1)	211.5(4)	C(2)–B(4)	157.4(7)
C(2)–B(5)	157.7(6)	C(2)–B(8)	166.0(6)
C(2)–C(2)(Me)	152.0(6)	C(3)–Rh(1)	208.9(4)
C(3)–B(6)	157.6(6)	C(3)–B(7)	156.7(7)
C(3)–B(9)	164.8(6)	B(4)–Rh(1)	236.6(9)
B(4)–B(7)	192.7(7)	B(4)–B(8)	181.0(7)
B(4)–B(10)	180.9(7)	B(5)–Rh(1)	237.6(5)
B(5)–B(6)	190.4(7)	B(5)–B(8)	181.8(7)
B(5)–B(11)	180.6(6)	B(6)–B(9)	182.1(6)
B(6)–Rh(1)	239.6(5)	B(6)–B(11)	178.7(6)
B(7)–Rh(1)	237.4(5)	B(7)–B(9)	181.5(7)
B(7)–B(10)	179.5(7)	B(8)–B(10)	173.8(7)
B(8)–B(11)	174.1(7)	B(9)–B(10)	174.7(7)
B(9)–B(11)	173.2(7)	B(10)–B(11)	182.6(7)
C(ring)–Rh(1) mean	220.1(4)		
Angles			
C(2)(Me)–C(2)–Rh(1)	123.2(3)	C(2)–Rh(1)–C(3)	106.5(2)
B(4)–Rh(1)–C(2)	40.6(1)	B(4)–Rh(1)–C(3)	83.6(2)
B(4)–Rh(1)–B(5)	66.8(2)	B(6)–Rh(1)–C(2)	83.3(2)
B(6)–Rh(1)–C(3)	40.4(1)	B(6)–Rh(1)–B(4)	86.2(2)
B(6)–Rh(1)–B(5)	47.0(1)	B(6)–Rh(1)–B(7)	67.0(2)
B(7)–Rh(1)–C(2)	83.9(2)	B(7)–Rh(1)–C(3)	40.5(1)

[a] The following atoms are related by a crystallographic mirror plane at 1/4 in *b*: B(1) and B(3), B(5) and B(7), and B(10) and B(8).

Inspection of the structure in Fig. 3 shows that [5-Br-1-(η^6-C_6Me_6)-1,2,4-$RuC_2B_8H_9$] (**5-Br-3a**), by contrast, adopts an asymmetrical configuration **3**, with the B(7), C(2), C(4) and Ru(1) centres now constituting a well defined quadrilateral open face. This in accord with the structures of the similar compounds [2,4-Me_2-1-(η^6-*p*-$MeC_6H_4^iPr$)-*closo*-1,2,4-$RuC_2B_8H_8$] [11,12], [1,1,1-$H(PPh_3)_2$-*closo*-1,2,4-$IrC_2B_8H_{10}$] [9] and [1,1,1-$H(PMe_3)_2$-*closo*-1,2,4-$IrC_2B_8H_{10}$] [10] reported previously. In these, therefore, the expected *closo* cage structure, i.e. the one that would be consistent with the formal 24-electron count [15–17], is considerably distorted into an *isonido* type of configuration [9,31,71]. As mentioned above, the 24-electron eleven-vertex true *closo* cluster configuration is well-recognised to be fragile [31,71,72]. For example, $[B_{11}H_{11}]^{2-}$ and $[2\text{-}CB_{10}H_{11}]^-$ are both fluxional via a diamond-square-diamond rearrangement that implies open-faced *isonido* intermediates [73,74]. In the case of the asymmetrically constituted species **3**, the asymmetry itself, together with the tendency of carbon vertices to favour low-coordinate connectivities for themselves [61,69,70], as well as localisation of electrons in the intercarbon link [C(2)–C(4) is 147.5(10) pm in compound **5-Br-3a**] contributes to the stabilisation of this square-faced *isonido* shape. Also as mentioned above, and as discussed in detail in Refs. [28,31] for symmetrical species of type **5**, a transition-element centre in the 1-position may play a role in stabilising the observed geometries by having a higher orbital involvement. Aspects of this interesting *closo–isonido* variation are adequately discussed elsewhere [31,71,75], not only for eleven-vertex species, but also for nine- and ten-vertex species. A closely similar phenomenon is also apparent in recent work on 12-vertex boron-containing cluster species [76–82], and the long-recognised related phenomena within the slipped 12-vertex {3,1,2-MC_2B_8} metalladicarbaboranes should perhaps also be noted in this context [83–92].

3.3. NMR spectroscopy

All the new compounds of series **3** and **5** reported here were well characterised by NMR spectroscopy (Tables 5 and 6) [93–95]. In this characterisation, [^{11}B–^{11}B]-COSY [96,97] and ^1H-{^{11}B(selective)} [98] NMR experiments, combined in some cases with [^1H–^1H]-COSY-{^{11}B(broadband)} measurements [99], led to the complete assignments of all the resonances to the individual {BH} and {CH} cluster units for all the compounds encountered in this study. The NMR data for

Table 5
^{11}B- and ^{1}H-NMR chemical shifts for the metalladicarbaboranes [1-L-1,2,4-MC$_2$B$_8$H$_{10}$] (compounds **3**) in CD$_2$Cl$_2$ at 294–297 K; presented as δ(^{11}B) [a] (^1J(^{11}B–^{1}H) in parentheses) [δ(^{1}H) [a] in square brackets (positive unless otherwise signed)]

Comp	BH(3)	BH(3)	BH(5)	BH6)	BH(10)	BH(8)	BH(11)	BH(7)	CH(2)	CH(4)
3a	+63.5	+63.5	+0.6	+0.1	−14.9	−20.1	−26.3	−42.3	–	–
	(152)	(152)	(137)	(140)	(154)	(171)	(142)	(146)	–	–
	[7.19]	[7.19]	[1.92]	[1.21]	[0.77]	[1.91]	[+0.31]	[−2.39]	[3.77]	[3.64]
5-Br-3a	+65.1	+65.1	+1.7 [b]	−1.7	−14.4	−19.3	−24.7	−43.2	–	–
	(154)	(154)	(–)	(132)	(157)	(175)	(146)	(149)	–	–
	[7.39]	[7.39]	[–]	[1.19]	[0.70]	[2.25]	[0.66]	[−2.33]	[3.80]	[3.54]
7-Br-3a	+60.6	+60.6	1.7	−0.8	−13.4	−22.1	−24.7	−36.2 [b]	–	–
	(154)	(154)	(137)	(140)	(154)	(174)	(142)	(–)	–	–
	[7.20]	[7.20]	[1.12]	[2.04]	[1.16]	[1.81]	[0.40]	[–]	[3.95]	[3.61]
3b	62.0	62.0	0.1	−1.2	−14.4	−20.3	−26.5	−42.5	–	–
	(155)	(155)	(155) [c]	(155) [c]	(155)	(171)	(143)	(149)	–	–
	[7.74]	[7.74]	[2.29]	[1.46]	[0.88]	[1.94]	[0.38]	[−2.12]	[4.47]	[3.80]
3c	68.6	68.6	4.6	3.1	−9.0	−21.0	−23.9	−39.2	–	–
	(158)	(158)	(158) [c]	(175) [c]	(156)	(173)	(143)	(153)	–	–
	[7.39]	[7.39]	[2.19]	[1.68]	[1.25]	[1.83]	[0.55]	[−2.03]	[3.97]	[4.20]
3d	50.3	50.3	−4.6	−5.3	−15.6	−19.3	−28.3	−47.9	–	–
	(154)	(154)	(139) [c]	(136) [c]	(156)	(171)	(143)	(149)	–	–
	[8.10]	[8.10]	[2.15]	[1.81]	[−0.65]	[2.18]	[−0.32]	[−2.81]	[5.19]	[3.81]

[a] Assignment by relative intensities, [^{11}B–^{11}B]-COSY (measured for all compounds; typically observed crosspeaks: 3–6 s, 3–7 s, 3–9 s, 5–6 s, 5–8 w–m, 5–11 s, 6–9 s, 6–11 s, 7–9 w–m, 7–10 w, 8–10 m–s, 8–11 s, 9–10 s, 9–11 s, 10–11 s; s = strong, m = medium, w = weak), [^{1}H H–^{1}H]-COSY (measured for all compounds except for **5-Br-3a** and **7-Br-3a**; typical observed cross-peaks : 2–4 s, 2–5 s, 2–8 s, atom H(3) is not involved in the correlation due to extreme downfield position of ^{11}B(3) {see Ref. [81]}, 4–7 s, 4–8 w, 4–10 s, 5–6 m–s, 5–8 s?, 5–11 s, 6–9 w, 6–11 s, 7–9 ?–w, 8–10 m–s, 8–11 s, 9–10 s, 9–11 s, 10–11 s; ? = uncertain) and ^{1}H-{^{11}B(selective)} experiments (for ^{1}H); additional ^{1}H resonances for the η^6-arene and η^5-cyclopentadiene ligands: **3a**, +2.12 (18H, C$_6$Me$_6$); **5-Br-3a** +2.16 (18H, C$_6$Me$_6$); **7-Br-3a** +2.13 (18H, C$_6$Me$_6$); **3b** MeC$_6$H$_4^i$Pr aliphatics centred at +1.12, +1.17, +1.99, +2.59, {C$_6$H$_4$} at +5.67 to +5.95 (4H); **3c**, +1.86 (15H, C, C$_5$Me$_5$); **3d**, MeC$_6$H$_4^i$Pr aliphatics centred at +1.13, +1.19, +2.14, +2.59, {C$_6$H$_4$} at +5.65 to +5.85 (4H). ^{13}C-NMR spectrum of **3c**: C$_5$Me$_5$ at +103.26 [doublet, ^1J(^{103}Rh–^{13}C) 5.2 Hz] and +9.76 (quartet), C(2) and C(4) at +58.26 and +42.15.

[b] Singlet; Br-substituted position.

[c] Value uncertain due to peak overlap.

Table 6
^{11}B- and ^{1}H-NMR chemical shifts for metalladicarbaboranes [1-L-1,2,3-MC$_2$B$_8$H$_{10}$] (**5**); CD$_2$Cl$_2$ solution at 294–297 K; presented as δ(^{11}B) [a] (^1J(^{11}B–^{1}H) in parentheses) [δ(^{1}H) [a] in square brackets]

Compound	BH(8)	BH(9)	BH(4,5)	BH(6,7)	BH(10,11)	CH(2,3)
5	+7.9		−10.8		−24.3	–
	(152)		(145)		(141)	–
	[+3.20]		[+1.50]		[+0.25]	[+5.12]
5b	+8.2		−11.5		−24.6	–
	(153)		(149)		(139)	–
	[+3.23]		[+1.52]		[+0.20]	[+5.05]
5c	+6.0		−7.4		−22.5	–
	(153)		(152)		(140)	–
	[+3.04]		[+1.52]		[+0.36]	[+5.64]
2-Me-5c	+13.3	+4.5	−6.4		−22.4.	–
	(153)		(149)		(139)	–
	[+3.33]	[+2.96]	[+1.64]	[+1.51]	[+0.51]	[+2.63] [b]
						[+4.83] [c]
5d	+7.6		−17.2		−26.1	–
	(ca. 150)		(149)		(140)	–
	[+4.25]		[+1.42]		[−0.77]	[+6.00]

[a] Assignment by relative intensities, [^{11}B–^{11}B]-COSY [all theoretical ^1J(^{11}B–^{11}B) crosspeaks observed; observed cross-peaks for **2-Me-5c**: 8-4,5,6,7 s; 8-10,11 s, 9-4,5,6,7 s; 9-4,5,6,7 s; 9-10,11 s; 10,11-4,5,6,7 s; s = strong), and ^{1}H{^{11}B(selective)} experiments (for ^{1}H); additional ^{1}H resonances of the η^6-arene and η^5-cyclopentadiene ligands: **5a** +2.12 (18 H, C$_6$Me$_6$); **5b** MeC$_6$H$_4^i$Pr aliphatics centred at +1.22, +2.19, +2.70, and {C$_6$H$_4$} at +5.68 to +5.74 (4H); **5c** +1.93 (15 H, C$_5$Me$_5$); **5d** MeC$_6$H$_4^i$Pr aliphatics centred at +1.23, +2.28, +2.66, and {C$_6$H$_4$}at +5.06 to +5.71 (4H). ^{13}C-NMR spectrum of **5c**: C$_5$Me$_5$ at +103.85 [doublet ^1J(^{103}Rh–^{13}C) 6.1 Hz] and +9.44 (quartet), C(2,3) +79.9.

[b] Signal of methyl protons.

[c] Signal from CH(3) cluster-carbon protons.

compounds of type **3** are in Table 5 and those for compounds of type **5** are in Table 6, and illustrative points are depicted in Figs. 4 and 5.

As shown in Fig. 4 (bottom diagram) all complexes of the asymmetric $\{1,2,4\text{-}MC_2B_8\}$ constitution **3** exhibit eight different ^{11}B resonances and very similar boron nuclear shielding behaviour. Their ^{11}B spectra span a large range of about 100 ppm. The differences among the members of the series are attributable to the presence of different metal vertices at the six-coordinate 1-position and, in the case of compounds **5-Br-3a** and **7-Br-3a**, α and β substituent effects of the bromo substituents. As found previously for the structurally analogous compounds $[2,4\text{-}Me_2\text{-}1\text{-}(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)$-*closo*-$1,2,4\text{-}RuC_2B_8H_8]$ (**2,4-Me₂-3b**) [11,12] and $[1\text{-}(\eta^5\text{-}C_5H_5)$-*closo*-$1,2,4\text{-}CoC_2B_8H_{10}]$ [13,14], the spectra are characterised by eight signals between +65 and −50 ppm, with $^{11}B(7)$ to extreme high field at about −45 ppm, and $^{11}B(3)$ to extreme low field at about +60 ppm, with a close central grouping of all the other ^{11}B resonances. For all the compounds **3** the ordering is the same within this close grouping, so that the isospectrality [95,100] arising from isostructurality is readily apparent. These ^{11}B spectra bear little resemblance to those of either *nido* [1–4] or *arachno* [101] ten-vertex $\{5,6\text{-}C_2B_8\}$ skeletons, which suggests that the electronic structure of the metalladicarbaboranes **3** arises from more than just a simple addition of a metal vertex to replace bridging hydrogen atoms in the open face of the starting substrate.

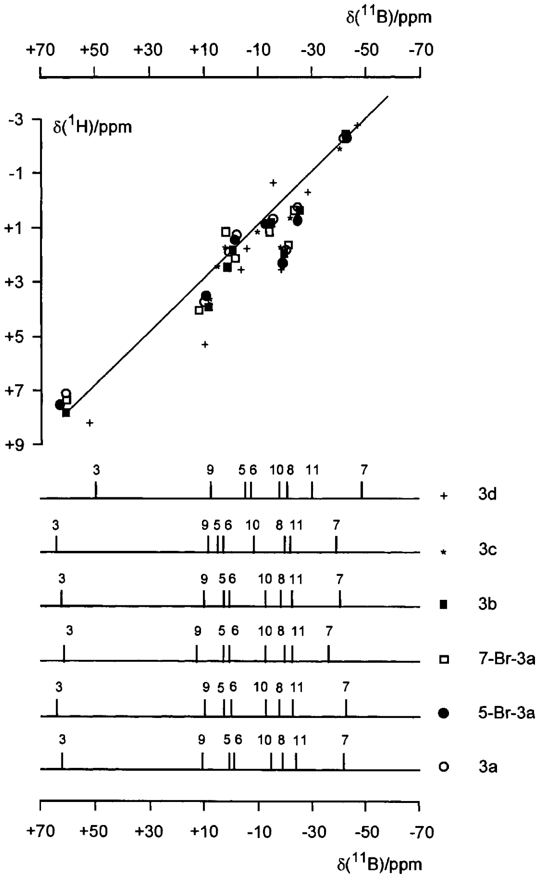

Fig. 4. The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B-NMR spectra of the eleven-vertex metalladicarbaboranes of general formulation $[1\text{-}L\text{-}1,2,4\text{-}MC_2B_8H_{10}]$ (**3**), where $\{ML\} = \{Ru(\eta^6\text{-}C_6Me_6)\}$ (**3a**), $\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$ (**3b**), $\{Rh(\eta^5\text{-}C_5Me_5)\}$ (**3c**), and $\{Os(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$ (**3d**), together with those for the substituted derivatives $[5\text{-}Br\text{-}1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}1,2,4\text{-}RuC_2B_8H_9]$ (**5-Br-3a**) and $[$**7-Br-1**$\text{-}(\eta^6\text{-}C_6Me_6)\text{-}1,2,4\text{-}RuC_2B_8H_9]$ (**7-Br-3a**). The upper diagram is a plot of δ (^1H) versus δ (^{11}B) for individual {BH} units for all compounds **3**; the correlation line drawn has slope corresponding to δ (^{11}B):δ (^1H) 11.5:1.

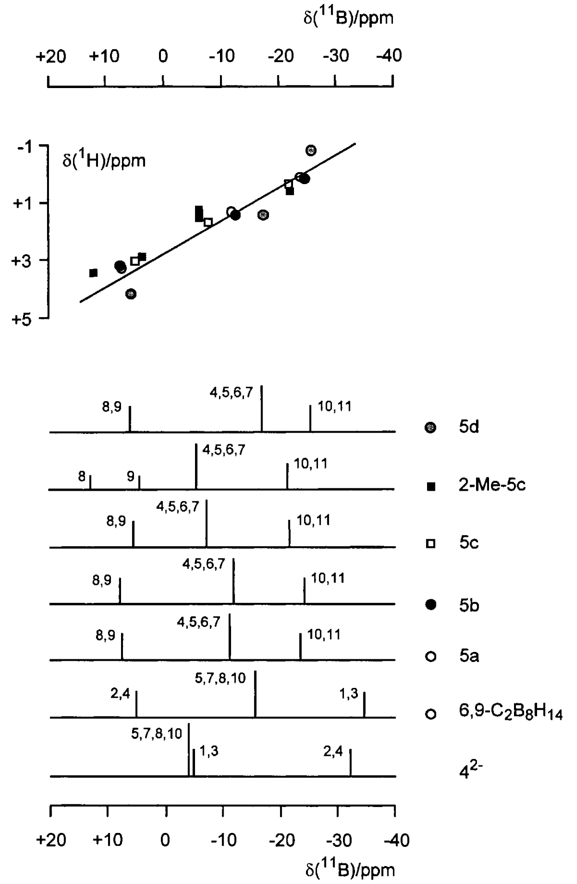

Fig. 5. The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B-NMR spectra of the eleven-vertex *closo*-structured metalladicarbaboranes of general formulation $[1\text{-}L\text{-}1,2,3\text{-}MC_2B_8H_{10}]$ (**5**), where $\{ML\} = \{Ru(\eta^6\text{-}C_6Me_6)\}$ (**5a**), $\{Ru(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$ (**5b**), $\{Rh(\eta^5\text{-}C_5Me_5)\text{-}C_5Me_5)\}$ (**5c**), and $\{Os(\eta^6\text{-}p\text{-}MeC_6H_4^iPr)\}$ (**5d**), together with those for the substituted complex $[2\text{-}Me\text{-}1\text{-}(\eta^5\text{-}C_5Me_5)$-*closo*-$1,2,3\text{-}RhC_2B_8H_9]$ (**2-Me-5c**), neutral *arachno*-$6,9\text{-}C_2B_8H_{14}$ (data from Ref. [28]), and the starting [*nido*-$6,9\text{-}C_2B_8H_{10}]^{2-}$ anion substrate (species $\mathbf{4}^{2-}$, data from Ref. [6]). The upper diagram is a plot of δ (^1H) versus δ (^{11}B) for individual {BH} units for all the compounds of type **5**; the correlation line drawn has slope corresponding to (^{11}B):δ (^1H) 7.5:1. Note that, in capping the *nido*/*arachno* ten-vertex shape (lowest two traces) to give the eleven vertex closed shape (**5**), the formal numbering changes as follows: (1,3)→(10,11), (2,4)→(8,9) and (5,7,8,10)→(4,5,6,7).

In accord with the time-average C_{2v} symmetry that the clusters of compounds **5** will have in solution, the ^{11}B-NMR spectra show typical 2:4:2 patterns of doublets as also found for other compounds of cluster constitution **5** previously reported [6,12,20–27,50] (Fig. 5). The less symmetric compound **2-Me-5c** should exhibit five ^{11}B resonances in 1:1:2:2:2 relative intensity ratio, but at 128 MHz exhibits an apparent 1:1:4:2 pattern. This arises because of coincidental overlap of the (4,5) and (6,7) ^{11}B resonances, these positions being readily differentiated in the ^{1}H-$\{^{11}$B$\}$ spectra. The ^{11}B spectra of these compounds of type **5** span a much narrower range than those of compounds of type **3**. They lack the extreme high and low field shifts of the ^{11}B(3) and ^{11}B(7) resonances of the latter, and are contained within the range $\delta(^{11}\mathrm{B}) + 10$ to -30 ppm. Although the spectrum of the ostensible model *closo* species [2,3-$C_2B_9H_{11}$] is also compact, there are no real parallels in shielding either (a) with this *closo* model or (b) with the [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ starting anion (species $\mathbf{4}^{2-}$), suggesting that the electronic structure is not (a) true *closo* or (b) bridged *nido*. As discussed above, the latter bridged *nido* case is also ruled out from considerations based on interatomic distances, and the former true *closo* may also not be favoured on this basis. In common with the $\{Pt(PMe_2Ph)_2\}$ analogue [1,1-$(PMe_2Ph)_2$-1,2,3-$PtC_2B_8H_{10}$], however, the ^{11}B shielding pattern shows quite a marked similarity with that [28] of the ten-vertex *arachno* species [6,9-$C_2B_8H_{14}$]. For the platinum compound this has been interpreted in terms of a replacement of the bonds to the two bridging and two *endo*-terminal hydrogen atoms of [6,9-$C_2B_8H_{14}$] by four bonds to the platinum centre [28]. The NMR and structural similarities between compounds **5** and the $\{Pt(PMe_2Ph)_2\}$ compound suggest that this four-orbital metal-to-cluster bonding interpretation should be also considered for compounds of series **5**.

As also seen from Figs. 4 and 5 (upper traces), there is an approximate linear correlation between cluster ^{11}B and ^{1}H chemical shifts for the {BH(*exo*)} units of all the compounds of type **3** and **5**. However, the gradients $\delta(^{11}\mathrm{B})$:$\delta(^{1}\mathrm{H})$ for compounds **3** (ca. 11.5:1) and compounds **5** (ca. 7.5:1) are clearly different, again suggesting different electronic constitutions for the two series.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, for compounds **5-Br-3a** (deposition no. 144316) and **2-Me-5c** (deposition no. 144317). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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