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Journal of Organometallic Chemistry 489 (1995) 43–50

Journal of Organometallic Chemistry

Organoruthenaborane chemistry. Part 10. [☆] Preparation, molecular structure, and nuclear magnetic resonance properties of $[6,9\text{-}(\eta^6\text{-pcym})_2\text{-}nido\text{-}6,9\text{-}Ru_2B_8H_{12}]$

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Received 16 May 1994

Abstract

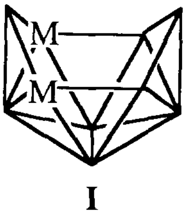
Reaction of the versatile organometallaborane synthon $[(\eta^6\text{-pcym})RuCl_2]_2$ (pcym = *p*-cymene, 1-Me-4′-Pr-C_6H_4) with *arachno*-$[B_9H_{14}]^-$ (as its NEt_4^+salt) and water affords the deep green compound $[6,9\text{-}(\eta^6\text{-pcym})_2\text{-}nido\text{-}6,9\text{-}Ru_2B_8H_{12}]$ (**1**) along with the previously reported [1] orange complex $[6\text{-}(\eta^6\text{-pcym})\text{-}nido\text{-}6\text{-}RuB_9H_{13}]$ (**2**) in yields of 4% and 30% respectively. A single crystal X-ray analysis has been carried out on (**1**). NMR spectroscopic data are also presented and briefly discussed. These, together with the molecular structure of (**1**), confirm the compounds to be *nido*-decaborane analogues; compound (**2**) with the HB (6) unit, and compound (**1**) with both the HB(6) and the HB(9) units, replaced by isolobal $\{Ru(\eta^6\text{-pcym})\}$ units.

Keywords: Ruthenium; Metallaborane; Crystal structure

1. Introduction

The development of high yielding reactions for some metallaboranes in recent years [2,3a,3b,4] has made possible investigation of the reactions of electron-donor ligands and other small molecules with metallaboranes. This has proved to be a rich field of study [5]. Whilst many reactions have given interesting and novel products, reactions involving water and oxygen are much less straightforward. In most instances these reactions lead to cluster degradation, giving an array of uncharacterisable products. The formation of the ferraoxaborane $[2\text{-}(\eta^6\text{-}C_6H_3Me_3)Fe\text{-}6\text{-}O\text{-}B_8H_{10}]$ [6], and the rhodaoxaboranes $[7\text{-}(\eta^5\text{-}C_5Me_5)\text{-}8\text{-}Cl\text{-}11\text{-}(PMe_2Ph)\text{-}nido\text{-}7,12\text{-}RhOB_{10}H_9]$ [4,7] and $[7\text{-}(\eta^5\text{-}C_5Me_5)\text{-}10\text{-}(NEt_3)\text{-}nido\text{-}7,12\text{-}RhOB_{10}H_{10}]$ [8] together with the oxygen-coupled rhodaborane $[\mu\text{-}9,9'\text{-}O\text{-}\{5\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}5\text{-}RhB_9H_{12}\}_2]$ [8] have been attributed to the presence of either water or oxygen.

Metallaborane analogues of *nido*-$B_{10}H_{14}$ are known for a number of metals [9] including all four possible isomers of $[(\eta^6\text{-}C_6Me_6)RuB_9H_{13}]$ [1,3a,10]. Dimetalladecaboranes are rare, only three of the 21 possible isomers being known. The 5,7-(configuration **I**), and 6,9-isomers (configuration **II**) of $[(\eta^5\text{-}C_5Me_5)_2\text{-}Co_2B_8H_{12}]$ were isolated from the reaction of *arachno*-$[B_9H_{14}]^-$ with $CoCl_2$ and $Li^+[C_5Me_5]^-$ [11] and characterised by NMR spectroscopy and X-ray



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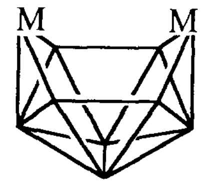

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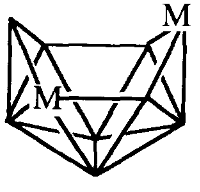

III

[☆] Part 9 see Ref. [1].

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SSDI 0022-328X(94)05119-4

Table 1
Selected interatomic distances (Å) for [6,9-(η^6-MeC$_6$H$_4$-4-^{i}Pr)$_2$-*nido*-6,9-Ru$_2$B$_8$H$_{12}$] (2) with estimated standard deviations in parentheses

Molecule a				Molecule b				Molecule c			
(i) To the ruthenium atom											
Ru(1)–C(11)	2.23(1)	Ru(2)–C(21)	2.18(1)	Ru(3)–C(31)	2.20(1)	Ru(4)–C(41)	2.20(1)	Ru(5)–C(51)	2.23(1)	Ru(6)–C(61)	2.20(1)
Ru(1)–C(12)	2.19(1)	Ru(2)–C(22)	2.17(1)	Ru(3)–C(32)	2.23(1)	Ru(4)–C(42)	2.21(1)	Ru(5)–C(52)	2.24(1)	Ru(6)–C(62)	2.22(1)
Ru(1)–C(13)	2.16(1)	Ru(2)–C(23)	2.19(1)	Ru(3)–C(33)	2.24(1)	Ru(4)–C(43)	2.21(1)	Ru(5)–C(53)	2.22(1)	Ru(6)–C(63)	2.22(1)
Ru(1)–C(14)	2.17(1)	Ru(2)–C(24)	2.22(1)	Ru(3)–C(34)	2.21(1)	Ru(4)–C(44)	2.19(1)	Ru(5)–C(54)	2.20(1)	Ru(6)–C(64)	2.20(1)
Ru(1)–C(15)	2.21(1)	Ru(2)–C(25)	2.23(1)	Ru(3)–C(35)	2.18(1)	Ru(4)–C(45)	2.17(1)	Ru(5)–C(55)	2.20(1)	Ru(6)–C(65)	2.18(1)
Ru(1)–C(16)	2.24(1)	Ru(2)–C(26)	2.21(1)	Ru(3)–C(36)	2.17(1)	Ru(4)–C(46)	2.18(1)	Ru(5)–C(56)	2.22(1)	Ru(6)–C(66)	2.18(1)
Ru(1)–B(12)	2.24(2)	Ru(2)–B(10)	2.26(2)	Ru(3)–B(22)	2.18(2)	Ru(4)–B(20)	2.23(2)	Ru(5)–B(32)	2.22(2)	Ru(6)–B(30)	2.22(2)
Ru(1)–B(15)	2.24(2)	Ru(2)–B(14)	2.21(2)	Ru(3)–B(25)	2.25(2)	Ru(4)–B(24)	2.20(2)	Ru(5)–B(35)	2.21(2)	Ru(6)–B(34)	2.25(2)
Ru(1)–B(17)	2.24(2)	Ru(2)–B(18)	2.27(2)	Ru(3)–B(27)	2.25(2)	Ru(4)–B(28)	2.25(2)	Ru(5)–B(37)	2.23(2)	Ru(6)–B(38)	2.24(2)
(ii) Boron–boron											
B(11)–B(12)	1.78(2)	B(13)–B(14)	1.81(2)	B(21)–B(22)	1.79(3)	B(23)–B(24)	1.80(3)	B(31)–B(32)	1.79(3)	B(33)–B(34)	1.81(3)
B(11)–B(13)	1.83(3)	B(13)–B(17)	1.71(3)	B(21)–B(23)	1.78(3)	B(23)–B(27)	1.77(3)	B(31)–B(33)	1.80(3)	B(33)–B(37)	1.68(3)
B(11)–B(14)	1.85(3)	B(13)–B(18)	1.67(3)	B(21)–B(24)	1.80(3)	B(23)–B(28)	1.78(3)	B(31)–B(34)	1.82(3)	B(33)–B(38)	1.73(3)
B(11)–B(15)	1.72(3)	B(14)–B(18)	1.77(3)	B(21)–B(25)	1.73(3)	B(24)–B(28)	1.76(3)	B(31)–B(35)	1.77(3)	B(34)–B(38)	1.84(3)
B(11)–B(10)	1.75(3)	B(14)–B(10)	1.82(3)	B(21)–B(20)	1.72(3)	B(24)–B(20)	1.79(3)	B(31)–B(30)	1.78(3)	B(34)–B(30)	1.80(3)
B(12)–B(13)	1.79(3)	B(15)–B(10)	2.02(3)	B(22)–B(23)	1.76(3)	B(25)–B(20)	2.09(3)	B(32)–B(33)	1.78(3)	B(35)–B(30)	2.09(3)
B(12)–B(15)	1.75(3)	B(17)–B(18)	2.02(3)	B(22)–B(25)	1.77(3)	B(27)–B(28)	2.05(3)	B(32)–B(35)	1.81(3)	B(37)–B(38)	2.08(3)
B(12)–B(17)	1.82(3)			B(22)–B(27)	1.79(3)			B(32)–B(37)	1.75(3)		
(iii) Others											
C(ring)–C(Me)(range)		1.50(2)–1.60(3)									
C–C(Me)(range)		1.51(3)–1.59(3)									

crystallography [11a]. The 5,9-isomer (configuration **III**) was isolated from a similar reaction with *nido*-$[B_5H_8]^-$ and characterised by NMR spectroscopy [11b].

We describe here the synthesis and characterization of a *nido*-6,9-dimetalladecaborane of ruthenium.

2. Results and discussion

Reaction of $[(\eta^6\text{-pcym})RuCl_2]_2$ with *arachno*-$[B_9H_{14}]^-$ (from the NEt_4^+ salt) and water in dichloromethane solution for 16 h, followed by chromatographic separation, yielded deep green (**1**, 4%) and bright orange (**2**, 30%) air-stable metallaborane products. These were characterised as $[6,9\text{-}(\eta^6\text{-pcym})_2\text{-}nido\text{-}6,9\text{-}Ru_2B_8H_{12}]$ (**1**) and $[6\text{-}(\eta^6\text{-pcym})\text{-}nido\text{-}6\text{-}RuB_9H_{13}]$ (**2**) by NMR spectroscopy and, in the case of compound (**1**), by a single-crystal X-ray diffraction analysis. Compound (**2**) was satisfactorily identified as $[6\text{-}(\eta^6\text{-pcym})\text{-}nido\text{-}6\text{-}RuB_9H_{13}]$ by comparison of its NMR data with published data [1].

The reaction giving the major product, (**2**), may be represented stoichiometrically by Eq. (1)

$$[(\eta^6\text{-pcym})RuCl_2]_2 + 2[NEt_4][B_9H_{14}] \rightarrow 2[6\text{-}(\eta^6\text{-pcym})RuB_9H_{13}] + 2NEt_4Cl + 2HCl \qquad (1)$$

Compound (**1**) may be thought of as being derived from compound (**2**) by hydrolysis followed by reaction with another ruthenium centre. This may be represented stoichiometrically by Eqs. (2) and (3).

$$[6\text{-}(\eta^6\text{-pcym})RuB_9H_{13}] + 3H_2O \rightarrow [4\text{-}(\eta^6\text{-pcym})\text{-}arachno\text{-}RuB_8H_{14}] + B(OH)_3 \qquad (2)$$

$$2[4\text{-}(\eta^6\text{-pcym})\text{-}arachno\text{-}RuB_8H_{14}] + [(\eta^6\text{-pcym})RuCl_2]_2 \rightarrow 2[6,9\text{-}(\eta^6\text{-pcym})_2\text{-}nido\text{-}6,9\text{-}Ru_2B_8H_{12}] + 4HCl \qquad (3)$$

Hydrolysis of compound (**2**) (Eq. (2)) may lead to a nine-vertex *arachno*-ruthenaborane intermediate having the skeletal structure of *iso-arachno*-B_9H_{15} or *arachno*-$[B_9H_{14}]^-$ (conformation **IV**). Attempts to degrade compound (**2**) under conditions identical with those used to synthesise *arachno*-$[B_9H_{14}]^-$, with a view to preparing a nine-vertex metallaborane analogue of *arachno*-$[B_9H_{14}]^-$, have been reported to give $[5\text{-}(\eta^6\text{-pcym})\text{-}6\text{-}(OEt)\text{-}nido\text{-}5\text{-}RuB_9H_{12}]$ [12]. Metallaboranes having the structural motif of *iso-arachno*-B_9H_{15} are known for a number of transition metals [13,14] but not for ruthenium. Reaction of such a nine-vertex ruthen-

Table 2
Selected bond angles (°) for $[6,9\text{-}(\eta^6\text{-MeC}_6H_4\text{-}4\text{-}^iPr)_2\text{-}nido\text{-}6,9\text{-}Ru_2B_8H_{12}]$ (**2**) with estimated standard deviations in parentheses

Molecule a		Molecule b		Molecule c	
(i) At the ruthenium atom					
B(12)–Ru(1)–B(15)	46.1(7)	B(22)–Ru(3)–B(25)	47.0(7)	B(32)–Ru(5)–B(35)	48.3(7)
B(12)–Ru(1)–B(17)	48.0(8)	B(22)–Ru(3)–B(27)	47.8(7)	B(32)–Ru(5)–B(37)	46.3(8)
B(15)–Ru(1)–B(17)	81.0(8)	B(25)–Ru(3)–B(27)	82.1(7)	B(35)–Ru(5)–B(37)	81.8(8)
B(10)–Ru(2)–B(14)	48.0(7)	B(20)–Ru(4)–B(24)	47.6(7)	B(30)–Ru(6)–B(34)	47.6(8)
B(10)–Ru(2)–B(18)	80.7(7)	B(20)–Ru(4)–B(28)	82.1(7)	B(30)–Ru(6)–B(38)	82.7(7)
B(14)–Ru(2)–B(18)	46.6(6)	B(24)–Ru(4)–B(28)	46.6(8)	B(34)–Ru(6)–B(38)	48.3(8)
(ii) Ruthenium–Boron–Boron					
Ru(1)–B(12)–B(11)	118.6(11)	Ru(3)–B(22)–B(21)	120.0(12)	Ru(5)–B(32)–B(31)	117.8(10)
Ru(1)–B(12)–B(13)	116.3(12)	Ru(3)–B(22)–B(23)	122.0(12)	Ru(5)–B(32)–B(33)	116.8(12)
Ru(1)–B(12)–B(15)	66.9(10)	Ru(3)–B(22)–B(25)	68.7(9)	Ru(5)–B(32)–B(35)	65.4(9)
Ru(1)–B(12)–B(17)	66.2(9)	Ru(3)–B(22)–B(27)	68.1(9)	Ru(5)–B(32)–B(37)	67.0(10)
Ru(1)–B(15)–B(10)	122.3(13)	Ru(3)–B(25)–B(20)	122.2(10)	Ru(5)–B(35)–B(30)	121.9(13)
Ru(1)–B(15)–B(11)	121.9(12)	Ru(3)–B(25)–B(21)	119.3(12)	Ru(5)–B(35)–B(31)	119.4(12)
Ru(1)–B(15)–B(12)	67.0(9)	Ru(3)–B(25)–B(22)	64.2(9)	Ru(5)–B(35)–B(32)	66.2(9)
Ru(1)–B(17)–B(12)	65.9(9)	Ru(3)–B(27)–B(22)	64.1(8)	Ru(5)–B(37)–B(32)	66.7(10)
Ru(1)–B(17)–B(13)	119.6(12)	Ru(3)–B(27)–B(23)	118.2(11)	Ru(5)–B(37)–B(33)	121.0(14)
Ru(1)–B(17)–B(18)	123.9(10)	Ru(3)–B(27)–B(28)	125.1(11)	Ru(5)–B(37)–B(38)	123.8(11)
Ru(2)–B(10)–B(11)	120.6(12)	Ru(4)–B(20)–B(21)	120.0(11)	Ru(6)–B(30)–B(31)	120.3(12)
Ru(2)–B(10)–B(14)	64.5(9)	Ru(4)–B(20)–B(24)	65.2(9)	Ru(6)–B(30)–B(34)	66.9(10)
Ru(2)–B(10)–B(15)	123.6(11)	Ru(4)–B(20)–B(25)	123.4(11)	Ru(6)–B(30)–B(35)	122.8(12)
Ru(2)–B(14)–B(10)	67.5(9)	Ru(4)–B(24)–B(20)	67.1(9)	Ru(6)–B(34)–B(30)	65.5(10)
Ru(2)–B(14)–B(11)	118.7(10)	Ru(4)–B(21)–B(21)	118.2(11)	Ru(6)–B(34)–B(31)	117.1(12)
Ru(2)–B(14)–B(13)	117.2(10)	Ru(4)–B(24)–B(23)	120.9(13)	Ru(6)–B(34)–B(33)	114.6(13)
Ru(2)–B(14)–B(18)	68.7(9)	Ru(4)–B(24)–B(28)	68.3(10)	Ru(6)–B(34)–B(38)	65.7(9)
Ru(2)–B(18)–B(13)	120.2(11)	Ru(4)–B(28)–B(23)	118.8(13)	Ru(6)–B(38)–B(33)	118.5(12)
Ru(2)–B(18)–B(14)	64.7(7)	Ru(4)–B(28)–B(24)	65.1(10)	Ru(6)–B(38)–B(34)	66.0(9)
Ru(2)–B(18)–B(17)	121.8(10)	Ru(4)–B(28)–B(27)	121.3(11)	Ru(6)–B(38)–B(37)	120.7(11)

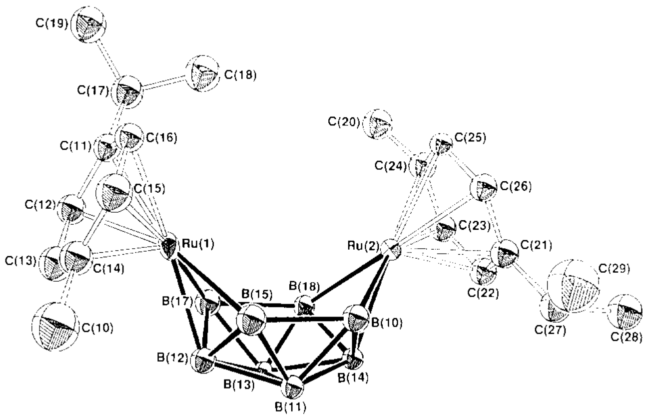
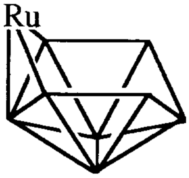


Fig. 1. Thermal ellipsoid diagram (probability level 50%) of $[6,9\text{-}(\eta^6\text{-pcym})_2\text{-}nido\text{-}6,9\text{-}Ru_2B_8H_{12}]$ (**1**) (molecule a). There are another two crystallographically distinct molecules that differ in the angle of twist of the two (η^6-pcym) groups bound to the ruthenium atoms relative to the $\{Ru_2B_8H_{12}\}$ cluster.

aborane intermediate with another ruthenium centre, in a reaction similar to that leading initially to the formation of compound (**2**), would lead to the formation of the ten-vertex diruthanaborane compound (**1**), as represented stoichiometrically by Eq. (3).



IV

A crystal of compound (**1**) suitable for X-ray analysis was obtained from a dichloromethane solution by diffusion of *n*-hexane. There are three crystallographically independent molecules in the unit cell (a,b and c) that differ primarily in the orientation of the metal-bound *p*-cymene ligands relative to the $\{Ru_2B_8H_{12}\}$ cluster. The structure of molecule a is shown in Fig. 1.

Selected interatomic distances and angles are given in Tables 1 and 2, respectively. Atomic coordinates and isotropic temperature factors are listed in Table 3. Compound (**1**) is readily seen to be a *nido*-6,9-dimetalladecaborane and to have a structure based upon that of *nido*-$B_{10}H_{14}$ in which HB(6) and HB(9) have been replaced by $\{Ru(\eta^6\text{-pcym})\}$ units. The boron–boron and ruthenium–boron interatomic distances are unexceptional for a *nido*-metalladecaborane [9] [$Ru\text{–}B_{(range)}$ = 2.17(2)–2.27(2) Å; $B\text{–}B_{(range)}$ = 1.69(3)–1.85(3) Å for the three independent molecules]. The interatomic distances of those parts of the cluster that have no direct bond to either metal centre are very similar to those in $B_{10}H_{14}$ itself [15], and the overall structure is very similar to that of the only reported analogue, $[6,9\text{-}(\eta^5\text{-}C_5Me_5)_2\text{-}6,9\text{-}nido\text{-}Co_2B_8H_{12}]$ [11]. The B(15)–B(10) and B(17)–B(18) inter-boron distances of molecule a are both diagnostically long, at 2.02(3) Å, as are the corresponding distances in molecules *b* [2.09(3), 2.05(3) Å] and *c* [2.09(3), 2.08(3) Å], as observed in the parent cluster *nido*-$B_{10}H_{14}$ [15]. There are variations in the $Ru\text{–}C_{(aryl)}$ distances [$Ru\text{–}C_{(aryl)(range)}$ = 2.16(1)–2.24(1) Å] although these are within the range typically found in (arene)ruthenium metallaboranes [16] and have been attributed [2] to differential *trans* influences or steric effects of the nearest neighbour components of the borane cluster. Although the hydrogen atoms associated with the borane moieties could not be located with any certainty, and were consequently omitted from the calculations, they could be clearly identified from the NMR results.

The measured NMR properties of compound (**1**) are shown in Table 4. The $^{11}B\text{-}\{^1H\}$ NMR spectrum exhibits three resonances with relative intensities 2 : 2 : 4, and indicates a time-averaged C_{2v} symmetry. Selective $^1H\text{-}\{^{11}B\}$ NMR experiments related the hydrogen atom resonances to their directly bound boron atoms, and revealed that all had directly bound *exo* hydrogen atoms. One high-field ^1H resonance ($\delta^1H = -8.49$ ppm (4H)) is present, and is attributable to four Ru–Hμ–B bridging hydrogen atoms. The ^1H NMR data for the *p*-cymene ligands are consistent with the $\{Ru_2B_8H_{12}\}$ cluster having time-averaged C_{2v} symmetry. The overall ^{11}B shielding pattern is very similar to that shown by the only other established 6,9-dimetalladecaborane, $[6,9\text{-}(\eta^5\text{-}C_5Me_5)\text{-}nido\text{-}6,9\text{-}Co_2B_8H_{12}]$ [11b]. For comparison purposes, the NMR data for this compound are shown in Table 4 with those for compound (**1**).

In accord with the broad metallaborane shielding patterns observed elsewhere [17], the general ^{11}B shielding pattern of compounds (**1**) and (**2**) are very similar to that of *nido*-$B_{10}H_{14}$ (shown in Fig. 2).

On introduction of a metal centre into the B(6) position in the *nido*-decaboranyl unit it is only the boron atoms adjacent to the metal centre, B(2) and B(5, 7), that show significant deshielding. The sites distant to the metal centre, B(1, 3), B(4) and B(8, 10), are little affected by the introduction of the metal centre ($\Delta\delta(^{11}B) < 5$ ppm). Only the boron *trans* to the metal centre, B(4), shows a slightly larger shift ($\Delta\delta(^{11}B) = +7.6$ ppm). On the introduction of a second metal centre into the *nido*-decaboranyl unit a similar deshielding is observed. Only those adjacent to the metal centre change significantly, whereas those distant from the additional metal centre remain relatively unchanged. Again the boron *trans* to the metal centre, B(2), shows a slightly larger change in shift, $\Delta\delta(^{11}B) = +11.4$ ppm. In compounds (**1**) and (**2**) a general deshielding of the B(2) and B(5, 7) nuclei [and with compound (**1**), B(4) and B(8, 10) additionally] adjacent to the metal centre may be expected since the metal-to-boron bonding electrons are expected to have access to lower excited states associated with the metal centre.

Table 3
Atom coordinates and isotropic thermal parameters for [6,9-(η^6-pcym)$_2$-*nido*-6,9-Ru$_2$B$_8$H$_{12}$]

Atom	x	y	z	U
RU(1)	0.50186(17)	0.77748(10)	0.25268(5)	
RU(2)	0.28263(15)	0.55607(9)	0.14744(5)	
RU(3)	0.41617(15)	0.16922(9)	0.20723(5)	
RU(4)	0.20341(16)	−0.05451(10)	0.09822(5)	
RU(5)	0.14647(15)	0.40348(10)	0.56746(4)	
RU(6)	−0.01084(15)	0.20637(9)	0.43340(5)	
C(11)	0.3748(10)	0.8572(9)	0.3074(4)	0.030(4)
C(12)	0.4977(10)	0.8348(9)	0.3350(4)	0.033(4)
C(13)	0.6280(10)	0.8540(9)	0.3165(4)	0.043(5)
C(14)	0.6354(10)	0.8955(9)	0.2704(4)	0.039(5)
C(15)	0.5125(10)	0.9179(9)	0.2427(4)	0.046(5)
C(16)	0.3821(10)	0.8988(9)	0.2612(4)	0.030(4)
C(17)	0.2243(26)	0.8311(16)	0.3266(8)	0.043(5)
C(18)	0.1235(30)	0.7810(18)	0.2832(9)	0.051(6)
C(19)	0.1562(30)	0.9149(18)	0.3459(10)	0.051(6)
C(10)	0.7838(38)	0.9181(25)	0.2502(13)	0.073(8)
C(21)	0.2086(13)	0.4910(8)	0.0696(4)	0.031(4)
C(22)	0.2106(13)	0.4302(8)	0.1067(4)	0.031(4)
C(23)	0.1370(13)	0.4440(8)	0.1519(4)	0.030(4)
C(24)	0.0613(13)	0.5188(8)	0.1600(4)	0.032(4)
C(25)	0.0593(13)	0.5796(8)	0.1228(4)	0.021(3)
C(26)	0.1330(13)	0.5657(8)	0.0776(4)	0.028(4)
C(27)	0.2876(23)	0.4699(14)	0.0201(7)	0.034(4)
C(28)	0.2198(27)	0.3893(16)	−0.0125(9)	0.045(5)
C(29)	0.2929(49)	0.5459(29)	−0.0155(15)	0.092(11)
C(20)	−0.0119(24)	0.5369(15)	0.2105(8)	0.040(5)
B(11)	0.6394(20)	0.6192(13)	0.1681(7)	0.020(3)
B(12)	0.6573(22)	0.6776(14)	0.2326(7)	0.025(4)
B(13)	0.5928(18)	0.5666(11)	0.2262(6)	0.015(3)
B(14)	0.5060(20)	0.5280(12)	0.1619(6)	0.019(3)
B(15)	0.5844(25)	0.7235(15)	0.1768(8)	0.032(4)
B(17)	0.5157(23)	0.6382(14)	0.2694(7)	0.027(4)
B(18)	0.4217(21)	0.5368(13)	0.2218(7)	0.020(3)
B(10)	0.4823(23)	0.6255(14)	0.1284(7)	0.027(4)
C(31)	0.6113(12)	0.2459(7)	0.2000(3)	0.022(3)
C(32)	0.6493(12)	0.1695(7)	0.2212(3)	0.025(3)
C(33)	0.5917(12)	0.1462(7)	0.2669(3)	0.024(3)
C(34)	0.4960(12)	0.1991(7)	0.2914(3)	0.026(3)
C(35)	0.4580(12)	0.2755(7)	0.2702(3)	0.029(4)
C(36)	0.5156(12)	0.2988(7)	0.2245(3)	0.031(4)
C(37)	0.6740(21)	0.2768(13)	0.1502(7)	0.031(4)
C(38)	0.7104(22)	0.2013(13)	0.1108(7)	0.032(4)
C(39)	0.8036(24)	0.3350(15)	0.1665(8)	0.038(4)
C(30)	0.4233(21)	0.1701(13)	0.3390(7)	0.031(4)
C(41)	0.3298(11)	−0.1366(9)	0.0467(4)	0.030(4)
C(42)	0.3187(11)	−0.1759(9)	0.0934(4)	0.021(3)
C(43)	0.1867(11)	−0.1938(9)	0.1109(4)	0.029(4)
C(44)	0.0657(11)	−0.1725(9)	0.0815(4)	0.045(5)
C(45)	0.0768(11)	−0.1332(9)	0.0347(4)	0.043(5)
C(46)	0.2089(11)	−0.1152(9)	0.0173(4)	0.040(5)
C(47)	0.4761(24)	−0.1199(15)	0.0264(8)	0.037(4)
C(48)	0.5418(26)	−0.2067(15)	0.0111(8)	0.042(5)
C(49)	0.5789(27)	−0.0623(17)	0.0691(9)	0.045(5)
C(40)	−0.0807(35)	−0.1889(22)	0.1024(12)	0.066(7)
B(21)	0.0659(22)	0.1087(14)	0.1769(7)	0.025(4)
B(22)	0.1986(22)	0.1957(14)	0.1850(7)	0.023(4)
B(23)	0.1163(23)	0.1613(14)	0.1213(7)	0.027(4)
B(24)	0.0558(23)	0.0488(14)	0.1122(7)	0.026(4)
B(25)	0.2089(21)	0.1052(13)	0.2224(7)	0.023(4)
B(27)	0.3002(21)	0.1838(13)	0.1284(7)	0.023(4)
B(28)	0.1987(25)	0.0841(15)	0.0786(8)	0.031(4)
B(20)	0.1120(21)	0.0018(13)	0.1714(7)	0.023(4)
C(51)	−0.0022(9)	0.4646(8)	0.6220(4)	0.027(3)
C(52)	0.0074(9)	0.5151(8)	0.5796(4)	0.021(3)
C(53)	0.1385(9)	0.5467(8)	0.5673(4)	0.025(3)
C(54)	0.2600(9)	0.5277(8)	0.5972(4)	0.037(4)
C(55)	0.2504(9)	0.4772(8)	0.6395(4)	0.036(4)
C(56)	0.1193(9)	0.4457(8)	0.6519(4)	0.032(4)
C(57)	−0.1490(24)	0.4307(15)	0.6345(8)	0.039(4)
C(58)	−0.2306(28)	0.5073(17)	0.6568(9)	0.048(5)
C(59)	−0.2348(34)	0.3793(20)	0.5885(10)	0.061(7)
C(50)	0.4060(25)	0.5623(16)	0.5829(8)	0.041(5)
C(61)	−0.2002(12)	0.1184(7)	0.4243(4)	0.029(4)
C(62)	−0.2419(12)	0.2009(7)	0.4140(4)	0.023(3)
C(63)	−0.1786(12)	0.2445(7)	0.3758(4)	0.027(3)
C(64)	−0.0736(12)	0.2057(7)	0.3479(4)	0.039(5)
C(65)	−0.0318(12)	0.1233(7)	0.3582(4)	0.034(4)
C(66)	−0.0951(12)	0.0796(7)	0.3964(4)	0.027(4)
C(67)	−0.2686(22)	0.0686(14)	0.4658(7)	0.033(4)
C(68)	−0.3042(24)	0.1260(15)	0.5157(8)	0.038(4)
C(69)	−0.4109(25)	0.0234(15)	0.4377(8)	0.041(5)
C(60)	−0.0113(23)	0.2552(14)	0.3067(7)	0.036(4)
B(31)	0.3302(20)	0.2671(12)	0.4858(7)	0.022(3)
B(32)	0.3120(21)	0.3093(13)	0.5529(7)	0.023(4)
B(33)	0.2542(23)	0.1998(15)	0.5313(8)	0.028(4)
B(34)	0.2089(25)	0.1757(15)	0.4607(8)	0.030(4)
B(35)	0.2683(24)	0.3729(14)	0.4981(8)	0.030(4)
B(37)	0.1575(24)	0.2606(15)	0.5719(8)	0.030(4)
B(38)	0.0817(22)	0.1672(13)	0.5108(7)	0.025(4)
B(30)	0.1945(24)	0.2800(15)	0.4354(8)	0.029(4)

The molecule is notionally based upon *nido*-B$_{10}$H$_{14}$ with the HB(6) and HB(9) positions replaced by isoelectronic and isolobal {Ru(η^6-pcym)} moieties. The ruthenium centres are thereby formally eighteen-electron d^6 Ru(II) centres contributing three orbitals and two electrons to the cluster bonding scheme.

In contrast to the reaction between [(η^6-pcym)-RuCl$_2$]$_2$ and [NEt$_4$][B$_9$H$_{14}$] in the presence of water similar reactions involving [(η^5-C$_5$Me$_5$)RhCl$_2$]$_2$ [2] and [(η^6-C$_6$Me$_6$)RuCl$_2$]$_2$ [3] yielded only the expected 6-metalla-*nido*-decaboranes, albeit in lower yields and with a significantly increased amount of chromatographically immobile material. Unlike the 6-metalla-*nido*-decaboranes [6-(η^5-C$_5$Me$_5$)-*nido*-6-RhB$_9$H$_{13}$] [5a] and [6-(η^6-C$_6$Me$_6$)-*nido*-6-RuB$_9$H$_{13}$] [3b] compound **1** shows no sign of reaction with tertiary phosphines (PMe$_2$Ph, PMePh$_2$, PPh$_3$, dppm) even upon extended periods of time in refluxing in dichloromethane. Reaction of compound **1** with MeNC in dichloromethane at room temperature was, however, instantaneous, and gave an unstable yellow complex that has yet to be characterized.

3. Experimental details

3.1. General

Reactions were carried out under dry nitrogen in dried and degassed solvents, but subsequent manipula-

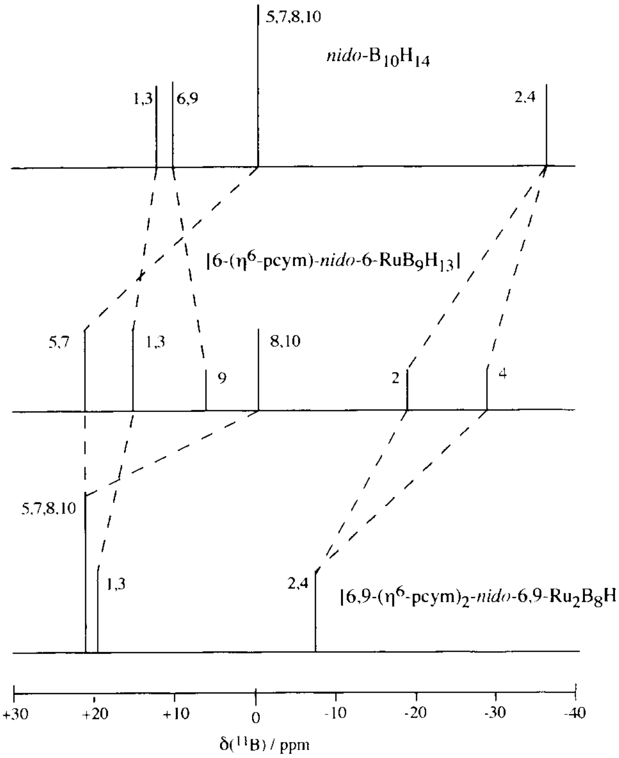


Fig. 2. Diagram showing the ^{11}B NMR resonance positions for *nido*-$B_{10}H_{14}$ [25], [6-(η^6-pcym)-*nido*-6-RuB_9H_{13}] [1], and [6,9-(η^6-pcym)$_2$-*nido*-6,9-$Ru_2B_8H_{12}$].

tions and separations were carried out in air. [(η^6-pcym)RuCl_2]$_2$ [18] and [NEt_4][B_9H_{14}] [13] were prepared as previously described; other starting materials were obtained commercially. Preparative thin layer chromatography (TLC) used 1 mm layers of silica (Kieselgel GF54; Fluka) on glass plates of dimensions 20 × 20 cm^2; these were made in the laboratory as required, from an acetone slurry followed by drying in air at ca. 60°C.

3.2. Nuclear magnetic resonance spectroscopy

This was performed at 9.40 Tesla on a Brucker AM400 instrument. The procedure used for ^{1}H{^{11}B} spectroscopy has been described elsewhere [19] Other NMR spectroscopy was straightforward. Chemical shifts $\delta(^1H)$ and $\delta(^{11}B)$ are given in ppm to high frequency (low field) of Ξ100 (SiMe4) and 32.083971 MHz (nominally $BF_3(OEt)_2$ in $CDCl_3$) [20], respectively.

3.3. Reaction of [(η^6-pcym)RuCl_2]$_2$, [NEt_4][B_9H_{14}] and water

[(η^6-pcym)RuCl_2]$_2$ (0.2 g; 0.327 mmol), [NEt_4][B_9H_{14}] (0.167 g; 0.69 mmol) and water (13 μl; 0.72 mmol) were stirred in CH_2Cl_2 solution (50 cm^3) for 16 h. The resulting brown solution was reduced in volume (rotary evaporator) and subjected to preparative TLC with CH_2Cl_2 as eluant. Two mobile products were present as a dark green TLC band (compound (**1**), R_f0.80) and an intense orange-yellow TLC band (compound (**2**), R_f0.95); these were purified by repeated chromatography and recrystallization from CH_2Cl_2/*n*-hexane (1 : 1), and identified as [6,9-(η^6-pcym)$_2$-*nido*-6,9-$Ru_2B_8H_{12}$] (**1**) (0.015 g; 0.026 mmol; 4%) and [6-(η^6-pcym)-*nido*-6-RuB_9H_{13}] (**2**) (0.073 g; 0.195 mmol; 30%) as described in the text.

Table 4
Measured NMR parameters for [6,9-(η^6-pcym)$_2$-*nido*-6,9-$Ru_2B_8H_{12}$] compound (**1**), and, for comparison purposes, data for [6,9-(η^5-C_5Me_5)$_2$-*nido*-6,9-$Co_2B_8H_{12}$] [11b]

Assignment [c]	[6,9-(η^6-pcym)$_2$-*nido*-6,9-$Ru_2B_8H_{12}$] [a]			[6,9-(η^6-C_5Me_5)$_2$-*nido*-6,9-$Co_2B_8H_{12}$] [h]		
	$\delta(^{11}B)$ [de] (ppm)	$^1J(^{11}B-^1H)$ [f] (Hz)	$\delta(^1H)$ [gh] (ppm)	$\delta(^{11}B)$ [de] (ppm)	$^1J(^{11}B-^1H)$ [f] (Hz)	$\delta(^1H)$ [gh] (ppm)
2,4	−7.4 (2B)	137	+2.12 (2H)	+2.3 (2B)	134	
1,3	+19.7 (2B)	133	+4.09 (2H)			+4 [j]
				+20.8 (6B)	116	
5,7,8,10	+20.8 (4B)	133	+4.56 (4H)			
6,9	Ru	–	– [i]	Co	–	– [k]
5,6; 6,7; 8,9; 9,10			−8.94 (4H)			−11.65 (4H)

[a] $CDCl_3$ solution at 297 K.

[h] $CDCl_3$ solution at ambient temperature.

[c] Tentative assignments made by comparison with NMR data from [6-(η^6-pcym)-*nido*-6-RuB_9H_{13}] [1].

[d] ± 0.5 ppm.

[c] To high frequency of $BF_3(OEt_2)$.

[f] ± 5 Hz; measured from ^{11}B spectrum with resolution enhancement to achieve baseline separation of doublet components.

[g] ± 0.05 ppm to high frequency of $SiMe_4$.

[h] ^{1}H resonances related to directly bound ^{11}B resonances by selective ^{1}H–^{11}B] experiments.

[i] $\delta(^1H)$(MeC_6H_4-4-^{i}Pr) *Me*, +2.31 ppm; C_6H_4, +5.79 ppm (doublet) and +5.74 ppm (doublet) [mutual splitting 5.7 Hz]; C*H*Me_2, +2.76 ppm (heptet) [$^3J(^1H-^1H)$ = 6.9 Hz]; CH*Me*$_2$, +1.28 ppm (doublet) [^3J(1H-1H) = 6.9 Hz].

[j] BH overlapped quartets.

[k] δ(1H)(C_5Me_5) + 1.80 ppm.

3.4. Crystal structure analysis

Crystals of compound (**1**), suitable for data collection, were obtained from CH_2Cl_2 by the slow liquid-liquid diffusion of *n*-hexane. Syntex diffractometer, graphite-monochromated Mo Kα radiation, $C_{60}H_{120}$-Ru_2B_{24}, $M = 569.21$. Crystals were triclinic, space group $P\bar{1}$, with $a = 9.555(5)$, $b = 15.463(6)$, $c = 25.379(9)$ Å, $\alpha = 95.64(3)$, $\beta = 94.48(4)$, $\gamma = 92.44(4)°$, $U = 3715.4$ Å^3 and $Z = 6$, $D_c = 1.526$ g cm^{-1}, μ(Mo Kα) = 11.97 cm^{-1}, $F(000) = 1728$.

3.5. Data collection and processing

Data were collected and processed at the University of Canterbury. A total of 8340 unique data were measured (the merging $R = 0.039$) at low temperatures (−125°C) using the ω scan technique ($2 < \Theta < 22.5°$; $\pm h \pm k + l$). Intensities of three reflections were monitored during the data collection and showed a variation of $\leq 4\%$ and the data were corrected accordingly. Empirical absorption corrections were based on ψ scans with minimum and maximum corrections of 0.500 and 0.762 respectively being calculated.

3.6. Structure solution and refinement

The structure was solved by direct methods [21] and refined by a full-matrix least-squares method [22]. As already mentioned three crystallographically distinct diruthenaborane units were distinguished. The final refinement cycle converged with values of 0.065 for both R and R_w for the 325 variables and 5440 data for which $F^2 > 3\sigma(F^2)$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with the weight defined as $1.0198/(\sigma^2(F) + 0.003081F^2)$. The atoms of the *p*-cymene ligands were treated as rigid groups with the H in calculated positions (C–H, 0.96 Å). The borane H and those involved in bridging between Ru and B atoms could not be located with any certainty and were not included in the calculations. Anisotropic thermal motion was assumed for the six Ru atoms only. Atomic scattering factors for Ru were taken from the tabulations of Cromer and Mann [23], anomalous dispersion corrections were by Cromer and Liberman [24]. Tables of thermal parameters, hydrogen atom coordinates and full lists of bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank Massey University Research Fund for a post-doctoral Fellowship (MB), the NZ University Grants Committee for equipment, and Drs. John D. Kennedy and Xavier L.R. Fontaine of the University of Leeds for carrying out high-field NMR spectroscopy. We are also grateful to Dr. W.T. Robinson of the University of Canterbury for collecting the crystallographic data.

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