Ruthenium butterfly boride clusters with (η⁶-arene) ligands

Jane R. Galsworthy [a], Catherine E. Housecroft [b,*], Dorn M. Nixon [a], Arnold L. Rheingold [c]

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB1 2EW, UK*
[b] *Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel, Switzerland*
[c] *Department of Chemistry, University of Delaware, Newark, DE 19716, USA*

Received 11 July 1996

Abstract

The ruthenaborane anions $[Ru_3(CO)_9BH_4]^-$ and $[Ru_3(CO)_9B_2H_5]^-$ can be used as building blocks to assemble tetraruthenium butterfly clusters incorporating a wingtip $Ru(\eta^6\text{-Ar})$ fragment in place of the isolobal $Ru(CO)_3$ fragment present in the previously reported compound $[Ru_4H(CO)_{12}BH_2]$. The syntheses and spectroscopic characterizations of $[Ru_4H(\eta^6\text{-Ar})(CO)_9BH_2]$ (Ar = C_6H_6, C_6H_5Me, $MeC_6H_4\text{-}4\text{-CHMe}_2$) are reported. A single crystal structure determination of $[Ru_4H(\eta^6\text{-}C_6H_5Me)(CO)_9BH_2]$ confirms the location of the η^6-arene ligand in a wingtip site but reveals that the butterfly framework is essentially unperturbed in going from an $Ru(CO)_3$ to $Ru(\eta^6\text{-Ar})$ cluster fragment.

Keywords: Ruthenium; Boron; Ruthenium butterfly boride cluster; Crystal structure

1. Introduction

Work from our group concerning low oxidation state transition metal clusters containing interstitial and semi-interstitial boron atoms has focused on clusters with carbonyl or η^5-cyclopentadienyl ligands and, most significantly, on clusters containing $Ru(CO)_3$ or $Rh(\mu^5\text{-}C_5Me_5)$ fragments [1,2]. Perturbation of the electronic structure of a cluster and thus its chemistry can be achieved by changes in the ligands, or by going from a homometallic to a heterometallic framework. We have addressed both these issues, firstly with the substitution of phosphine for carbonyl ligands [1,3] and secondly in a comparison of some aspects of the chemistries of the isoelectronic clusters $[Ru_4H(CO)_{12}BH_2]$ **1** and $[RhRu_3H(\eta^5\text{-}C_5Me_5)(CO)_9BH_2]$ [1,4].

Of the boride clusters studied, we have found, perhaps not surprisingly, that it is the semi-interstitial environment that best lends itself to participation in chemical transformations and compound **1** has been a key precursor in our work. In this paper we report the incorporation of one $Ru(\eta^6\text{-arene})$ unit in place of a wingtip $Ru(CO)_3$ unit in **1**, and thereby illustrate the

formation of a new group of clusters containing a semi-interstitial boron atom.

1
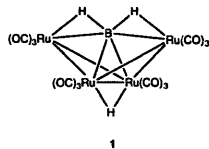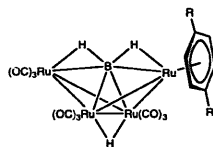
2: R = R' = H
3: R = Me, R' = H
4: R = ʲPr, R' = Me

2. Experimental section

2.1. General

Fourier transform NMR spectra were recorded on a Bruker WM 250 spectrometer; ^1H shifts are reported

with respect to δ 0 for Me$_4$Si; ^{11}B NMR with respect to δ 0 for F$_3$B·OEt$_2$; downfield chemical shifts are positive. Solution infrared spectra were recorded on a Perkin–Elmer FT 1710 spectrophotometer, and fast atom bombardment (FAB) mass spectra using Kratos instruments (3-NBA matrix = 3-nitrobenzyl alcohol).

All reactions were carried out under argon by using standard Schlenk methods. Solvents were pre-dried and distilled under N$_2$. Separations were achieved by using thin layer plate chromatography with Kieselgel 60-PF-254 (Merck). The compounds [{Ru(CO)$_3$Cl$_2$}$_2$] and [{Ru(η^6-C$_6$H$_4$-4-CHMe$_2$)Cl$_2$}$_2$] were used as received (Aldrich) and [(Ph$_3$P)$_2$N][Ru$_3$(CO)$_9$BH$_4$] [5], [(Ph$_3$P)$_2$N][Ru$_3$(CO)$_9$B$_2$H$_5$] [6], [{Ru(η^6-Ar)-Cl$_2$}$_2$] (Ar = C$_6$H$_6$ or C$_6$H$_5$Me) and [Ru(η^6-C$_6$H$_6$)(MeCN)$_3$][BF$_4$]$_2$ [7] were prepared according to published procedures. [Ru(η^6-C$_6$H$_6$)(PhCN)$_3$][BF$_4$]$_2$, [Ru(η^6-C$_6$H$_5$Me)(MeCN)$_3$][BF$_4$]$_2$ and [Ru(η^6-C$_6$H$_5$Me)(MeCN)$_3$][PF$_6$]$_2$ were prepared in a similar manner to [Ru(η^6-C$_6$H$_6$)(MeCN)$_3$][BF$_4$]$_2$ [7]. Yields are with respect to the starting clusters [(Ph$_3$P)$_2$N]-[Ru$_3$(CO)$_9$BH$_4$] or [(Ph$_3$P)$_2$N][Ru$_3$(CO)$_9$B$_2$H$_5$].

2.2. Preparation of [Ru$_4$H(CO)$_{12}$BH$_2$]

A solution of the compound [{Ru(CO)$_3$Cl$_2$}$_2$] (50 mg, 0.1 mmol) in CH$_2$Cl$_2$ (10 cm^3) was added to a solution of [(Ph$_3$P)$_2$N][Ru$_3$(CO)$_9$BH$_4$] (111 mg, 0.1 mmol) in CH$_2$Cl$_2$ (10 cm^3). The solution was stirred for 1 h, and then solvent was removed in vacuo and products were separated by TLC, eluting with hexane. The known cluster [Ru$_4$H(CO)$_{12}$BH$_2$] was obtained in 90% yield and was characterized by comparison of the IR, ^{1}H and ^{11}B NMR spectroscopic and mass spectral data with those in the literature [8,9].

2.3. Preparation of [Ru$_4$H(η^6-C$_6$H$_6$)(CO)$_9$BH$_2$] 2

Method I. A solution of the compound [(Ph$_3$P)$_2$N][Ru$_3$(CO)$_9$B$_2$H$_5$] (44 mg, 0.04 mmol) in CH$_2$Cl$_2$ (5 cm^3) was added to solid [Ru(η^6-C$_6$H$_6$)(PhCN)$_3$][BF$_4$]$_2$ (52 mg, 0.08 mmol). The brown solution was stirred for 1 h and the reaction was monitored by IR spectroscopy. After removal of solvent, the products were separated by TLC, eluting with hexane/CH$_2$Cl$_2$ (2:1). The first fraction (yellow) consisted of [Ru$_4$H$_4$(CO)$_{12}$] [10] and [Ru$_3$H(CO)$_9$B$_2$H$_5$] [11] in trace amounts. The second fraction (orange, 45%) was identified as [Ru$_4$H(η^6-C$_6$H$_6$)(CO)$_9$BH$_2$] 2. Intractable material remained on the baseline. For 2: NMR (CDCl$_3$, 298 K): ^{1}H (400 MHz), δ +5.58 (s, C$_6$H$_6$), −9.7 (br, B–H–Ru), −20.96 (s, Ru–H–Ru); [11]B (128 MHz), δ +102 (t, J_{BH} 60 Hz); IR (hexane, cm^{-1}) ν_{CO} 2081s, 2045vs, 2017s, 1997m, 1987m, 1982s; FAB mass spectrum: m/z 748 (M$^+$) with 7 CO losses (calc. for ^{12}C$_{15}$^{1}H$_9$^{11}B^{16}O$_9$^{101}Ru$_4$ 748).

Method II. A solution of [Ru(η^6-C$_6$H$_6$)-(MeCN)$_3$][PF$_6$]$_2$ (118 mg, 0.2 mmol) CH$_2$Cl$_2$ (10 cm^3) was added to a solution of [(Ph$_3$P)$_2$N]-[Ru$_3$(CO)$_9$BH$_4$] (110 mg, 0.1 mmol) in CH$_2$Cl$_2$ (10 cm^3). After stirring for 1 h, the yellow solution had become orange. Solvent was removed in vacuo and the products separated by TLC, eluting with hexane. Initial yellow fractions consisted of [Ru$_3$(CO)$_9$BH$_5$] [12], [Ru$_3$H(CO)$_9$B$_2$H$_5$] [11] and [Ru$_4$H(CO)$_{12}$BH$_2$] [8,9], and the fourth fraction (orange, 20%) was identified as compound 2. The baseline on the TLC plate was further eluted with CH$_2$Cl$_2$/hexane (2:1), and three fractions were collected. The first (yellow) band consisted of a mixture of boron-containing products (by ^{11}B NMR spectroscopy) but was not separated further due to the small quantities of material. The second (major) fraction was [(Ph$_3$P)$_2$N][Ru$_6$(CO)$_{17}$B] [6,13,14] and the third was identified as [(Ph$_3$P)$_2$N][H$_2$Ru$_5$(CO)$_{14}$(μ_4-COH)] (5%) [15].

Method III. In a reaction similar to Method II, the compound [{Ru(η^6-C$_6$H$_6$)Cl$_2$}$_2$] (1:1 ratio with [(Ph$_3$P)$_2$N][Ru$_3$(CO)$_9$BH$_4$]) can be used in place of [Ru(η^6-C$_6$H$_6$)(MeCN)$_3$][PF$_6$]$_2$. Compound 2 is obtained in approximately 20% yield.

2.4. Preparations of [Ru$_4$H(η^6-C$_6$H$_5$Me)(CO)$_9$BH$_2$] 3 and [Ru$_4$H(η^6MeC$_6$H$_4$-4-CHMe$_2$)(CO)$_9$BH$_2$] 4

Compounds 3 and 4 can be prepared in approximately 15% and 10% yields respectively by using Methods II or III above, with the appropriate η^6-arene ligand. Compound 3 was also prepared by Method I (but yields were poor) or by the reaction of [(Ph$_3$P)$_2$N][Ru$_3$(CO)$_9$B$_2$H$_5$] with [{Ru(η^6-C$_6$H$_6$)Cl$_2$}$_2$] in a manner analogous to Method III above. The addition of less than an equivalent of thallium(I) hexafluorophosphate aids chloride abstraction. Yields of compound 3 from this route were typically around 10%.

For 3: NMR (CDCl$_3$, 298 K): ^{1}H (400 MHz), δ +5.74 (d, J_{HH} 5.8 Hz, 2H), +5.51 (t, J_{HH} 5.9 Hz, 2H), +5.42 (t, J_{HH} 5.8 Hz, 1H) (for assignments, see text), +2.34 (s, 3H, Me), −9.6 (br, B–H–Ru), −20.88 (s, Ru–H–Ru); [11]B (128 MHz), δ +101 (t, J_{BH} 55 Hz); IR (hexane, cm^{-1}) ν_{CO} 2108w, 2081s, 2066w, 2055w, 2045vs, 2040m, 2016s, 1997m, 1988m, 1981s; FAB mass spectrum: m/z 763 (M$^+$) with 4 CO losses (calc. for ^{12}C$_{16}$^{1}H$_{11}$^{11}B^{16}O$_9$^{101}Ru$_4$ 762).

For 4: NMR (CDCl$_3$, 298 K): ^{1}H (400 MHz), δ +5.53 (d, J_{HH} 5.9 Hz, 2H), +5.47 (t, J_{HH} 5.9 Hz, 2H), +2.12 (s, Me), +1.26 (d, J_{HH} 7 Hz, CH*Me*), −9.7 (br, B–H–Ru), −20.89 (s, Ru–H–Ru); [11]B (128 MHz), δ +101; IR (CH$_2$Cl$_2$, cm^{-1}) ν_{CO} 2077m, 2040vs, 2008w, 1980s; FAB mass spectrum: m/z 804 (M$^+$) with 3 CO losses (calc. for ^{12}C$_{19}$^{1}H$_{17}$^{11}B^{16}O$_9$^{101}Ru$_4$ 804).

Table 1
Crystallographic data for 3

formula	$C_{16}H_{11}BO_9Ru_4$
formula weight	762.3
crystal system	monoclinic
space group	$P2_1/n$
a, b, c (Å)	9.213(2), 12.490(3), 19.301(5)
β (deg)	101.79(2)
volume (Å^3)	2174.2(8)
Z	4
D_x (g cm^{-3})	2.329
μ(Mo Kα) (cm^{-1})	27.7
T (K)	242
diffractometer	Siemens P4
	(graphite monochromator)
2θ range (deg)	4–55 ($\pm h, +k, \pm l$)
reflections (collected,	7846, 4377, 3705 (5σF_o)
independent, observed)	
$R(F), R(wF)$ [a] (%)	2.08, 3.16
$R(F), R(wF)$ [a] (%, all data)	2.85, 3.65
GOF	1.05
N_o/N_v	13.0

[a] $R(F) = \Sigma \Delta / \Sigma(F_o); \quad R(wF) = \Sigma[\Delta w^{1/2}]/[F_o w^{1/2}]; \quad \Delta = |F_o - F_c|; \; w^{-1} = \sigma^2(F_o) + g F_o^2.$

Table 2
Atomic coordinates ($\times 10^4$) for compound 3

Atom	x	y	z
Ru(1)	2065(1)	3822(1)	7765(1)
Ru(2)	−450(1)	3987(1)	8422(1)
Ru(3)	174(1)	1956(1)	9082(1)
Ru(4)	2399(1)	3561(1)	9268(1)
B(1)	1180(5)	2741(3)	8331(2)
O(1)	−2324(4)	3264(3)	7022(2)
O(2)	−326(4)	6362(3)	8050(2)
O(3)	−3070(3)	4128(3)	9168(2)
O(4)	−2685(4)	782(4)	8443(2)
O(5)	−955(5)	2705(3)	10387(2)
O(6)	1993(5)	115(3)	9860(2)
O(7)	2652(4)	3369(3)	10865(2)
O(8)	5020(4)	2094(3)	9251(2)
O(9)	3961(4)	5728(3)	9320(2)
C(1)	−1640(5)	3527(3)	7547(2)
C(2)	−377(4)	5478(3)	8178(2)
C(3)	−2065(4)	4068(3)	8912(2)
C(4)	−1634(6)	1218(4)	8694(3)
C(5)	−518(5)	2445(4)	9902(2)
C(6)	1304(5)	804(4)	9573(2)
C(7)	2516(5)	3439(3)	10271(2)
C(8)	4059(5)	2650(3)	9263(2)
C(9)	3420(5)	4909(4)	9293(2)
C(10)	1570(5)	5184(3)	7009(2)
C(11)	2730(5)	5483(3)	7580(2)
C(12)	4018(5)	4857(4)	7747(3)
C(13)	4156(5)	3929(3)	7361(3)
C(14)	2989(5)	3620(3)	6806(2)
C(15)	1681(5)	4247(4)	6612(2)
C(16)	470(7)	3910(5)	5995(3)
H(1)	773(56)	4298(40)	9259(26)
H(2)	1013(57)	1702(44)	8498(27)
H(3)	1656(51)	2610(40)	7807(24)

2.5. X-ray structural determination

Crystallographic data for compound 3 are collected in Table 1. Deep red block crystals were photographically characterized and determined to belong to the monoclinic crystal system. Systematic absences in the diffraction data uniquely determined the space group. An empirical correction for absorption was applied to the diffraction data ($T_{\text{max/min}} = 1.5$). The structure was solved by direct methods, completed from Fourier difference maps, and refined with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were idealized except for H(1), H(2) and H(3) which were located and refined.

All computations used SHELXTL-PLUS v4.2 software [16]. Atomic coordinates for 3 are given in Table 2. Supplementary data [atomic coordinates, bond parameters, anisotropic thermal parameters and idealized H-atom coordinates (5 pages) and structure factors (16 pages)] are available from the authors (A.L.R.).

3. Results and discussion

3.1. Syntheses and spectroscopic characterizations of compounds 2 to 4

Clusters containing arene ligands are now well established [17] and the ligand can be introduced either as an organic entity or an organometallic fragment. An example of the former method is seen in the preparation of $[Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ in which the benzene ligand caps the trimetal framework [17,18]. Examples of the second strategy include the reaction of the dianion $[Os_3(CO)_9(RC_2R')]^{2-}$ (R or R' = H, Me, Et, Ph) with $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ to yield the heterometallic compound $[Os_3Ru(\eta^6\text{-}C_6H_6)(CO)_9RC_2R')]$ in which the $\{Ru(\eta^6\text{-}C_6H_6)\}^{2+}$ fragment caps the open Os_2C_2 face of the anionic precursor [19]. We have previously reported [5] that, on photolysis, $[Ru_3(CO)_9BH_5]$ undergoes cluster expansion to form a mixture of $[Ru_4H(CO)_{12}BH_2]$ and $[Ru_6(CO)_{17}B]$, and we have made extensive use of the anion $[Ru_3(CO)_9BH_4]^-$ as a building block in the syntheses of heterometallic butterfly clusters containing Ru$_3$MB cores [1,2]. A natural progression of these reactions is the reaction of $[Ru_3(CO)_9BH_4]^-$ with sources of the $\{Ru(\eta^6\text{-}Ar)\}^{2+}$ (Ar = arene) fragment to give unsymmetrical but homometallic boron-containing clusters as shown in Fig. 1. An alternative precursor is $[Ru_3(CO)_9B_2H_5]^-$ which we have already reported can give heterometallic clusters containing only one boron atom [11].

Before attempting to synthesise the arene-substituted clusters, we tested the reaction between $[Ru_3(CO)_9BH_4]^-$ and $[\{Ru(CO_3)Cl_2\}_2]$ to confirm that cluster expansion to the known compound 1 was feasible.

Fig. 1. Schematic representation of the reaction between the anion [Ru$_3$(CO)$_9$BH$_4$] and an {Ru(η^6-arene)}$^{2+}$ fragment to yield products of the type [Ru$_4$H(η^6-arene)(CO)$_9$BH$_2$]. Note that in solution the cluster-bound H atoms in [Ru$_3$(CO)$_9$BH$_4$]$^-$ appear to be involved in a fluxional process [5].

We observed that this reaction proceeds smoothly to give 1 in ≥ 90% yield.

The reaction of [Ru$_3$(CO)$_9$BH$_4$]$^-$ and [Ru(η^6-C$_6$H$_6$)(MeCN)$_3$]$^{2+}$ produced compound 2 in about 20% yield. Self-cluster condensation from [Ru$_3$(CO)$_9$BH$_4$]$^-$ to [Ru$_6$(CO)$_{17}$B]$^-$ competed with the formation of 2. Increased yields of compound 2 were obtained from the reaction of [Ru$_3$(CO)$_9$B$_2$H$_5$]$^-$ with [Ru(η^6-C$_6$H$_6$)(PhCN)$_3$]$^{2+}$. Compound 2 exhibited a triplet (J_{BH} 60 Hz) in the ^{11}B NMR spectrum at δ + 102, characteristic of a BH$_2$ unit residing in an Ru$_4$ butterfly framework. The chemical shift of the signal was at significantly lower field compared to that of the starting cluster, and the shift indicated that the boron atom in the product possessed additional boron–metal bonding interactions [20,21]. The coupling constant of 60 Hz is characteristic of attachment to B–H–M bridging protons and is similar to that observed in [Ru$_4$H(CO)$_{12}$BH$_2$] [8,9]. The parent ion in the mass spectrum of compound 2 and its isotopic distribution were consistent with a formulation of [Ru$_4$H(η^6-C$_6$H$_6$)(CO)$_9$BH$_2$]. In the ^{1}H NMR spectrum, a singlet at δ + 5.58 was assigned to the benzene protons and a singlet at δ − 20.96 was consistent with the presence of an Ru–H–Ru bridging proton. The proposed structure (Fig. 1) places the two B–H–Ru bridging protons in different environments but only one broad resonance (δ − 9.7) was observed at 298 K. On cooling to 183 K, the only change to the spectrum was a sharpening of this signal due to the effects of thermal decoupling of the ^{11}B and ^{1}H spins. Although these ^{1}H NMR spectroscopic data indicated the possibility of the Ru(η^6-C$_6$H$_6$) unit residing in a hinge rather than a wingtip site, we favoured the wingtip site on the grounds of our previous experience [5,11,22]. Attempts to grow crystals of compound 2 were unsuccessful, and we turned our attention to the syntheses of the derivatives [Ru$_4$H(η^6-C$_6$H$_5$Me)(CO)$_9$BH$_2$] 3 and [Ru$_4$H(η^6-MeC$_6$H$_4$-4-CHMe$_2$)(CO)$_9$BH$_2$] 4.

The reaction of [Ru$_3$(CO)$_9$B$_2$H$_5$]$^-$ with [Ru(η^6-C$_6$H$_6$)(PhCN)$_3$]$^{2+}$ produced compound 3 in low yield. Improved yields (although still ≤ 20%) were obtained from the reactions of [Ru$_3$(CO)$_9$B$_2$H$_5$]$^-$ or [Ru$_3$(CO)$_9$BH$_4$]$^-$ with [{Ru(η^6-C$_6$H$_6$)Cl$_2$}$_2$]. Compound 4 was prepared by treating [Ru$_3$(CO)$_9$BH$_4$]$^-$ with [Ru(η^6-C$_6$H$_6$)(PhCN)$_3$]$^{2+}$ or [{Ru(η^6-C$_6$H$_6$)Cl$_2$}$_2$]. The infrared spectra in the carbonyl region of compounds 3 and 4 were very similar, and also resembled that of 2, indicating that the three clusters were structurally related. Compound 3 exhibited a triplet in the ^{11}B NMR spectrum at δ + 101 (J_{BH} 55 Hz), and in the ^{1}H NMR a broad resonance at δ − 9.6 was assigned to B–H–Ru bridging protons. The ^{11}B NMR spectrum of compound 4 also showed a signal at δ + 101 but no coupling was resolved; a broad resonance at δ − 9.7 was consistent with the presence of B–H–Ru bridging protons. For each of compounds 3 and 4, singlets at δ − 20.9 were assigned to an Ru–H–Ru bridging hydride.

Thus, although spectroscopic and mass spectrometric data were consistent with the formulation of products 2–4 as the family of compounds [Ru$_4$H(η^6-Ar)(CO)$_9$BH$_2$] (Ar = C$_6$H$_6$, C$_6$H$_5$Me, MeC$_6$H$_4$-4-CHMe$_2$), they did not permit an unambiguous assignment of the proposed structure shown in Fig. 1.

3.2. Crystal structure of [Ru$_4$H(η^6-C$_6$H$_5$Me)-(CO)$_9$BH$_2$] 3

Crystals of [Ru$_4$H(η^6-C$_6$H$_5$Me)(CO)$_9$BH$_2$] 3 were grown from a dichloromethane solution layered with hexane. The molecular structure of compound 3 is shown in Fig. 2, and selected bond distances and angles are listed in Table 3. The structural determination confirmed that 3 contains an Ru$_4$ butterfly skeleton containing a semi-interstitial boron atom and that, in the solid state, the {Ru(η^6-C$_6$H$_5$Me)} fragment occupied a wingtip site. The Ru–Ru bond distances to the {Ru(η^6-C$_6$H$_5$Me)} unit in 3 are somewhat lengthened compared to the Ru$_{CO}$–Ru$_{CO}$ edges in 3 and the non-hydrogen
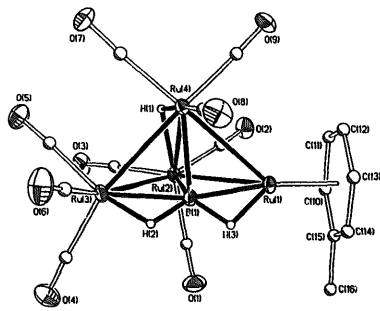
Fig. 2. Molecular structure of [Ru$_4$H(η^6-C$_6$H$_5$Me)(CO)$_9$BH$_2$] 3.

Table 3
Selected bond distances and angles for 3

(a) Bond distances (Å)

Ru(1)–Ru(2)	2.868(1)	Ru(1)–Ru(4)	2.873(1)
Ru(2)–Ru(3)	2.844(1)	Ru(2)–Ru(4)	2.845(1)
Ru(3)–Ru(4)	2.837(1)	Ru(1)–B(1)	2.011(4)
Ru(2)–B(1)	2.196(4)	Ru(3)–B(1)	2.115(5)
Ru(4)–B(1)	2.181(4)	Ru(1)–H(3)	1.57(5)
B(1)–H(3)	1.19(5)	B(1)–H(2)	1.35(6)
Ru(3)–H(2)	1.53(6)	Ru(2)–H(1)	1.81(5)
Ru(4)–H(1)	1.76(5)	Centroid–Ru(1)	1.718(3)

(b) Bond angles (deg)

Ru(1)–Ru(2)–Ru(4)	60.4(1)	Ru(1)–Ru(4)–Ru(2)	60.2(1)
Ru(3)–Ru(2)–Ru(4)	59.8(1)	Ru(2)–Ru(4)–Ru(3)	60.1(1)
Ru(2)–Ru(1)–Ru(4)	59.4(1)	Ru(2)–Ru(3)–Ru(4)	60.1(1)
Ru(1)–B(1)–Ru(3)	165.1(2)	Ru(2)–B(1)–Ru(4)	81.1(1)
Ru(1)–H(3)–B(1)	92.6(30)	Ru(3)–H(2)–B(1)	94.4(32)
Ru(2)–H(1)–Ru(4)	105.7(27)	Centroid–Ru(1)–Ru(2)	137.6(1)
Centroid–Ru(1)–Ru(4)	138.2(1)	Centroid–Ru(1)–B(1)	169.7(3)
Centroid–Ru(1)–H(1)	133(1)		

bridged Ru–Ru edges in cluster 1 [8]. The internal dihedral angle of the Ru$_4$ butterfly in 3 is 111° compared to 118° in compound 1. The boron atom forms a shorter bonding contact with atom Ru(1) (2.011(4) Å) than with the carbonyl associated atoms Ru(2), Ru(3) and Ru(4) (average 2.164(5) Å). The cluster bound hydrogen atoms were crystallographically located and corresponded to bridging sites analogous to those in compound 1.

If the crystallographically determined structure is representative of the bulk sample, and the solid state structure is retained in solution, then the appearance of a single resonance for the two B–H–Ru bridges suggests either a fluxional process or a coincidence of signals. Since the variable temperature ^{1}H NMR spectrum of [Ru$_4$H(η^6-C$_6$H$_6$)(CO)$_9$BH$_2$] showed no indication of fluxional behaviour, we favour the second explanation.

4. Conclusion

The use of the triruthenaborane cluster [Ru$_3$-(CO)$_9$BH$_4$]$^-$ as a building block for homo- and heterometallic butterfly clusters containing a semi-interstitial boron atom has been extended to produce homometallic species with an Ru(η^6-arene) unit in place of a wingtip Ru(CO)$_3$ fragment. Although [Ru$_3$(CO)$_9$-B$_2$H$_5$]$^-$ may also be used as a precursor, it appears favourable for the reaction to proceed with extrusion of one boron atom. Intra-skeleton structural differences between the all-carbonyl cluster 1 and the arene-substituted cluster 3 are small, and it will now be of interest to see whether reactivity patterns of the arene-sub-

stituted cluster parallel that of the all-carbonyl compound.

References

[1] C.E. Housecroft, *Chem. Soc. Rev.*, 24 (1995) 215.
[2] C.E. Housecroft, *Coord. Chem. Rev.*, 143 (1995) 297.
[3] S.M. Draper, C.E. Housecroft, J.S. Humphrey and A.L. Rheingold, *J. Chem. Soc., Dalton Trans.*, (1995) 3789.
[4] J.R. Galsworthy, C.E. Housecroft and A.L. Rheingold, *J. Chem. Soc., Dalton Trans.*, (1995) 2639.
[5] S.M. Draper, C.E. Housecroft, A.K. Keep, D.M. Matthews, X. Song and A.L. Rheingold, *J. Organomet. Chem.*, 423 (1992) 241.
[6] C.E. Housecroft, D.M. Matthews, A. Waller, A.J. Edwards and A.L. Rheingold, *J. Chem. Soc., Dalton Trans.*, (1993) 3059.
[7] M.A. Bennett and A.K. Smith, *J. Chem. Soc., Dalton Trans.*, (1974) 233.
[8] F.-E. Hong, D.A. McCarthy, J.P. White, C.E. Cottrell and S.G. Shore, *Inorg. Chem.*, 29 (1990) 2874.
[9] A.K. Chipperfield, C.E. Housecroft and A.L. Rheingold, *Organometallics*, 9 (1990) 681.
[10] C.R. Eady, B.F.G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1977) 477.
[11] C.E. Housecroft, D.M. Matthews, A.L. Rheingold and X. Song, *J. Chem. Soc., Dalton Trans.*, (1992) 2855.

[12] A.K. Chipperfield and C.E. Housecroft, *J. Organomet. Chem.*, *349* (1988) C17.

[13] F.-E. Hong, T.J. Coffy, D.A. McCarthy and S.G. Shore, *Inorg. Chem.*, *28* (1989) 3284.

[14] C.E. Housecroft, D.M. Matthews, A.L. Rheingold and X. Song, *J. Chem. Soc., Chem. Commun.*, (1992) 842.

[15] J.R. Galsworthy, C.E. Housecroft, R.L. Ostrander and A.L. Rheingold, *J. Organomet. Chem.*, *492* (1995) 211.

[16] G. Sheldrick, SHELXTL-PC v4.2, Siemens XRD, Madison, WI, 1990.

[17] D. Braga, P.J. Dyson, F. Grepioni and B.F.G. Johnson, *Chem. Rev.*, *94* (1994) 1585.

[18] B.F.G. Johnson, J. Lewis, M. Martinelli, A.H. Wright, D. Braga and F. Grepioni, *J. Chem. Soc., Chem. Commun.*, (1990) 364; D. Braga, F. Grepioni, B.F.G. Johnson, J. Lewis, C.E. Housecroft and M. Martinelli, *Organometallics*, *10* (1991) 1260.

[19] A.T. Brooker, P.A. Jackson, B.F.G. Johnson, J. Lewis and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1991) 707.

[20] N.P. Rath and T.P. Fehlner, *J. Am. Chem. Soc.*, *110* (1988) 5345.

[21] C.E. Housecroft, *Adv. Organomet. Chem.*, *33* (1991) 1 (table of NMR spectroscopic data).

[22] J.R. Galsworthy, C.E. Housecroft, D.M. Matthews, R. Ostrander and A.L. Rheingold, *J. Chem. Soc., Dalton Trans.*, (1994) 69.