

Preliminary communication

 $\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_6$: A metal-rich ruthenaborane analogue of pentaborane(9) and a model for a triruthenium supported unsaturated hydrocarbon**Ann K. Chipperfield, Catherine E. Housecroft * and Dorn M. Matthews***University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (U.K.)*

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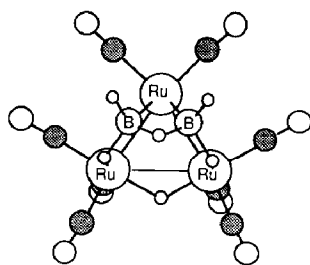
Abstract

The preparation by two independent routes, the isolation, and the characterisation of the metal-rich ruthenaborane $\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_6$ are reported. The cluster is formally derived from pentaborane(9) by the replacement of three {BH} by {Ru(CO)₃} units, and it is also an isoelectronic analogue of $\text{Ru}_3(\text{CO})_9\text{C}_2\text{H}_4$. Deprotonation occurs by loss of an Ru–H–Ru proton. The anion $[\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_5]^-$ is static on the NMR timescale, thereby behaving in a similar manner to the related anion $[\text{Fe}_2(\text{CO})_6\text{B}_3\text{H}_7]^-$ whilst contrasting with the isolobal $[\text{B}_5\text{H}_8]^-$ anion which is fluxional.

We recently described the characterization of several metal-rich ruthenaborane clusters [1–3]. The use of $\text{Ru}_3(\text{CO})_{12}$ as a precursor of these compounds gives a degree of specificity to the synthesis, since the relative strength of the Ru–Ru bond mitigates against Ru–Ru bond cleavage; hence Ru_3 ring opening or fragmentation is minimized. One aim of our investigations is to use the Ru_3 framework as a surface upon which to carry out borane transformations, e.g. the systematic coupling or cleavage of small borane units. Homologation of $\text{BH}_3 \cdot \text{thf}$ takes place at mononuclear transition metal centres [4–9], and recently Messerle has illustrated that the reaction of $[\text{BH}_4]^-$ with $\{(\text{Me}_5\text{C}_5)\text{Ta}\}_2(\mu\text{-X})_4$, (X = Cl, Br) provides a model for the conversion of CH_4 into C_2H_6 [10]. We describe below two routes to a new ruthenaborane, $\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_6$, both starting from $\text{Ru}_3(\text{CO})_{12}$, but differing in that one involves the homologation of $\text{BH}_3 \cdot \text{thf}$ while the second involves transformation of the $[\text{B}_3\text{H}_8]^-$ ion to a trimetal supported diborane unit.

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with $\text{BH}_3 \cdot \text{thf}$ and $\text{Li}[\text{BHEt}_3]$ gives a mixture of cluster anions, which, after acidification and chromatographic separation, yields $\text{Ru}_3(\text{CO})_9\text{BH}_5$ ($\approx 10\%$ yield) [1] and $\text{Ru}_4(\text{CO})_{12}\text{BH}_3$ ($\approx 10\%$ yield) [3]. A minor product ($\leq 5\%$ yield) of the reaction has now been isolated and spectroscopically

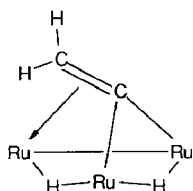
characterized as $\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_6$ (I) [11*]. A higher yield, ($\geq 10\%$), of I is obtained from the reaction of $[\text{Me}_4\text{N}][\text{B}_3\text{H}_8]$ with $\text{Ru}_3(\text{CO})_{12-x}(\text{MeCN})_x$ ($x = 1,2$) [12] in acetonitrile. Our infrared data in the carbonyl region for I agree with those given some twelve years ago by Lewis and Johnson [13] when, on the basis of mass and infrared spectral data, they proposed the formation of I as a very minor product from the reaction of $\text{Ru}_3(\text{CO})_{12}$ and $[\text{BH}_4]^-$. No structural assignment was made, and it has since been pointed out [14] that a molecular mass consistent with $\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_6$ would also match that of $\text{H}_3\text{Ru}_3(\text{CO})_9\text{BCH}_2$, an analogue of the structurally characterized osmaborane $\text{H}_3\text{Os}_3(\text{CO})_9\text{BCH}_2$ [15]. From our complete spectroscopic characterization of I, we are now able to establish the existence of this metal-rich metallaborane, and assign a structure as detailed below.



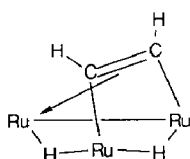
(I)

Cluster I is a *nido*-ruthenaborane, formally derived from pentaborane(9) by the isolobal replacement of 3BH by $3\text{Ru}(\text{CO})_3$ units. Three isomers (Fig. 1) are possible but only isomer **A** is consistent with the combined ^1H and ^{11}B NMR data; *endo*-hydrogen sites are in a ratio of $1(\text{B}-\text{H}-\text{B})/2(\text{Ru}-\text{H}-\text{B})/1(\text{Ru}-\text{H}-\text{Ru})$ and there is a single boron environment. Isomer **A** is the expected structure, since it exhibits a closed triangle of ruthenium atoms and should therefore be energetically preferred over **B** and **C** in which the Ru_3 -framework is an open one.

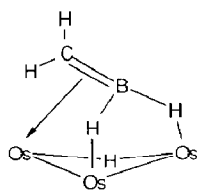
Compound I is of particular interest because it fills a gap in the series of 5-vertex *nido*-metallaboranes. Taking B_5H_9 as the parent compound, isolobal substitutions may be made using metal fragments to replace BH units [16]. Compounds with an MB_4 -core are known for Fe, Ru, Os, Co and Rh [17], while $\text{Fe}_2(\text{CO})_6\text{B}_3\text{H}_7$ is the only *nido*-derivative having an M_2B_3 -core [8,18]. I is the first isolobal analogue of B_5H_9 which possesses an M_3B_2 -core, and the first metal-rich derivative, since no example of a *nido*-metallaborane having an M_4B -core is documented. $\text{Fe}_4(\text{CO})_{12}\text{BH}_3$ [19] and $\text{Ru}_4(\text{CO})_{12}\text{BH}_3$ [3,13,20] are both known but are classed as *arachno* clusters [19]; a *nido*- M_4B cluster of this type should have the formulation $\text{M}_4(\text{CO})_{12}\text{BH}_5$, ($\text{M} = \text{group 8 metal}$).



(II)



(III)



(IV)

* Reference number with asterisk indicates a note in the list of references.

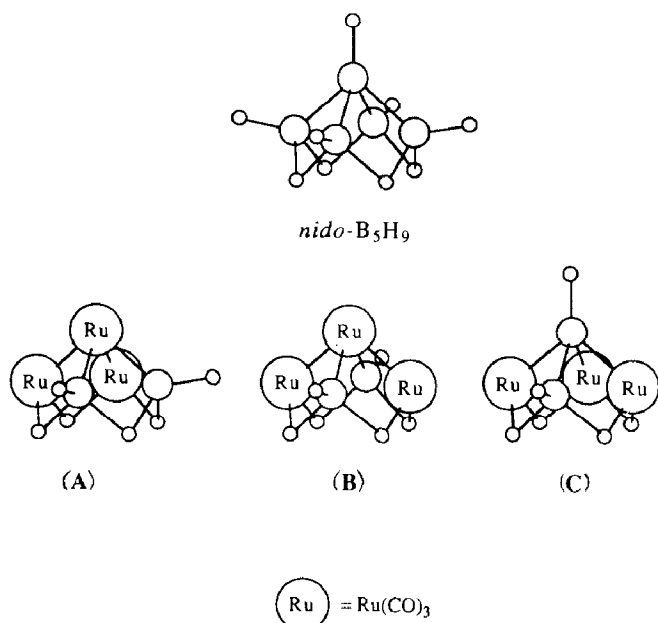
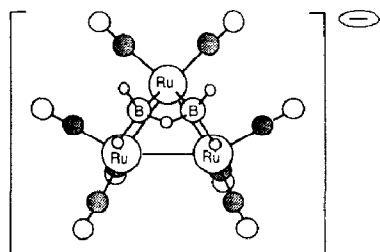


Fig. 1. Schematic representation of the three possible isomers of I and their relationship to *nido-B₅H₉*.

Compound I is isoelectronic with $\text{Ru}_3(\text{CO})_9\text{C}_2\text{H}_4$ and is therefore a borane analogue of a trimetal supported unsaturated hydrocarbon. Note that C_2H_4 , BCH_5 , and B_2H_6 comprise a series of isoelectronic main group ligands. $\text{Ru}_3(\text{CO})_9\text{C}_2\text{H}_4$ exists in two isomeric forms (II and III). In each structure, $2\text{Ru}-\text{H}-\text{Ru}$ interactions are present, and the residual C_2H_2 unit bonds are either parallel or perpendicular to one edge of the Ru_3 -triangle [21–23]. In the perpendicular mode, the organic fragment becomes a vinylidene ligand, confirmed crystallographically for $\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}=\text{CH}_2)$ [23,24]. The same perpendicular orientation is observed for the borylidene ligand in $\text{H}_3\text{Os}_3(\text{CO})_9(\text{B}=\text{CH}_2)$ [15] (IV) with no reported isomerism to a give a parallel bonded BCH_2 -ligand. In I, spectroscopic evidence supports a parallel bonding mode for the diborane ligand. Presumably this reflects the fact that each boron atom makes most efficient use of its bonding electrons if it is an integral part of the metallaborane cluster. A perpendicular bonding mode for a B_2H_2 akin to those illustrated for the CCH_2 or BCH_2 units in III and IV would make unacceptable demands upon the 3 valence electrons of the terminal boron atom. Thus, in going from $\text{Ru}_3(\text{CO})_9\text{C}_2\text{H}_4$ to $\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_6$, the orientation of the main group fragment is controlled by the bonding capabilities of C vs. B.

Deprotonation of I to $[\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_5]^-$ (V) occurs via the removal of an $\text{Ru}-\text{H}-\text{Ru}$ bridging proton, deduced on the basis of ^{11}B and ^1H NMR spectroscopic



data [25*]. Apart from the disappearance of the metal hydride signal in the ^1H NMR spectrum, the data for I and V are extremely similar, thereby indicating that the borane fragment undergoes no significant structural perturbation upon deprotonation of I. The Ru–H–B and B–H–B protons in the anion are static at room temperature on the 400 MHz timescale. This situation mimics that observed for *nido*- $[\text{Fe}_2(\text{CO})_6\text{B}_3\text{H}_6]^-$ [8], but contrasts with the fluxional behaviour exhibited by *nido*- $[\text{B}_5\text{H}_8]^-$ [26]. We have previously noted that introduction of an M–H–B in place of B–H–B interaction tends to raise the activation barrier for *endo*-hydrogen mobility [8], and the observation of a static structure both for I and V supports this observation. The results of a Fenske–Hall quantum chemical study for neutral I are consistent with the observation that deprotonation occurs preferentially by removal of an Ru–H–Ru bridging hydrogen atom.

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- 11 $\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_6$: $m/e P^+$ 584 (isotopic distribution agrees with simulated pattern for $\text{B}_2\text{C}_9\text{H}_6\text{O}_9\text{Ru}_3$) with 9CO losses observed; IR (hexane): $\nu(\text{BH})$ 2360 vw, 2300 vw, $\nu(\text{CO})$ 2108 w, 2082 s, 2067 w, 2061 w, 2055 vs, 2042 m, 2031 m, 2012 w, 1997 w cm^{-1} ; 128 MHz ^{11}B NMR (CDCl_3 , 298 K): δ +17.0 (br, FWHM 310 Hz, $^{11}\text{B}\{^1\text{H}\}$ FWHM 170 Hz); 400 MHz ^1H NMR (CDCl_3 , 298 K) δ +4.5 (br, 2H), –1.2 (br, 1H), –12.3 (br, 2H), –19.0 (s, 1H).
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25 $[\text{Ru}_3(\text{CO})_9\text{B}_2\text{H}_5]^-$: FAB $m/e P^-$ 583 (isotopic distribution agrees with simulated pattern for $\text{B}_2\text{C}_9\text{H}_5\text{O}_9\text{Ru}_3$) with 9CO losses observed; IR (CH_2Cl_2): $\nu(\text{BH})$ 2338 w, 2304 w, $\nu(\text{CO})$ 2057 w, 2005 s, 1978 m, 1952 w cm^{-1} ; 128 MHz ^{11}B NMR (CD_2Cl_2 , 298 K): δ +18.4 (br. FWHM 300 Hz, $^{11}\text{B}\{^1\text{H}\}$ FWHM 120 Hz); 400 MHz ^1H NMR (CD_2Cl_2 , 298 K): δ +4.5 (br. 2H), -0.4 (br. 1H), -12.8 (br. 2H).

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