Condensed metallaborane clusters: synthesis and structure of $Fe_2(CO)_6(\eta^5\text{-}C_5Me_5RuCO)(\eta^5\text{-}C_5Me_5Ru)B_6H_{10}$

Sundargopal Ghosh,* Thomas P. Fehlner and Bruce C. Noll

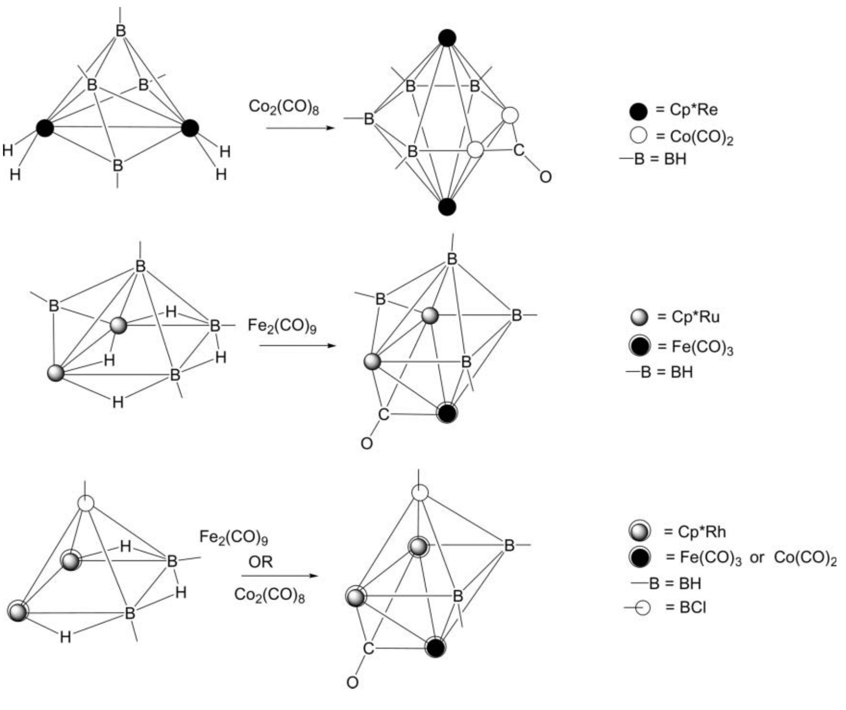
Received (in Berkeley, CA, USA) 18th February 2005, Accepted 6th April 2005
First published as an Advance Article on the web 11th May 2005
DOI: 10.1039/b502559a

Mild pyrolysis of $(\eta^5\text{-}C_5Me_5Ru)_2B_6H_{12}$ with $Fe_2(CO)_9$ yields the 12 skeletal electron pair (sep) $Fe_2(CO)_6(\eta^5\text{-}C_5Me_5RuCO)(\eta^5\text{-}C_5Me_5Ru)B_6H_{10}$ cluster; the title compound represents a novel class of hybrid multiple cluster in which a Fe_2B_2 tetrahedron has been fused to a ruthenaborane substrate.

The majority of high nuclearity transition metal clusters are derived by the condensation of smaller tetrahedral, octahedral, and trigonal-prismatic fragments.[1] The putative fusion of polyhedra to form extended and infinite solids fascinates chemists such as those investigating structural modifications of elemental boron and chalcogenides of early transition metals.[2] One advantage offered by the study of metallaboranes is that the limited bonding capabilities of the borane fragment can be used to circumscribe the behavior of the metal fragment. This is an advantage because the properties of metal and borane clusters are very different due to the presence of *d* orbitals on transition metal fragments not available to main group fragments. Thus, for example, variation of the boron-to-metal ratio for a given cluster size allows the unique properties of the metal centers to be expressed.[3]

Unfortunately, lack of good synthetic routes to metallaborane compounds in the past severely limited such exploration.[4,5] We have recently described a general route to dimetallaboranes of groups 6–9, based on the reaction of monocyclopentadienylmetal chloride and monoboranes.[6,7] As with transition metal cluster compounds, $Fe_2(CO)_9$ and $Co_2(CO)_8$ are versatile reagents for metal-cluster building reactions in metallaborane chemistry (Scheme 1).[8,9] The production of *nido*-$(\eta^5\text{-}C_5Me_5Ru)_2B_6H_8(CO)_2$,[10] **2** from the reaction of $(\eta^5\text{-}C_5Me_5Ru)_2B_6H_{12}$, **1** with $Co_2(CO)_8$ (Scheme 2) led us to investigate the reactivity of **1** with $Fe_2(CO)_9$. It reacts in a surprisingly different fashion to yield a new metallaborane $Fe_2(CO)_6(\eta^5\text{-}C_5Me_5RuCO)(\eta^5\text{-}C_5Me_5Ru)B_6H_{10}$, **3**.†

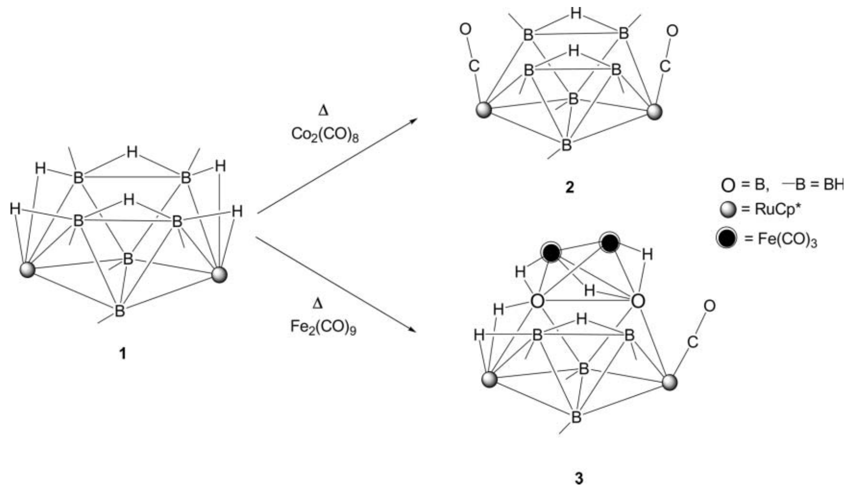
Compound **3** has been isolated in modest yield and characterized spectroscopically as well as by a single crystal X-ray diffraction study.‡ The parent ion in the mass spectrum fragments by the sequential loss of seven CO molecules and the molecular mass corresponds to $Cp^*{}_2Ru_2Fe_2B_6(CO)_7H_{10}$. The IR spectrum in the carbonyl region shows five terminal carbonyl frequencies. The highest frequencies, 2063, 2021, 1998 and 1992 cm^{-1}, have been assigned to a $Fe_2(CO)_6$ fragment as they are not unlike those reported for $Fe_2(CO)_6Se_2$[11] and $B_2H_6Fe_2(CO)_6$.[12] The lowest



Scheme 1

---

*sghosh@nd.edu



Scheme 2

frequency, 1962 cm^{-1}, has been assigned to Ru(CO) which is similar to that observed in **2**. The ^{1}H and ^{11}B NMR spectra suggest the absence of a plane of symmetry. Besides the BH terminal protons (1 : 1 : 1 : 1) one BHB, three FeHB and two RuHB protons are observed. The broad resonances at δ −6.1, −10.4 and −10.9 ppm are assigned to three BHFe protons while the resonances at −12.9 and −14.02 ppm are assigned to two BHRu protons.

However, the framework structure of **3** only became clear when the solid state structure was determined (Fig. 1). **3** displays the open structure of $Cp^*{}_2Ru_2B_6$ but with one B–B-edge of the open face bonded to two $Fe(CO)_3$ fragments. Effectively an external cluster $\{Fe_2B_2\}$ tetrahedron is fused to the ruthenaborane cluster through two common boron atoms. In addition, two of the Ru–H–B protons of **1** are replaced by one CO ligand at one Ru center while the other Ru center remains unchanged. Although the B–B and Ru–B distances are comparable to those found in $Fe(CO)_4(\eta^5\text{-}C_5Me_5Ru)_2B_4H_4$[7] the average of the Fe–B distances (2.23 Å) in **3** is about 0.15 Å longer.

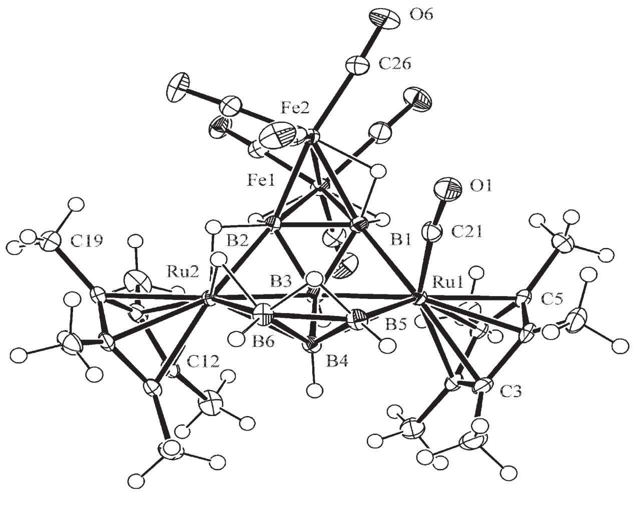


Fig. 1 Molecular structure of $Fe_2(CO)_6(\eta^5\text{-}C_5Me_5RuCO)(\eta^5\text{-}C_5Me_5Ru)B_6H_{10}$ (**3**). Ru(1)–B(5) 2.194(4), Ru(1)–B(3) 2.255(4), Ru(1)–B(4) 2.315(4), Fe(2)–Fe(1) 2.5694(9), Fe(1)–B(1) 2.260(5) Å, B(5)–Ru(1)–B(1) 104.80(16), B(5)–Ru(1)–B(3) 84.18(17), B(3)–Ru(1)–B(4) 45.99(15), B(2)–Fe(2)–B(1) 46.61(16), B(2)–Fe(2)–Fe(1) 55.64(11)°.

A large number of transition metal-carbonyl clusters can be described by the fusion of smaller cluster fragments.[13] These cluster types required an extension of the electron counting rules.[14,15] The bonding of **3** can be considered from two different viewpoints: Mingos's polyhedral fusion formalism[1,16] or by Jemmis's mno rule.[17] In the Mingos approach a condensed cluster is regarded as being generated from two polyhedra sharing a vertex, edge or face. The total electron count in such a condensed cluster is equal to the sum of the electron counts for the parent polyhedra minus the electron count of the shared unit (atom, pair of atoms *etc.*). *nido*-$(\eta^5\text{-}C_5Me_5Ru)_2B_6H_{12}$, **1** and $Fe_2(CO)_6(\eta 5\text{-}C_5Me_5RuCO)(\eta 5\text{-}C_5Me_5Ru)B_6H_{10}$, **3** are formally isolobal with B_8H_{12} and $B_{10}H_{14}$ respectively. Therefore, as shown in eqn. (1), **3** can be viewed as formed from condensation of B_4H_8 and B_8H_{12} with elimination of B_2H_6.

$$[B_4H_8]_{(\mathrm{cve}\,=\,20)} + [B_8H_{12}]_{(\mathrm{cve}\,=\,36)} \rightarrow [B_{10}H_{14}]_{(\mathrm{cve}\,=\,44)} + [B_2H_6]_{(\mathrm{cve}\,=\,12)} \qquad (1)$$

On the other hand, considering a {Cp*Ru} fragment as a three-orbital, one-electron fragment, the formal electron count for **3** is 12 sep. The mno rule gives: $m = 2$, $n = 10$ and $o = 0$ for $m + n + o = 12$ (where m is the number of polyhedra, n the number of vertices in the fused cluster, and o the number of single vertex shared atoms), also consistent with the composition of **3**.

The metallaborane reported here represents a novel class of hybrid multiple cluster synthesized from an edge sharing condensation of $(\eta^5\text{-}C_5Me_5Ru)_2B_6H_{12}$ and $Fe_2(CO)_9$, in which a Fe_2B_2 tetrahedron has been fused to a ruthenaborane substrate. This new metallaborane is interesting in its own right but it also suggests other related species should be accessible.

Sundargopal Ghosh,* Thomas P. Fehlner and Bruce C. Noll
Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA. E-mail: sghosh@nd.edu

Notes and references

† Synthetic procedure for **3**: In a typical reaction $(\eta^5\text{-}C_5Me_5Ru)_2B_6H_{12}$, **1** (0.19 g, 0.34 mmol) in hexane (20 mL) was stirred with 3 equivalent of $Fe_2(CO)_9$ (0.37 g, 1.02 mmol) for 3 h at 55 °C. The solvent was removed *in vacuo*, the residue was extracted in hexane, and passed through Celite. The filtrate was concentrated and kept at −40 °C to remove $Fe_3(CO)_{12}$. The mother liquor was concentrated and the residue chromatographed on silica gel TLC plates. Elution with pure hexane yielded brown $Fe_2(CO)_6(\eta^5\text{-}C_5Me_5RuCO)(\eta^5\text{-}C_5Me_5Ru)B_6H_{10}$, **3** (0.11 g, 40%). MS (FAB) P^+(max) 855 (isotopic pattern for 2 Ru, 2 Fe and 6 B atoms), $^{12}C_{27}{}^{1}H_{40}{}^{11}B_6{}^{101}Ru_2,{}^{55}Fe_2{}^{16}O_7$ calcd: 858.0118; obsd: 858.0115. ^{11}B NMR (C_6D_6, 22 °C): $\delta = 47.1$ (br, 1B-H*t*), 37.1 (br, 1B-H*t*); $\delta = 29.9$ (d, $J_{B\text{–}H} = 110$ Hz, 1B-H*t*), 1.37 (br, 2B; 1B-Fe and 1B-H*t*, accidental overlap); $\delta = -2.7$ {s, 1B (Fe-B)}; ^1H NMR (C_6D_6, 22 °C): $\delta = 6.39$ (pcq, 1 BH_t), 5.80 (pcq, 1BH_t), 2.78 (pcq, 1 BH_t), 0.82 (pcq, 1BH_t), 1.56 (s, 15 H, 1Cp*), 1.55 (s, 15 H, 1Cp*), −0.87 (s, br, 1B-H-B); −6.12 (pcq, 1Fe-H-B); −10.42 (pcq, 1Fe-H-B); −10.99 (pcq, 1Fe-H-B); −12.94 (pcq, 1Ru-H-B); −14.02 (s, br, 1Ru-H-B); ^{13}C NMR (C_6D_6, 22 °C): $\delta = 216$, 210, 209.5 (Fe-CO), 204 (Ru-*CO*), 101.4, 96.1 ($2C_5(CH_3)_5$), 9.8, 9.6 ($C_5(CH_3)_5$); IR (hexane, cm^{-1}): 2508 w, 2478w (B-H*t*), 2063s, 2021s, 1998s, 1992m (Fe-CO), 1962s (Ru-*CO*).

‡ Crystal data for **3**: Data collected on Bruker D8-Apex diffractometer equipped with an Oxford Cryosystems 700 Series low-temperature apparatus operating at 100 K. Crystal system, space group: monoclinic, *P*2(1)/*n*. Unit cell dimensions, $a = 9.6024(10)$ Å, $\alpha = 90°$, $b = 22.536(2)$ Å, $\beta = 99.642(2)°$, $c = 16.0264(16)$ Å, $\gamma = 90°$; $Z = 4$. Final R indices $[I > 2\sigma(I)]$ $R1 = 0.0580$, $wR2 = 0.1066$. CCDC 234013. See http://www.rsc.org/suppdata/cc/b5/b502559a/ for crystallographic data in CIF or other electronic format.

1 D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 706.

2 J. D. Corbett, *Acc. Chem. Res.*, 1981, **14**, 239.

3 T. P. Fehlner, in *Electron Deficient Boron and Carbon Clusters*, Eds. G. A. Olah, K. Wade and R. E. Williams, Wiley, New York, 1991, p. 287.

4 J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519; J. D. Kennedy, *Prog. Inorg. Chem.*, 1986, **34**, 211.

5 R. N. Grimes, in *Metal Interactions with Boron clusters*, Ed. R. N. Grimes, Plenum, New York, 1982, p. 269.

6 Y. Nishihara, K. J. Deck, M. Shang, T. P. Fehlner, B. S. Haggerty and A. L. Rheingold, *Organometallics*, 1994, **13**, 4510; J. Ho, K. J. Deck, Y. Nishihara, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1995, **117**, 10292; S. Aldridge, T. P. Fehlner and M. Shang, *J. Am. Chem. Soc.*, 1997, **119**, 2339; X. Lei, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1998, **120**, 2686; S. Ghosh, X. Lei, M. Shang and T. P. Fehlner, *Inorg. Chem.*, 2000, **39**, 5373.

7 X. Lei, M. Shang and T. P. Fehlner, *J. Am. Chem. Soc.*, 1999, **121**, 1275.

8 C. E. Housecroft, in *Boranes and Metalloboranes*, Ellis Horwood, Chichester, UK, 1990.

9 D. F. Shriver and H. D. Kaesz, in *The Chemistry of Metal Cluster Complexes*, Ed. R. D. Adams, VCH, New York, 1990.

10 S. Ghosh, A. M. Beatty and T. P. Fehlner, *Angew. Chem., Int. Ed.*, 2003, **42**, 4678.

11 P. Mathur, D. Chakrabarty, Md. M. Hossain, R. S. Rasid, V. Rugmini and A. L. Rheingold, *Inorg. Chem.*, 1992, **31**, 1106.

12 E. L. Anderson and T. P. Fehlner, *J. Am. Chem. Soc.*, 1978, **100**, 4606.

13 K.-S. Wong, J. R. Bowser, J. R. Pipal and R. N. Grimes, *J. Am. Chem. Soc.*, 1978, **100**, 5045; R. N. Grimes, *Coord. Chem. Rev.*, 1995, **143**, 71; J. D. Kennedy, in *Advances in Boron Chemistry*, Ed. W. Siebert, Royal Society of Chemistry, Cambridge, 1997, p. 451.

14 K. Wade, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 559; K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1; K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67.

15 D. M. P. Mingos, *Nature (London) Phys. Sci.*, 1972, **236**, 99.

16 D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311; D. M. P. Mingos and R. L. Johnston, *Struct. Bonding (Berlin)*, 1987, **68**, 31.

17 E. D. Jemmis, M. M. Balakrishnarajan and P. D. Pancharatna, *J. Am. Chem. Soc.*, 2001, **123**, 4313.