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Cluster Compounds

A Family of Heterometallic Cubane-Type Clusters with an *exo*-$Fe(CO)_3$ Fragment Anchored to the Cubane**

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Metal-rich boron clusters are members of a rapidly growing family of metallaborane "hybrid" systems which bridges the gap between metal clusters and polyhedral boranes.[1] Clusters such as $[Cp_4Ni_4B_4H_4]$[2] and $[Cp_4Co_4B_4H_4]$[3] ($Cp = \eta^5\text{-}C_5H_5$) can be linked with the well-studied class of tetranuclear metal complexes known as cubanes.[4] Recently, a metal-rich metallaborane with the same geometry, namely, $[(Cp^*Ru)_3(\mu_3\text{-}CO)Co(CO)_2B_3H_3]$ ($Cp^* = \eta^5\text{-}C_5Me_5$), was reported by Fehlner et al.[5] Cubane is quite a popular shape, especially for combinations of heterometal and main group elements.[6] These compounds are of interest not only because of their contribution to the development of organometallic chemistry, but also for their potential use as models for various industrial and biological catalytic processes.[7–9]

As a part of our ongoing studies on metallaboranes and their derivatives,[10] we recently reported the synthesis of $[(Cp^*Mo)_2B_4H_4E_2]$[11] (**1**: E = S; **2**: E = Se) and *arachno*-$[(Cp^*RuCO)_2B_2H_6]$[12] (**3**) in good yields. Until now we have focused on the chemistry of metallaboranes with boranes, main group elements, and small organic molecules.[10–13] We have now extended our studies to transition metal carbonyl compounds such as $[Fe_2(CO)_9]$, $[Mn_2(CO)_{10}]$, and $[Co_2(CO)_8]$, since earlier work suggested their potential as versatile reagents in cluster-building reactions.[14] Reaction with $[Co_2(CO)_8]$ led to decomposition, whereas mild pyrolysis of $[Fe_2(CO)_9]$ with **1**–**3** in hexane led to hybrid clusters $[(Cp^*M)_2(\mu_3\text{-}E)_2B_2H(\mu\text{-}H)\{Fe(CO)_2\}_2Fe(CO)_3]$ (**4**: M = Mo, E = S; **5**: M = Mo, E = Se; **6**: M = Ru, E = CO). The identities of **5** and **6** were established by a single-crystal X-ray diffraction study, which together with spectroscopic studies demonstrated the existence of novel capped-cubane cluster cores. Although X-ray quality crystals of **4** have not been obtained yet, its identity is inferred by comparison to selenium analogue **5**.

The overall structure of **5** is intriguing and its geometry can be viewed in a few different ways. The more obvious approach is to recognize the cubane shape made of two Mo, two Fe, two Se, and two B atoms, capped by a third Fe atom attached to one of the B-Fe-Fe faces of the cube (Figure 1).[15] An alternative description of **5** is as a Mo_2Fe_2 tetrahedron face-capped by two selenium and two boron atoms. Capping one of the resulting Fe_2B faces with another $Fe(CO)_3$ group generates capped cubane **5**.

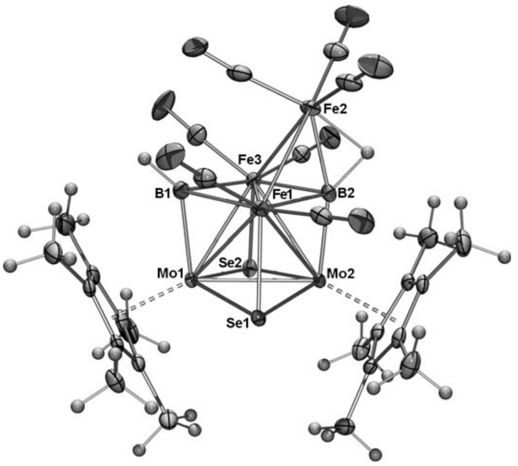

Figure 1. Molecular structure of **5** (40% probability ellipsoids). Selected bond lengths [Å]: Mo1–Mo2 2.9216(3), Mo1–B1 2.115(3), Fe1–B1 2.128(3), Mo1–Se2 2.4253(3), Fe1–Se1 2.4064(4), Fe3–Se2 2.4027(4), Fe1–Fe3 2.5220(4), Fe1–Fe2 2.6294(4).

Cubane-type sulfido clusters have been extensively investigated,[16] but the corresponding selenido derivatives have received little attention, and the only structurally characterized examples are the Mo, Sn, and Pd species with $[M_3M'Se_4]$ single-cube structure.[17] Compound **5** is the first heterobimetallic selenido cuboidal cluster containing a boride unit (B2) as one of the vertices. The Mo–Mo bond length in **5** is 0.08 Å longer than the corresponding distances in $[Mo_3CuSe_4Cl_4(dmpe)_3]PF_6$ (dmpe = 1,2-bis(dimethylphosphino)ethane).[17c] The Fe1–Fe3 distance of 2.5220(4) Å is 0.2 Å shorter than those observed in single- and double-cubane clusters, while the mean Mo–Fe distance of 2.792 Å is not unusual.[18] The third iron atom (Fe2) is *exo*-bonded to the cubane at the B2-Fe1-Fe3 face with a long Fe–Fe distance of 2.632 Å and a short Fe–B_{boride} bond length of 2.026(3) Å. The average Mo–

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Se distance of **5** (2.439 Å) is significantly shorter than that of diselenamolybdaborane **2** (2.585 Å).

Consistent with the X-ray results, the ^{11}B NMR of **4** and **5** confirm the presence of two boron resonances in the ratio of 1:1. The ^{11}B{^{1}H} NMR spectra of **4** and **5** feature one broad downfield resonance at $\delta = 143.4$ and 144.1 ppm respectively, in the range usually associated with metal-rich boride clusters.[19] The ^{13}C NMR spectra contain signals attributable to the two types of Cp* ligands and the $Fe(CO)_3$ fragment. The ^{77}Se NMR spectrum of **5** displayed single resonance at $\delta = 995$ ppm for the bridged μ_3-Se atoms.

In a similar fashion, mild pyrolysis of **3** with $[Fe_2(CO)_9]$ generated **6**, together with triply bridged borylene complexes $[\{(\mu_3\text{-BH})(Cp^*Ru)Fe(CO)_3\}_2(\mu\text{-CO})]$ (**I**)[12] and $[(\mu_3\text{-BH})_3(Cp^*Ru)_2\{Fe(CO)_3\}_2]$ (**II**; see the Supporting Information). The FAB mass spectrum of **6** showed the parent peak at m/z 915 and successive loss of nine carbonyl ligands before further fragmentation. The ^{11}B{^{1}H} NMR spectrum displayed two resonances with equal intensities; the peak at $\delta = 128.5$ ppm was assigned to the borylene boron atom, and the most downfield resonance at $\delta = 158.5$ ppm, which implies a greater degree of boron–metal interaction, to the boride boron atom. The ^{1}H NMR spectrum of **6** features two Cp* resonances at $\delta = 2.17$ and 1.84 ppm, indicative of two different Ru environments, as well as signals for one BH and one Fe-H-B proton. The IR spectrum shows three absorption bands, two of which correspond to terminal carbonyl [2029 (s), 1978 cm^{-1} (vs)] and one to a bridging carbonyl [1730 cm^{-1} (m)].

The structure of **6** (Figure 2)[15] consists of an array of four metal atoms at the corners of a tetrahedron with two CO, one BH, and one boride unit capping a face of the tetrahedron. In addition, one of the Fe_2B faces of the cubane is capped by an $Fe(CO)_3$ fragment. The coordination sphere of the Ru atoms is completed by Cp* ligands, and each iron atom has terminal CO ligands. Furthermore, the packing of the unit cell of **6** shows an intermolecular CH···O distance of 2.482 Å, which is shorter than the normal van der Waals H···O separation of 2.6 Å, and may possibly reflect weak hydrogen bonding between a methyl hydrogen atom of Cp* and a terminal carbonyl oxygen atom.[20]

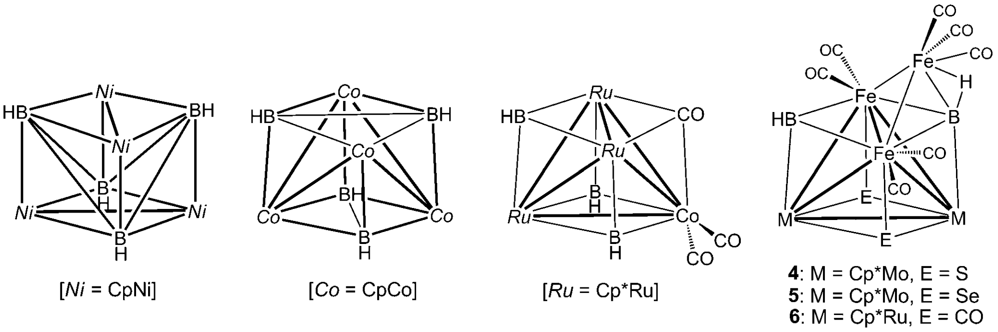


Figure 3. Metal-rich metallaboranes with cubane-type geometry.

The metal–metal distances of 2.7167(4) (Ru–Ru), 2.6573 ± 0.009 (Ru–Fe), and 2.4838(8) Å (Fe–Fe) are all consistent with single bonds between the metal atoms. All M-M-M angles in a regular tetrahedron are 60°, and the observed angles in **6** are very close to this ideal value. The average triply bridging M–CO (M = Ru, Fe) bond length of 2.088 Å compares favorably with the average value of 2.059 Å observed for the similar triply bridging carbonyl ligand in $[(Cp^*Ru)_3(\mu_3\text{-CO})Co(CO)_2B_3H_3]$.[5]

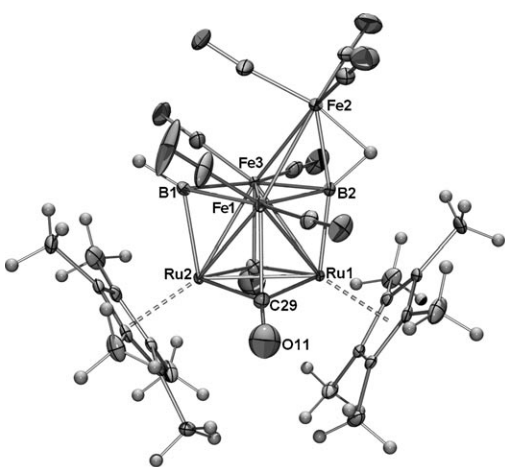
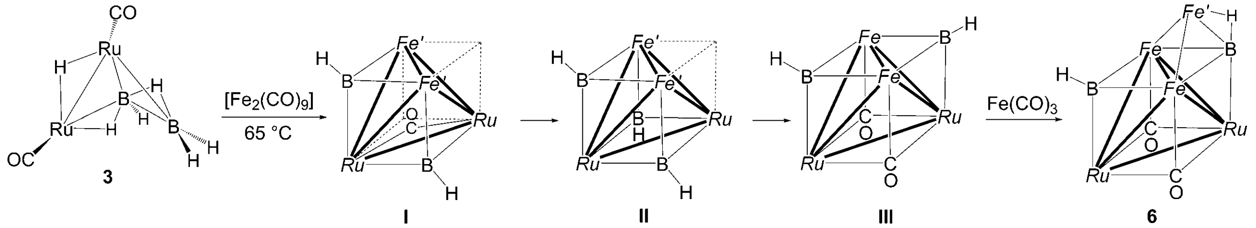


Figure 2. Molecular structure of **6** (30% probability ellipsoids). Selected bond lengths [Å]: Ru1–Ru2 2.7167(4), Ru1–Fe3 2.6663(6), Ru1–Fe1 2.6573(5), Fe2–Fe3 2.6800(7), Fe1–Fe2 2.6735(8), Fe1–Fe3 2.4838(8), Ru2–Fe3 2.64996, Ru2–Fe1 2.6354(6), Ru1–B2 1.985(4), Fe1–B2 2.029(4).

Although the qualitative shape of the cubane clusters shown in Figure 3 is the same, the M–M distances reflect changes in cluster electronic structure accompanying addition and loss of electrons.[21] Kennedy[22] described $[(CpNi)_4B_4H_4]$[2] and $[(CpCo)_4B_4H_4]$[3] as 68- and 64-electron clusters with two and four metal–metal bonds. Further, he suggested that the putative $[(CpFe)_4B_4H_4]$ cluster with 60 electrons should exhibit a cubane structure with six Fe–Fe bonds and a fully bonded metal tetrahedron. Metallaborane $[(Cp^*Ru)_3(\mu_3\text{-CO})Co(CO)_2B_3H_3]$, which connects these clusters, has 60 cluster valence electrons (cve) and a cubane geometry with six M–M bonds.[5] Compounds **4**–**6** are also 60-cve tetrametal metallaboranes which can be compared to those discussed above. Viewing these metallaboranes as a cubane, rather than a tetracapped tetrahedron with six skeletal electron pairs (sep) provides an satisfying solution to a long-standing anomaly in metallaborane chemistry, that is, the existence of $[(CpCo)_4B_4H_4]$ and $[(CpNi)_4B_4H_4]$ with eight and ten sep.[21,23]

Reaction of **3** with $[Fe_2(CO)_9]$ leads to 60-cve complex **6**. The reaction pathway whereby cubane **6** is formed is unknown; however, the isolation and characterization of



Scheme 1. A plausible pathway for the formation of capped cubane cluster **6** from **3**. *Ru* = Cp*Ru, *Fe′* = Fe(CO)$_3$, *Fe* = Fe(CO)$_2$.

bis- and tris-borylene complexes **I** and **II**[15] with 60 cve reveal a plausible pathway for the formation of **6** (see Figure S1 of the Supporting Information). As shown in Scheme 1, the core geometry of **6** is similar to those of **I** and **II**, that is, a cubane with two and one missing vertices respectively. Formation of **II** can be considered to be replacement of the μ-CO ligand in **I** by the isoelectronic {BH} fragment. Thus, it is reasonable to assume that under thermolytic conditions **II** rearranges to intermediate [(μ_3-BH)$_2$(Cp*Ru)$_2${Fe(CO)$_2$}$_2$(μ_3-CO)$_2$] (**III**) with elimination of one BH group. Intermediate **III** is a cubane with two electrons fewer than required for a regular cubane cluster. Therefore, as the reaction progresses, one of the cubane faces of **III** (Fe-Fe-B) may possibly be capped by an Fe(CO)$_3$ fragment to give 60-cve **6**.

In conclusion, to the best of our knowledge, these are the first examples of a family of heterobimetallic cuboidal clusters with a boride unit as one of the vertices. Further, systematic reactivity studies combined with theoretical treatments are required to fully understand these systems. Such work is in progress.

Experimental Section

4–6: In a typical reaction, compound **1** (0.07 g, 0.12 mmol) in hexane (15 mL) was stirred with 3 equiv of [Fe$_2$(CO)$_9$] (0.14 g, 0.36 mmol) for 4 h at 65 °C. The solvent was removed in vacuo, and the residue extracted with 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 was subjected to chromatography on silica gel TLC plates. Elution with a hexane/CH$_2$Cl$_2$ (9/1) afforded **4** (0.005 g, 4 %). The yield of Se analogue **5** from **2** was 19 % (0.02 g). In a similar fashion, **3** (0.075 g, 0.13 mmol) provided **6** (0.02 g, 16 %), along with borylene complexes **I** (0.03 g, 27 %) and **II** (0.005 g, 5 %); see the Supporting Information for **II**.

4: ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$, 25 °C): δ = 143.4 (br, 1 B), 107.2 ppm (br, 1 B); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 9.95 (br, 1 BH$_t$), 1.74 (s, 15 H, 1 Cp*), 1.68 (s, 15 H, 1 Cp*), −7.86 ppm (s, 1 H, Fe-H-B); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 215.5, 203.4 (s, CO), 108.6, 105.9 (s, C_5Me$_5$), 13.1, 12.8 ppm (s, C$_5$$Me_5$); IR (hexane): $\tilde{\nu}$ = 2029, 1978 cm^{-1} (CO); MS (FAB) P$^+$(max): *m*/*z* (%) 913.

5: ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$, 25 °C): δ = 144.1 (br, 1 B), 108.1 ppm (br, 1 B); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 9.98 (br, 1 BH$_t$), 1.73 (s, 15 H, 1 Cp*), 1.66 (s, 15 H, 1 Cp*), −7.78 ppm (s, 1 H, Fe-H-B); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 216.2, 203.8 (s, CO), 112.9, 104.7 (s, C_5Me$_5$), 12.8, 12.3 ppm (s, C$_5$$Me_5$); ^{77}Se NMR (95 MHz, CDCl$_3$, 25 °C): δ = 995 (s, 2 Se). IR (hexane): $\tilde{\nu}$ = 2022, 1976 cm^{-1} (CO); MS (FAB) P$^+$(max): *m*/*z* 1007; elemental analysis (%) calcd for C$_{27}$H$_{32}$B$_2$Fe$_3$Mo$_2$O$_7$Se$_2$: C 32.19, H 3.20; found: C 33.02, H 3.36.

6: ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$, 25 °C): δ = 158.5 (br, 1 B), 128.5 ppm (br, 1 B); ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 8.48 (br, 1 BH$_t$), 2.17 (s, 15 H, 1 Cp*), 1.84 (s, 15 H, 1 Cp*), −8.48 ppm (s, 1 H, Fe-H-B); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C): δ = 215.5, 209.4 (s, CO), 120.3, 119.9 (s, C_5Me$_5$), 13.1, 9.0 ppm (s, C$_5$$Me_5$). IR (hexane): $\tilde{\nu}$ = 2029, 1978 (CO), 1730 cm^{-1} (μ_3-CO); MS (FAB) P$^+$(max): *m*/*z* 915; elemental analysis (%) calcd for C$_{29}$H$_{32}$B$_2$Fe$_3$Ru$_2$O$_9$: C 38.03, H 3.52; found: C 39.28, H 3.72.

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[15] Crystal data for **5** and **6** were collected on an Oxford Diffraction Xcalibur-S CCD system equipped with graphite-monochromated Mo$_{K\alpha}$ radiation at 150 K. Crystal data for **II** were collected and integrated on a Bruker AXS Kappa APEX2 CCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ (λ = 0.71073 Å) radiation at 173 K. The structures were solved by

heavy-atom methods using SHELXS-97 or SIR92 and refined using SHELXL-97. Crystal data for **5**: $C_{27}H_{32}B_2Fe_3O_7Mo_2Se_2$ $M_r = 1007.50$, monoclinic, space group $P2_1/c$, $a = 12.2619(4)$, $b = 13.3712(3)$, $c = 21.2481(6)$ Å, $\beta = 106.675(3)°$, $Z = 4$, $\rho_{calcd} = 2.005\ \mathrm{Mg\,m^{-3}}$, $R_1 = 0.0172$, $wR^2 = 0.0416$, 5867 independent reflections and 406 parameters. Crystal data for **6**: $C_{29}H_{32}B_2Fe_3O_9Ru_2$ $M_r = 915.86$, triclinic, space group $P\bar{1}$, $a = 10.3081(4)$, $b = 10.8988(5)$, $c = 16.0185(7)$ Å, $\alpha = 74.054(4)$, $\beta = 81.082(3)$, $\gamma = 67.255(4)°$, $Z = 2$, $\rho_{calcd} = 1.909\ \mathrm{Mg\,m^{-3}}$, $R_1 = 0.0257$, $wR^2 = 0.0750$, 5578 independent reflections and 424 parameters. Crystal data for **II**: $C_{26}H_{33}B_3Fe_2O_6Ru_2$ $M_r = 787.79$, monoclinic, space group $P2_1$, $a = 9.3791(8)$, $b = 14.9670(14)$, $c = 10.9142(9)$ Å, $\beta = 106.910(4)$, $Z = 2$, $\rho_{calcd} = 1.785\ \mathrm{Mg\,m^{-3}}$, $R_1 = 0.0136$, $wR^2 = 0.0341$, 5135 independent reflections and 375 parameters. CCDC 756488 (**5**), 796129 (**6**) and 804017 (**II**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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