

## Heterometallic cubane-type clusters containing group 13 and 16 elements\*

K. Geetharani, Shubhankar Kumar Bose, and Sundargopal Ghosh<sup>‡</sup>

*Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India*

*Abstract:* Heterometallic cubane-type clusters were synthesized from the reaction of group 6 and 8 metallaboranes using transition-metal carbonyl compounds. Structural and spectroscopic study revealed the existence of novel “capped-cubane” geometry. In addition, the crystal structure of these clusters distinctly confirms the presence of boride unit as one of the vertices. These clusters possess 60 cluster valence electrons (cve) and six metal–metal bonds. A plausible pathway for the formation of ruthenium-capped cubane has been described.

*Keywords:* boranes; boride; cluster compounds; cubane; iron; metallaboranes; molybdenum; ruthenium; selenium.

### INTRODUCTION

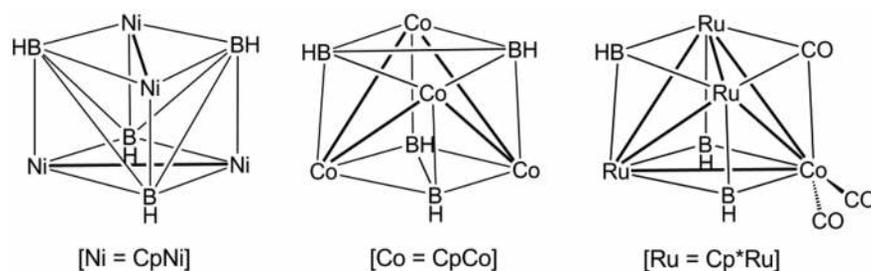
Cubic structures had been observed in inorganic chemistry before cubane, a hydrocarbon with the formula  $C_8H_8$ , was first prepared in 1964 by Eaton and Cole [1]. Cubane-related metal complexes have aroused much interest not only because of their contribution to the development of modern chemistry, but also for their potential use as models for various industrial and biological catalytic processes [2–4]. In addition, these complexes have recently been utilized as optical limiters and contrast agents [5–8]. The cube, aesthetically satisfying for its high symmetry, is well-represented in elements in both the p-block and d-block and in combinations of the two. The chemistry of cubane-type clusters has been extended to the homometallic clusters of a variety of metals such as Ru [9], Co [10], Rh [11], Ir [12], Ti [13], V [14], Mo [15], etc., and also to the heterometallic clusters. Heterometal clusters containing the cubane-type core has been largely motivated by the geometrical resemblance of their six-coordinate, to those in the native clusters of nitrogenase [16,17] and by the possibility of using these species as precursors in the synthesis of clusters related to those in the enzyme [18].

Transition-metal chalcogenide clusters with a cubane-type structure, where the metal and chalcogen atoms occupy adjacent vertices in a cube, are a unique area within cluster chemistry [15,19]. The first cuboidal cluster to be identified contained the  $Fe_4S_4$  core, a redox-active unit present in the electron-transfer protein ferredoxin [20]. In the past decades, several review articles have appeared covering the most important aspects of the chemistry of cubane-like clusters, which contain tetrahedral structural units of four transition-metal atoms, and four main group non-metal atoms [21–25]. Metal-rich metallaborane polyhedra are compositionally intermediate between the polyhedral boranes and the metal clusters, and may be regarded as “hybrid” species which in a structural and electronic sense are members of both families [26]. The stable existence of such compounds provide concrete support for the theory, first advanced by Wade [27] and subsequently developed by several authors [28], that the

\**Pure Appl. Chem.* **84**, 2183–2498 (2012). A collection of invited papers based on presentations at the 14<sup>th</sup> International Meeting on Boron Chemistry (IMEBORON-XIV), Niagara Falls, Canada, 11–15 September 2011.

<sup>‡</sup>Corresponding author

metal cluster, organometallic cluster, and borane families are related electronically and are amenable to the same kind of molecular orbital description. This idea is the basis for the widely used electron-counting rules [28a] that correlate cage structure with framework electron population. The cluster electron-counting rules and the concept of transition-metal fragments isolobal with a B–H fragment permit the vast majority of metallaborane structures to be simply related to the composition of the compound. The metal-rich boron clusters such as  $[(\text{Cp})_4\text{Ni}_4\text{B}_4\text{H}_4]$  [29] and  $[(\text{Cp})_4\text{Co}_4\text{B}_4\text{H}_4]$  [30] ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) made by Grimes, can be linked to the well-studied class of tetranuclear metal complexes known as cubanes [19,20]. Recently reported was also a metal-rich metallaborane by Fehlner with the same geometry,  $[(\text{Cp}^*\text{Ru})_3(\mu_3\text{-CO})\text{Co}(\text{CO})_2\text{B}_3\text{H}_3]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) (Chart 1) [31].



**Chart 1** Metal-rich metallaboranes with cubane-type geometry.

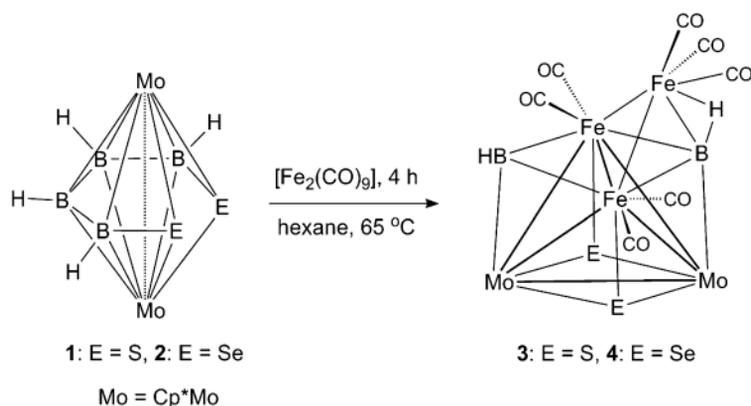
A synthetic goal in which our group has been interested is the preparation of “hybrid” clusters that contain metal and boron atoms in comparable numbers and exhibit properties common to both the borane and metal cluster families [32]. We have also been focusing on the chemistry of metallaboranes with boranes, main group elements, and small organic molecules, in which some of them showed interesting reaction chemistry [33,34]. We have now extended our studies to transition-metal carbonyl compounds, for example,  $[\text{Fe}_2(\text{CO})_9]$ ,  $[\text{Mn}_2(\text{CO})_{10}]$ , and  $[\text{Co}_2(\text{CO})_8]$  [35–37]. Transition-metal carbonyl compounds have received considerable attention in metallaborane chemistry in connection with their potential as versatile reagents in metal cluster-building reactions [38]. Thus, a general methodology for the synthesis of higher-nuclearity clusters by use of transition-metal carbonyl compounds would enable access to new types of heterometallic cubane-type clusters [35,36]. Here, we briefly review our recent discovery of hybrid cubane-type clusters, which can be considered as a new entry to the cubane family.

## SYNTHESIS OF CUBANE-TYPE CLUSTERS

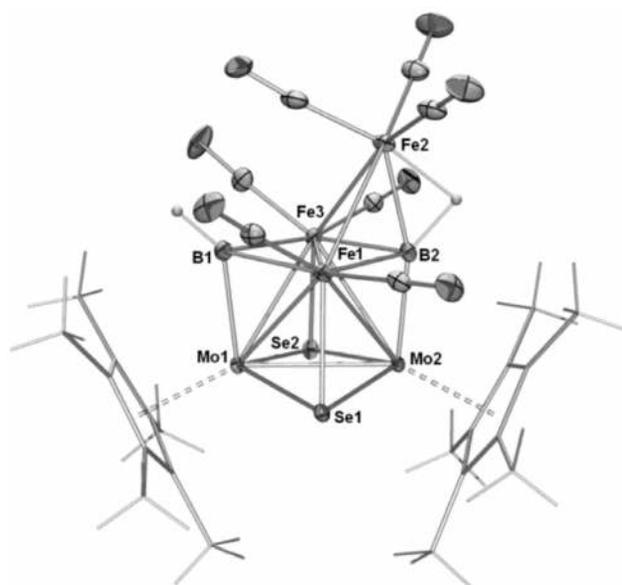
### Synthesis and characterization of dimolybdaborane cubane-type clusters

As a part of our ongoing studies, recently we have shown that the reaction of  $[\text{Cp}^*\text{MoCl}_4]$  with  $[\text{LiBH}_4\cdot\text{thf}]$ , followed by thermolysis in presence of chalcogen powders (S and Se), leads to dichalcocobalboranes  $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_4\text{E}_2]$  [34] (**1**: E = S; **2**: E = Se), in good yields. Therefore, upon availability of **1** and **2**, the chemistry was elaborated by means of cluster expansion reaction with  $[\text{Fe}_2(\text{CO})_9]$ , which led to the isolation of new type of hybrid clusters  $[(\text{Cp}^*\text{Mo})_2(\mu_3\text{-E})_2\text{B}_2\text{H}(\mu\text{-H})\{\text{Fe}(\text{CO})_2\}_2\text{Fe}(\text{CO})_3]$  (**3**: E = S; **4**: E = Se) (Scheme 1) [35].

The constitution of **4** was ascertained by an X-ray diffraction study on a suitable single crystal (Fig. 1), and displays the existence of a novel “capped cubane” cluster core. Although X-ray-quality crystals of **3** have not been obtained, its identity is inferred by comparison to the selenium analogue **4**. The overall structure of **4** 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, and its “cap”, a third Fe atom, is attached to one of the B–Fe–Fe faces of the cube. Alternatively,



**Scheme 1** Synthesis of dimolybdaborane cubane-type clusters **3** and **4**.



**Fig. 1** Crystal structure of **4** with 40 % thermal ellipsoids.

the observed geometry of **4** can be viewed as a tetracapped tetrahedron in which  $\text{Mo}_2\text{Fe}_2$  defines a tetrahedral framework. The triangular faces of this tetrahedron are capped by B1, B2, Se1, and Se2 atoms and one of the resulting triangular faces, Fe1–Fe3–B2, being capped by  $\text{Fe}(\text{CO})_3$  group; thereby generating capped cubane **4**.

Cubane-type sulfido clusters have been comprehensively investigated [2], in contrast the corresponding selenido derivatives have received little interest, the only structurally characterized examples being the Mo, Sn, and Pd derivatives with  $[\text{M}_3\text{M}'\text{Se}_4]$  single cube structure [39]. Compound **4** is the first heterobimetallic selenido cuboidal cluster containing a boride unit (B2) as one of the vertices. The Mo–Mo bond length in **4** is 0.08 Å longer than the corresponding distances in  $[\text{Mo}_3\text{CuSe}_4\text{Cl}_4(\text{dmpe})_3]\text{PF}_6$  [dmpe = 1,2-bis(dimethylphosphino)ethane] [39c]. The Fe1–Fe3 distance is 2.5220(4) Å, which is 0.2 Å shorter than those observed in single- and double-cubane clusters; while the mean Mo–Fe distances of 2.792 Å are not unusual [19]. *Exo*-bonded to the cubane at the

B2–Fe1–Fe3 face is the third Fe atom (Fe2) with a long Fe–Fe distance of 2.632 Å and the short Fe–B<sub>boride</sub> bond distance of 2.026(3) Å.

The <sup>1</sup>H and <sup>11</sup>B NMR spectra are consistent with the solid-state X-ray structure of **4**, which rationalizes the presence of two B resonances in the ratio of 1:1. The <sup>11</sup>B{<sup>1</sup>H} NMR spectra of **3** and **4** feature one broad downfield resonance at δ = 143.4 and 144.1 ppm, respectively, the range usually associated with resonance signals from metal-rich boride cluster [40]. The <sup>13</sup>C NMR spectra contain signals attributable to the two types of Cp\* ligands and the Fe(CO)<sub>3</sub> fragment. The <sup>77</sup>Se NMR spectra of **4** displayed single resonance at δ = 995 ppm for the bridged μ<sub>3</sub>-Se atoms.

### Synthesis and characterization of diruthenaborane cubane clusters

The monometalcarbonyl species such as [M(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>] (M = Cr, Mo) are known to add metal carbonyl fragments both in organometallic [41] and metallaborane chemistry [42]. In contrast, the reaction of diruthenaborane [1,2-(Cp\*RuH)<sub>2</sub>B<sub>3</sub>H<sub>7</sub>] [43] with [Mo(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>], yielded *arachno*-[(Cp\*RuCO)<sub>2</sub>B<sub>2</sub>H<sub>6</sub>] **5**, which presumably resulted from the cluster degradation followed by carbonylation at metal centers [32c] (Table 1). This new diruthenatetraborane has been isolated in high yield, and provides an interesting alternative to conventional methods of carbonylation using monometalcarbonyl fragments. No reaction of [1,2-(Cp\*RuH)<sub>2</sub>B<sub>3</sub>H<sub>7</sub>] observed with [W(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>] and all our attempts to generate **5** from [(η<sup>6</sup>-arene)Cr(CO)<sub>3</sub>] failed. Similar reaction was investigated with other metallaborane clusters such as [(Cp\*M)<sub>2</sub>B<sub>5</sub>H<sub>11</sub>] (M = Mo, W) [44,45] and [(Cp\*Ru)<sub>2</sub>B<sub>6</sub>H<sub>12</sub>] [46]. Unfortunately, all attempts to extend this chemistry to other clusters failed, even after several days.

**Table 1** Synthesis of *arachno*-[(Cp\*RuCO)<sub>2</sub>B<sub>2</sub>H<sub>6</sub>], **5** by monometal-carbonyl fragments.

$$[(\text{Cp}^*\text{RuH})_2\text{B}_3\text{H}_7] \xrightarrow[\text{(M=Cr, Mo, W; n, L = 1, THF; n, L = 3, CH}_3\text{CN)}]{[\text{M}(\text{CO})_{6-n}\text{L}_n]} [(\text{Cp}^*\text{RuCO})_2\text{B}_2\text{H}_6] \quad \mathbf{5}$$

Metallaborane	Monometal-carbonyl fragments	Solvent	T [°C]	t [h]	Yield [%] <sup>a</sup>
[(Cp*RuH) <sub>2</sub> B <sub>3</sub> H <sub>7</sub> ]	[Mo(CO) <sub>5</sub> ·THF]	THF	60	48	21
	[W(CO) <sub>5</sub> ·THF]	THF	60	18	26
	[Mo(CO) <sub>3</sub> (CH <sub>3</sub> CN) <sub>3</sub> ]	CH <sub>3</sub> CN	75	18	90
	[Cr(CO) <sub>3</sub> (CH <sub>3</sub> CN) <sub>3</sub> ]	CH <sub>3</sub> CN	75	15	74
	[W(CO) <sub>3</sub> (CH <sub>3</sub> CN) <sub>3</sub> ]	CH <sub>3</sub> CN	75	48	D <sup>b</sup>
	[(η <sup>6</sup> -arene)Cr(CO) <sub>3</sub> ]	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	75	48	D <sup>b</sup>
[(Cp*M) <sub>2</sub> B <sub>5</sub> H <sub>9</sub> ] (M = Mo, W)	CO gas	Hexane	RT <sup>c</sup>	02	NR <sup>d</sup>
	[Mo(CO) <sub>5</sub> ·THF]	THF	60	48	NR <sup>d</sup>
	[W(CO) <sub>5</sub> ·THF]	THF	60	48	NR <sup>d</sup>
	[Mo(CO) <sub>3</sub> (CH <sub>3</sub> CN) <sub>3</sub> ]	CH <sub>3</sub> CN	75	72	NR <sup>d</sup>
	[Cr(CO) <sub>3</sub> (CH <sub>3</sub> CN) <sub>3</sub> ]	CH <sub>3</sub> CN	75	48	NR <sup>d</sup>
	[(η <sup>6</sup> -arene)Cr(CO) <sub>3</sub> ]	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	75	48	NR <sup>d</sup>
[(Cp*Ru) <sub>2</sub> B <sub>6</sub> H <sub>12</sub> ]	[Mo(CO) <sub>5</sub> ·THF]	THF	60	48	NR <sup>d</sup>
	[W(CO) <sub>5</sub> ·THF]	THF	60	48	NR <sup>d</sup>
	[Mo(CO) <sub>3</sub> (CH <sub>3</sub> CN) <sub>3</sub> ]	CH <sub>3</sub> CN	75	72	NR <sup>d</sup>
	[Cr(CO) <sub>3</sub> (CH <sub>3</sub> CN) <sub>3</sub> ]	CH <sub>3</sub> CN	75	48	NR <sup>d</sup>
	[(η <sup>6</sup> -arene)Cr(CO) <sub>3</sub> ]	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	75	48	NR <sup>d</sup>

THF = tetrahydrofuran. CH<sub>3</sub>CN = acetonitrile. C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> = toluene.

<sup>a</sup>Yield based on Ru.

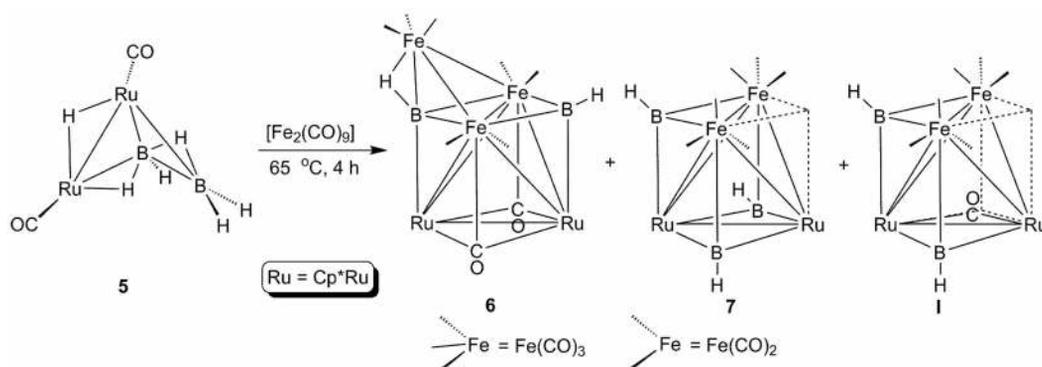
<sup>b</sup>Decomposition.

<sup>c</sup>Room temperature.

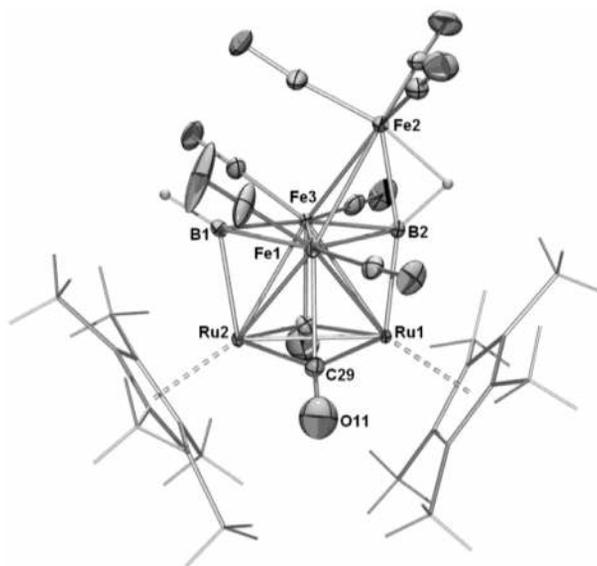
<sup>d</sup>No reaction.

Mild thermolysis of **5** with  $[\text{Fe}_2(\text{CO})_9]$  generated  $[(\text{Cp}^*\text{Ru})_2(\mu_3\text{-CO})_2\text{B}_2\text{H}(\mu\text{-H})\{\text{Fe}(\text{CO})_2\}_2\text{Fe}(\text{CO})_3]$  **6**, in parallel with the formation of an incomplete cubane cluster  $[(\mu_3\text{-BH})_3(\text{Cp}^*\text{Ru})_2\{\text{Fe}(\text{CO})_3\}_2]$ , **7** and triply bridged borylene complexes,  $[\{(\mu_3\text{-BH})(\text{Cp}^*\text{Ru})\text{Fe}(\text{CO})_3\}_2(\mu\text{-CO})]$ , (**I**, vide infra) (Scheme 2) [32c]. The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **6** displays two resonances with equal intensities, the peak at  $\delta = 128.5$  ppm has been assigned to the borylene boron, and the most downfield resonance at  $\delta = 158.5$  ppm has been assigned to the boride boron, which implies a greater degree of boron–metal interaction. The  $^1\text{H}$  NMR spectrum of **6** featured two Cp\* resonances at  $\delta = 2.17$  and 1.84 ppm, indicative of two different Ru environments. In addition, **6** showed the presence of one BH proton and one Fe–H–B proton.

The structure of **6**, shown in Fig. 2, consists of an array of four metal atoms at the corners of a tetrahedron with two CO, one BH, and one boride unit capping each faces of the tetrahedron. In addition, one of the  $\text{Fe}_2\text{B}$  faces of the cubane is capped by  $\text{Fe}(\text{CO})_3$  fragment. The coordination sphere of the Ru atoms is completed by Cp\* ligands, and each Fe atom has terminally bonded CO ligands. Furthermore, the packing of the unit cell of **6** shows intermolecular CH–O distance of 2.482 Å, which



**Scheme 2** Synthesis of diruthenaborane cubane clusters **6**, **7**, and triply bridged heterometallic borylene complex.



**Fig. 2** Crystal structure of **6** with 30 % thermal ellipsoids.

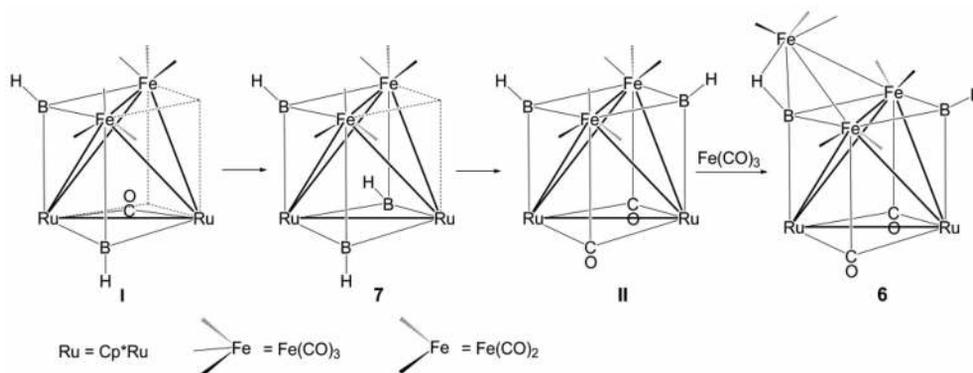
is shorter than the normal van der Waals  $H\cdots O$  separation of 2.6 Å, may possibly reflect weak hydrogen bonding between the methyl hydrogen of Cp\* and terminal carbonyl oxygen [47].

The metal–metal distances, 2.7167(4) Å (Ru–Ru),  $2.6573 \pm 0.009$  Å (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  $[(Cp^*Ru)_3(\mu_3-CO)Co(CO)_2B_3H_3]$  [31].

The geometry of **7** can be viewed as an incomplete cubane-type cluster made of two Ru, two Fe, and three B atoms (Scheme 2) [15,19]. It consists of a  $Ru_2Fe_2$  tetrahedron, in which three triangular faces Ru1–Ru2–Fe1, Ru1–Ru2–Fe2 and Ru2–Fe1–Fe2 are capped by a borylene ligand (BH) in a  $\mu_3$  fashion, thereby generating an overall tricapped tetrahedron structure. A formal electron count [28] for **7** is in agreement with the metallaborane,  $[(Cp^*Re)_2B_4H_8]$  [48], that is six skeletal electron pair (sep) appropriate for tetrahedral geometry. The interatomic Ru1–Ru2 distance of 2.7477(3) Å indicates the existence of a single bond between the Ru atoms; however, it is slightly longer than observed in **6**. The average B–Ru distance of 2.054 Å lies in the range of those reported for the transition-metal borylene complexes [49]. Compound **7** contains one semibridging carbonyl ligand that links the Cp\*Ru and  $Fe(CO)_2$  fragments. The  $^1H$  and  $^{11}B$  NMR spectra of **7** rationalize the presence of two B environments in a ratio of 2:1 at  $\delta$  126.2 and 92.9 ppm. The parent ion of **7** in the mass spectrum fragments by the sequential loss of six CO molecules and the molecular mass corresponds to  $Cp^*_2Ru_2Fe_2(CO)_6B_3H_3$ .

#### Reaction pathway

Reaction of **5** with  $[Fe_2(CO)_9]$  leads to the 60 cluster valence electrons (cve) complex **6**. The reaction pathway whereby the cubane **6** is formed is unknown; however, the isolation and characterization of *bis*-borylene complexes  $[\{(\mu_3-BH)(Cp^*Ru)Fe(CO)_3\}_2(\mu-CO)]$ , **I** and incomplete cubane **7** with 60 cve reveal a plausible pathway for the formation of **6**. As shown in Scheme 3, the core geometry of **6** is similar to that of **I** and **7**, a cubane with two and one missing vertices, respectively. The formation of **7** can be considered to be a replacement of the  $\mu-CO$  ligand in **I** by the isoelectronic {BH} fragment. Thus, it is reasonable to assume that under thermolytic condition **7** rearranges to an intermediate  $[(\mu_3-BH)_2(Cp^*Ru)_2\{Fe(CO)_2\}_2(\mu_3-CO)_2]$ , **II** by the removal of one BH group. Intermediate **II** is a cubane with 2 electrons fewer than required for a regular cubane cluster. Therefore, as reaction progresses, one of the cubane faces of **II** (Fe–Fe–B) may possibly be capped by  $Fe(CO)_3$  fragment to attain 60 cve **6**.



**Scheme 3** A plausible pathway for the formation of capped cubane cluster **6** from **3**.

### Geometrical comparison of cubane-type clusters containing group 13 element

Although the qualitative shape of the cubane clusters, shown in Chart 1 and Table 2, remain the same, the M–M distances reflect changes in cluster electronic structure accompanying the addition and loss of electrons [50]. Earlier, Kennedy in his review [51] described [(CpNi)<sub>4</sub>B<sub>4</sub>H<sub>4</sub>] [29] and [(CpCo)<sub>4</sub>B<sub>4</sub>H<sub>4</sub>] [30] as 68- and 64-electron clusters, with two and four metal–metal bonds. Further, he suggested that the putative [(CpFe)<sub>4</sub>B<sub>4</sub>H<sub>4</sub>] cluster with 60 electrons should exhibit a cubane structure with six Fe–Fe bonds and a fully bonded metal tetrahedron. The metallaborane that connects these clusters is 60 cve [(Cp\**Ru*)<sub>3</sub>(μ<sub>3</sub>-CO)Co(CO)<sub>2</sub>B<sub>3</sub>H<sub>3</sub>], a cubane geometry with six M–M bonds [31] (Table 2). Compounds **3**, **4**, and **6**, presented in this report, are also 60 cve tetrametal metallaboranes, which can be compared to those discussed above. In fact, the first member (and parent) of this particular class of cubane-like molecules, that is [Cp<sub>4</sub>Fe<sub>4</sub>(μ<sub>3</sub>-CO)<sub>4</sub>] [52], also represents a 60 cve cluster with six M–M bonds.

**Table 2** Structural and chemical shift (<sup>11</sup>B NMR spectra) comparison of **3**, **4**, **6**, and **7** and other related cubane-type clusters.

Compounds	cve	Avg. <i>d</i> (M–M) [Å]	Avg. <i>d</i> (M–B) [Å]	No. of M–M bonds	<sup>11</sup> B NMR [ppm]
[(Cp) <sub>4</sub> Ni <sub>4</sub> B <sub>4</sub> H <sub>4</sub> ]	68	2.35	2.03	2	56.2
[(Cp) <sub>4</sub> Co <sub>4</sub> B <sub>4</sub> H <sub>4</sub> ]	64	2.47	2.02	4	–121.4
[(Cp* <i>Ru</i> ) <sub>3</sub> (μ <sub>3</sub> -CO)Co(CO) <sub>2</sub> B <sub>3</sub> H <sub>3</sub> ]	60	2.74	2.08	6	134.5, 120
<b>3</b>	60	– <sup>a</sup>	– <sup>a</sup>	6	143.4, 107.2
<b>4</b>	60	2.92	2.08	6	144.1, 108.1
<b>6</b>	60	2.72	2.03	6	158.5, 128.5
<b>7</b>	60	2.74	2.05	6	126.2, 92.9

<sup>a</sup>Characterizations are based on the spectroscopic data only.

### CONCLUSIONS

In our contribution, we reveal an unprecedented family of heterometallic cubane-type clusters, [(Cp\**Mo*)<sub>2</sub>(μ<sub>3</sub>-E)<sub>2</sub>B<sub>2</sub>H(μ-H){Fe(CO)<sub>2</sub>}<sub>2</sub>Fe(CO)<sub>3</sub>] (E = S or Se) and [(Cp\**Ru*)<sub>2</sub>(μ<sub>3</sub>-CO)<sub>2</sub>B<sub>2</sub>H(μ-H){Fe(CO)<sub>2</sub>}<sub>2</sub>Fe(CO)<sub>3</sub>] containing a Fe(CO)<sub>3</sub> moiety *exo*-bonded to the cubane. These clusters demonstrate the existence of novel “capped cubane” geometry and confirm the presence of a boride unit, which is without precedent in metallaborane chemistry. These results demonstrate that metallaborane with its open face may possibly offer further cluster build-up reaction, particularly with metallaborane of early transition metals.

### ACKNOWLEDGMENTS

This work was supported by the Indo-French Centre for the Promotion of Advanced Research (IFC-PAR-CEFIPRA), No. 4405-1, New Delhi is gratefully acknowledged. KG thanks the Council of Scientific and Industrial Research (CSIR), India, for Research Fellowship.

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