

# Synthesis and Structure of Heterometallic Clusters (IrCo<sub>2</sub>, IrFe) Containing Bridging 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolato Ligands

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The 16-electron half-sandwich iridium complexes [Cp\*Ir{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}] [E = S (**1a**), Se (**1b**)] (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) [Cp\*Ir{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}] = η<sup>5</sup>-pentamethylcyclopentadienyl-[1,2-dicarba-*closo*-dodecaborane(12)-dichalcogenolato]iridium] reacted with Co<sub>2</sub>(CO)<sub>8</sub> in toluene solution to afford the trinuclear clusters [Cp\*Ir{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}]<sub>2</sub>{Co<sub>2</sub>(CO)<sub>5</sub>} [E = S (**2a**), Se (**2b**)] and mononuclear complexes [Cp\*Ir(CO){E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}] [E = S (**3a**), Se (**3b**)] as byproducts. Compounds **2a** and **2b** contain closed IrCo<sub>2</sub> triangle geometry with one Co–Co and two Ir–Co bonds. The dinuclear IrFe complexes [Cp\*Ir{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}]<sub>2</sub>{Fe(CO)<sub>3</sub>} [E = S (**4a**), Se (**4b**)] were obtained from the reactions of **1a** and **1b** with Fe(CO)<sub>5</sub> in the presence of Me<sub>3</sub>NO. The molecular structures of **2a**, **2b**, and **4b** have been determined by X-ray crystallography.

## Introduction

During the past decade, considerable attention has been devoted to metal complexes with *o*-carborane dichalcogenolato ligands, due to their unique molecular structure.<sup>1</sup> In the 16e half-sandwich complexes [Cp\*M-{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}] [M = Co,<sup>2</sup> Rh,<sup>3</sup> Ir;<sup>4</sup> E = S, Se], which contain the “pseudo-aromatic” metalladichalcogenolene five-membered ring, the metal centers, the metal–thiolato (or selenolato) bonds, and the B(3,6)–H bonds are reactive sites for interaction with unsaturated substrates.<sup>5</sup> In the course of our investigations we realized that the 16e half-sandwich complexes [Cp\*M-{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}] [M = Ir, Rh, Co; E = S, Se] can serve as promising precursors for the synthesis of mixed-metal clusters.<sup>6</sup> We have developed this methodology to build up clusters with oligonuclear framework, and some heterometallic clusters have been synthesized in such a manner that the products contain metal–metal bonds.<sup>7</sup>

The interaction of unsaturated hydrocarbons with carbonyl complexes such as Co<sub>2</sub>(CO)<sub>8</sub> and Fe(CO)<sub>5</sub> has been recognized as one of the most important reactions in the field of organometallic chemistry,<sup>8</sup> and the reactions of Co<sub>2</sub>(CO)<sub>8</sub> and Fe(CO)<sub>5</sub> with [CpCo(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] complexes have been reported very recently.<sup>9</sup> However, iridium–cobalt and iridium–iron mixed-metal clusters formed through an iridachalcogenolato heterocycle, supported by 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolates, have not been reported before, to the best of our knowledge. As an application of our cluster synthesis methodology, we report here the first examples of trinuclear and dinuclear complexes, obtained from the half-sandwich iridium compounds **1a,b** with Co<sub>2</sub>(CO)<sub>8</sub> and Fe(CO)<sub>5</sub>, respectively, in the presence of Me<sub>3</sub>NO to give [Cp\*Ir{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}]<sub>2</sub>{Co<sub>2</sub>(CO)<sub>5</sub>} (E = S (**2a**); Se (**2b**)) and [Cp\*Ir{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}]<sub>2</sub>{Fe(CO)<sub>3</sub>} (E = S (**4a**); Se (**4b**)), respectively.

## Results and Discussion

**Synthesis and Characterization of [Cp\*Ir{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}]<sub>2</sub>{Co<sub>2</sub>(CO)<sub>5</sub>} (E = S (**2a**); Se (**2b**)).** We have reported previously that treatment of [Cp\*<sub>2</sub>Ir<sub>2</sub>Cl<sub>2</sub>(μ<sub>2</sub>-Cl)<sub>2</sub>] with dilithium dichalcogenolato carboranes gives

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(1) (a) Hawthorne, M. F.; Zheng, Z. P. *Acc. Chem. Res.* **1997**, *30*, 267. (b) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1. (c) Jin, G.-X. *Coord. Chem. Rev.* **2004**, *248*, 587.

(2) (a) Kim, D. H.; Ko, J.; Park, K.; Cho, S.; Kang, S. O. *Organometallics* **1999**, *18*, 2738. (b) Won, J.-H.; Kim, D. H.; Kim, B. Y.; Kim, S.-J.; Lee, C.; Cho, S.; Ko, J.; Kang, S. O. *Organometallics* **2002**, *21*, 1443. (c) Hou, X. F.; Wang, X. C.; Wang, J.-Q.; Jin, G.-X. *J. Organomet. Chem.* **2004**, *689*, 2228. (d) Li, W.; Weng, L. H.; Jin, G.-X.; *Inorg. Chem. Commun.* **2004**, *7*, 1174.

(3) (a) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *587*, 252. (b) Kong, Q.; Jin, G.-X.; Cai, S. Y.; Weng, L.-H. *Chin. Sci. Bull.* **2003**, *48*, 1733.

(4) (a) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **1999**, 837. (b) Bae, J.-Y.; Park, Y.-I.; Ko, J.; Park, K.-I.; Cho, S.-I.; Kang, S. O. *Inorg. Chim. Acta* **1999**, *289*, 141. (c) Bae, J. Y.; Lee, Y.-J.; Kim, S.-J.; Ko, J.; Cho, S.; Kang, S. O. *Organometallics* **2000**, *19*, 1514.

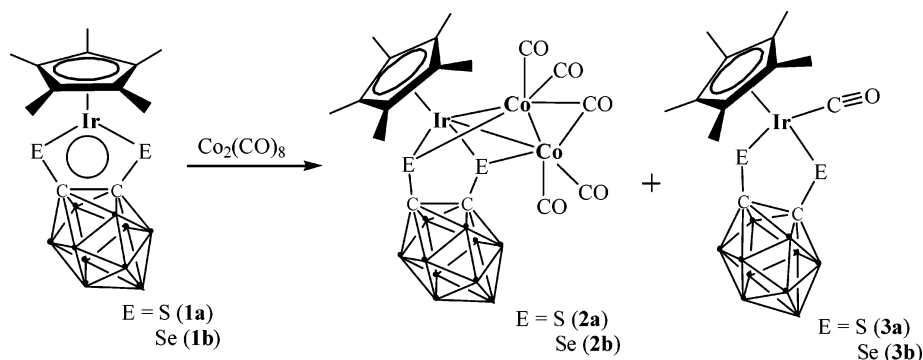
(5) (a) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3689. (b) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem. Eur. J.* **2000**, *6*, 3026. (c) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem. Eur. J.* **2002**, *8*, 388.

(6) (a) Lu, S.-X.; Jin, G.-X.; Eibl, S.; Herberhold, M.; Xin, Y. *Organometallics* **2002**, *21*, 2533. (b) Yu, X.-Y.; Jin, G.-X.; Hu, N.-H.; Weng, L.-H. *Organometallics* **2002**, *21*, 5540. (c) Yu, X.-Y.; Lu, S.-X.; Jin, G.-X.; Weng, L.-H. *Inorg. Chim. Acta* **2004**, *357*, 361. (d) Yu, X.-Y.; Jin, G.-X.; Hu, N.-H. *Chin. J. Chem.* **2003**, *21*, 446.

(7) Jin, G.-X.; Wang, J.-Q.; Zhang, Z.; Weng, L. H.; Herberhold, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 259.

(8) (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Hoffman, D. M.; Hoffman, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

(9) (a) Muratsugu, S.; Nakagawa, N.; Habe, S.; Namiki, K.; Murata, M.; Nishihara, H. In *5th Japan-China Joint Symposium on Metal Cluster Compounds*; Japan, 2004; p 59. (b) Nihei, M.; Nankawa, T.; Kurihara, M.; Nishihara, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1098.

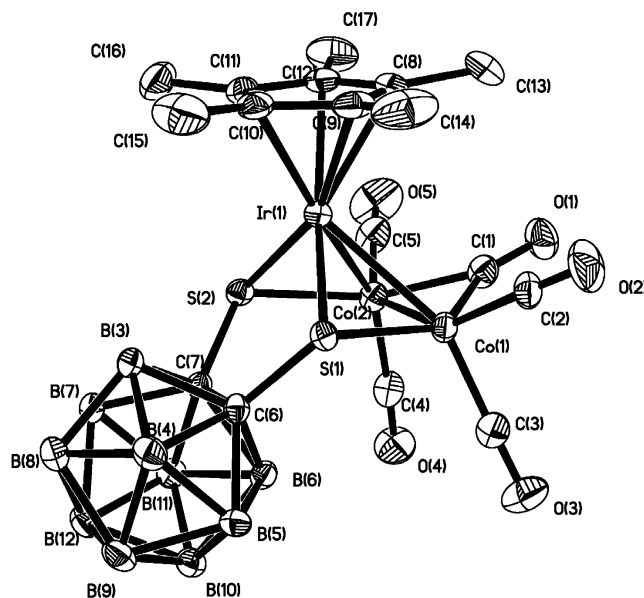
Scheme 1. Synthesis of **2a** and **2b**

the 16-electron dithiolene and diselenolene complexes **1a,b** and investigated the addition reactions at the iridium atom.<sup>4a</sup> Now, it has been found that **1a,b** in toluene solution can react with Co<sub>2</sub>(CO)<sub>8</sub> in a 1:1 molar ratio at room temperature, changing to deep red from blue or green. The dark red and orange products [Cp\*Ir{E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}{Co<sub>2</sub>(CO)<sub>5</sub>} (E = S (**2a**); Se (**2b**)) and the byproducts [Cp\*Ir(CO){E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}] (E = S (**3a**); Se (**3b**)) were formed in a yield of 76–79% and 5–6%, respectively (Scheme 1). Both compounds are neutral, diamagnetic, and slightly air-sensitive in solution. It is noteworthy that, in the presence of the decarbonylation reagent Me<sub>3</sub>NO, **2a** and **2b** are obtained in higher yields (80–85%) and without the concomitant formation of **3a** and **3b**.

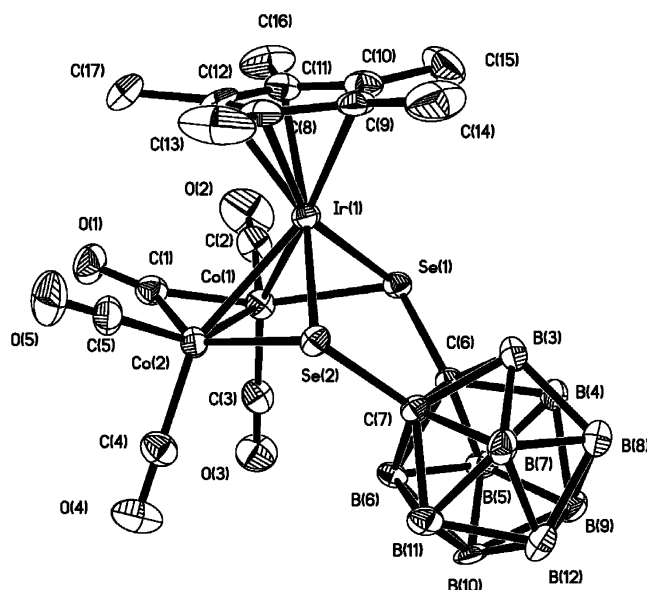
The characterization of the products **2a** and **2b** is based on elemental analyses and X-ray diffraction studies. The IR spectra of **2a** in the solid state exhibit, besides absorptions typical of the terminal CO groups at 2054(vs), 2031(vs), 2015(vs), and 1980(s) cm<sup>-1</sup>, two bands (1821(s), 1808(s) cm<sup>-1</sup>) in the region typical for CO bridges. Apparently, there are two kind of ν(CO) frequencies for the Co<sub>2</sub>(CO)<sub>5</sub> moieties. The <sup>13</sup>C NMR spectrum of **2a** in CDCl<sub>3</sub> solution shows only one resonance at δ = 169 for the CO groups.

The structures of **2a** and **2b** have been determined by X-ray analysis using single crystals grown from toluene–hexane, after chromatography on silica. The molecular structures of **2a** and **2b** are shown in Figures 1 and 2. Selected bond distances and angles are listed in Tables 1 and 2.

Compound **2a** has a closed IrCo<sub>2</sub> triangular core, in which the two Ir–Co edges are bridged by μ<sub>3</sub>-S ligands, and the Co–Co edge is bridged by a μ<sub>2</sub>-CO ligand. The Ir–Co distances (Ir(1)–Co(1) = 2.5967(11) Å, Ir(1)–Co(2) = 2.6244(11) Å) are very short and clearly indicative of bonding interactions. The Co(1)–Co(2) distance is 2.4452(12) Å, typical of a Co–Co single bond.<sup>10</sup> The Ir atom is further capped by a Cp\* ligand and coordinated to two μ<sub>3</sub>-S ligands. Due to the coordination of the S atoms to Co, the pseudoaromatic iridadiholato heterocyclic system is destroyed and bent with a dihedral angle of 161.5° along the S···S vector. The Co–S distances of 2.2717(19)–2.241(2) Å are slightly longer than the Co–S lengths in the 16-electron complex [CpCoS<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)] (2.129(8)–2.139(8) Å).<sup>2a</sup> Each Co



**Figure 1.** Molecular structure of **2a** with atom labeling, ellipsoids at the 30% probability level, all hydrogen atoms omitted for clarity.



**Figure 2.** Molecular structure of **2b** with atom labeling, ellipsoids at the 30% probability level, all hydrogen atoms omitted for clarity.

(10) (a) Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18. (b) Brown, D. A. *J. Chem. Phys.* **1960**, *33*, 1037. (c) Summer, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732. (d) Herberhold, M. Jin, G.-X., Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 656.

atom bears two terminal CO ligands; the remaining CO group bridges the Co(1)–Co(2) metal–metal bond. The Co(1)–C(1) and Co(2)–C(1) bonds are 1.902(7) and

**Table 1. Selected Bond Distances (Å) and Angles (deg) for 2a**

(a) Distances			
Ir(1)–Co(1)	2.5967(11)	Ir(1)–Co(2)	2.6244(11)
Ir(1)–S(1)	2.3050(16)	Ir(1)–S(2)	2.3127(16)
Co(1)–S(1)	2.2717(19)	Co(1)–C(1)	1.902(7)
Co(1)–C(3)	1.781(7)	Co(1)–Co(2)	2.4452(12)
Co(2)–S(2)	2.241(2)	Co(2)–C(1)	1.900(7)
Co(2)–C(5)	1.819(7)	C(1)–O(1)	1.171(8)
C(3)–O(3)	1.131(8)	C(5)–O(5)	1.117(8)
(b) Angles			
Ir(1)–Co(1)–Co(2)	62.65(3)	Ir(1)–Co(2)–Co(1)	61.50(3)
Ir(1)–S(1)–Co(1)	56.04(5)	Co(1)–Ir(1)–Co(2)	55.85(3)
Co(1)–S(1)–Ir(1)	54.83(5)	Co(1)–Co(2)–C(1)	80.1(3)
Co(1)–O(1)–C(1)	139.5(6)	Co(1)–O(3)–C(3)	178.1(7)

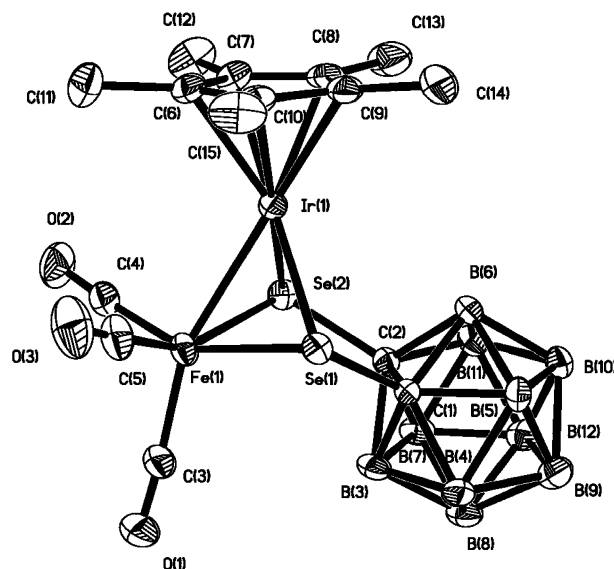
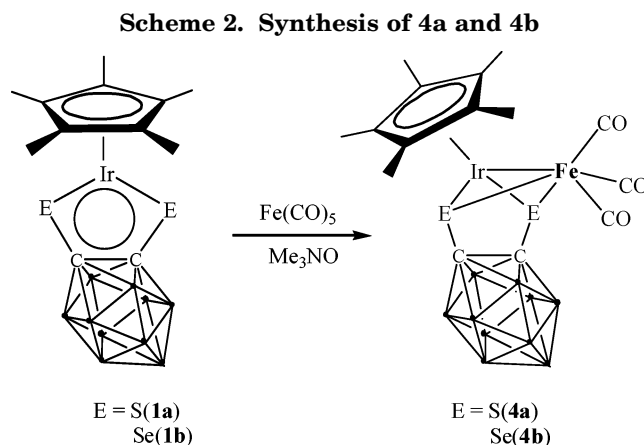
**Table 2. Selected Bond Distances (Å) and Angles (deg) for 2b**

(a) Distances			
Ir(1)–Co(1)	2.6460(13)	Ir(1)–Co(2)	2.6156(13)
Ir(1)–Se(1)	2.4246(10)	Ir(1)–Se(2)	2.4189(11)
Co(1)–Se(1)	2.3515(17)	Co(1)–C(1)	1.887(10)
Co(1)–C(3)	1.786(10)	Co(1)–Co(2)	2.4445(16)
Co(2)–Se(2)	2.3827(15)	Co(2)–C(1)	1.890(9)
Co(2)–C(5)	1.795(10)	C(1)–O(1)	1.183(10)
C(3)–O(3)	1.124(11)	C(5)–O(5)	1.115(10)
(b) Angles			
Ir(1)–Co(1)–Co(2)	61.69(4)	Ir(1)–Co(2)–Co(1)	62.95(4)
Ir(1)–Se(1)–Co(1)	67.26(4)	Co(1)–Ir(1)–Co(2)	55.37(4)
Co(1)–Se(1)–Ir(1)	67.26(4)	Co(1)–Co(2)–C(1)	49.6(3)
Co(1)–O(1)–C(1)	140.3(8)	Co(1)–O(3)–C(3)	179.0(9)

1.900(7) Å, similar to the bridging Co–C distances of  $\text{Co}_2(\text{CO})_8$  (mean value 1.92 Å)<sup>10c</sup> and longer than Co–C(3), Co–C(4), and Co–C(5) (range from 1.781(7) to 1.819(7) Å).

Complex **2b** crystallizes in the form of dark red prisms in the orthorhombic space group *Pbca* with eight molecules in the unit cell. Its molecular structure is similar to that of **2a**. Figure 2 depicts the molecular structure of **2b**, determined by X-ray structure analysis using a single crystal grown from toluene–hexane, after chromatography on silica. Compound **2b** also contains three metal atoms, with a triangular core similar to that of **2a**. There are three metal–metal bonds: Ir(1)–Co(1) = 2.6460(13) Å, Ir(1)–Co(2) = 2.6156(13) Å, and Co(1)–Co(2) = 2.4445(16) Å. The dihedral angle (165.6°) along the Se...Se vector is almost identical with that in **2a** (161.5°), whereas it is 180° in the parent diselenolene complex  $\text{Cp}^*\text{Ir}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$  (**2b**).

**Reaction with  $\text{Fe}(\text{CO})_5$ .** The 14-electron fragment  $\text{Co}(\text{CO})_3^+$  in **2a,b** is isolobal to an  $\text{Fe}(\text{CO})_3$  unit. To investigate the possible extension of our synthetic approach to IrFe clusters, we attempted to react the  $[\text{Cp}^*\text{Ir}\{\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})\}]$  (E = S (**1a**), Se (**1b**)) model complexes with  $\text{Fe}(\text{CO})_5$  in the presence of 2 equiv of  $\text{Me}_3\text{NO}$  (Scheme 2). The products **4a** and **4b** were isolated as red solids with yields of 63% and 56%, respectively. The IR spectrum of **4b** in the solid state exhibits absorptions at 2038(vs) and 1963(vs)  $\text{cm}^{-1}$ , which we ascribe to vibration of terminal CO ligands. The X-ray crystal structure of **4b** is shown in Figure 3, and selected bond lengths and angles are presented in Table 3. The Ir–Fe distance in **4b** (2.5762(11) Å) is found in the range expected for a single bond.<sup>11</sup> The Fe center in **4a** is coordinated by two Se atoms, one Ir atom, and three terminal CO groups in an approximately

**Figure 3.** Molecular structure of **4b** with atom labeling, ellipsoids at the 30% probability level, all hydrogen atoms omitted for clarity.**Table 3. Selected Bond Distances (Å) and Angles (deg) for 4b**

(a) Distances			
Ir(1)–Se(1)	2.4411(10)	Ir(1)–Se(2)	2.4316(9)
Ir(1)–Fe(1)	2.5762(11)	Fe(1)–C(3)	1.808(7)
Fe(1)–C(4)	1.783(8)	Fe(1)–C(5)	1.780(7)
Fe(1)–Se(1)	2.4072(13)	Fe(1)–Se(2)	2.4265(12)
C(1)–C(2)	1.607(7)	C(1)–O(4)	1.140(8)
C(2)–O(5)	1.131(8)	C(3)–O(6)	1.141(8)
(b) Angles			
Ir(1)–Se(1)–Fe(1)	64.19(3)	Ir(1)–Se(2)–Fe(1)	64.05(3)
Ir(1)–Fe(1)–Se(1)	58.54(3)	Ir(1)–Fe(1)–Se(2)	58.07(3)
Fe(1)–Ir(1)–Se(2)	57.88(3)	Fe(1)–Ir(1)–Se(10)	57.27(3)
Fe(1)–Se(1)–C(1)	103.36(16)	Fe(1)–Se(2)–C(2)	103.62(15)
Se(2)–Ir(1)–Se(1)	81.61(3)		

trigonal-bipyramidal geometry. The Ir–Se bond distances (2.4411(10) and 2.4316(9) Å) are similar to those found in **2b**, while the Fe–Se bond distances (2.4072(13) and 2.4265(12) Å) are close to complexes containing

(11) (a) Rosenberg, S.; Mahoney, W. S.; Hayes, J. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1065. (b) Crespi, A. M.; Sabat, M.; Shriver, D. F. *Inorg. Chem.* **1988**, *27*, 812. (c) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2544. (d) Della Pergola, R.; Garlaschelli, L.; Demartin, F.; Manassero, M.; Masciocchi, N.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1990**, 127. (e) Bruce, M. I.; Koutsantonis, G. A.; Tiekink, E. R. T. *J. Organomet. Chem.* **1991**, *407*, 391. (f) Della Pergola, R.; Ceriotti, A.; Garlaschelli, L.; Demartin, F.; Manassero, M.; Masciocchi, N.; Sansoni, M. *Inorg.*



Table 4. Crystallographic Data for Compounds 2a, 2b, and 4b

	2a	2b	4b
empirical formula	C <sub>17</sub> H <sub>25</sub> B <sub>10</sub> Co <sub>2</sub> IrO <sub>5</sub> S <sub>2</sub>	C <sub>17</sub> H <sub>25</sub> B <sub>10</sub> Co <sub>2</sub> IrO <sub>5</sub> Se <sub>2</sub>	C <sub>15</sub> H <sub>25</sub> B <sub>10</sub> FeIrO <sub>3</sub> Se <sub>2</sub>
fw	791.65	885.45	767.42
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> (Å)	10.146(3)	10.154(3)	18.076(7)
<i>b</i> (Å)	15.736(5)	16.051(4)	14.012(5)
<i>c</i> (Å)	34.459(12)	34.606(10)	19.787(7)
<i>V</i> (Å <sup>3</sup> )	5502(3)	5640(3)	5012(3)
<i>Z</i>	8	8	8
ρ <sub>calcd</sub> (g/cm <sup>3</sup> )	1.912	2.086	2.034
μ(Mo Kα) (mm <sup>-1</sup> )	6.198	8.479	8.806
no. of observations	4839	5551	4935
no. of params	350	350	299
goodness of fit	1.208	1.166	1.063
<i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0381	0.0490	0.0314
<i>wR</i> <sub>2</sub> <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0935	0.0965	0.0648
largest peak in diff map (e Å <sup>-3</sup> )	1.637	1.435	1.352

<sup>a</sup> *R*<sub>1</sub> = Σ||*F*<sub>o</sub>| - |*F*<sub>c</sub>|| (based on reflections with *F*<sub>o</sub><sup>2</sup> > 2σ(*F*<sup>2</sup>)). *wR*<sub>2</sub> = [Σ(*wF*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)/Σ(*wF*<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>; *w* = 1/[σ(*F*<sub>o</sub><sup>2</sup>) + (0.095*P*)<sup>2</sup>]; *P* = [max(*F*<sub>o</sub><sup>2</sup>, 0) + 2*F*<sub>c</sub><sup>2</sup>]/3 (also with *F*<sub>o</sub><sup>2</sup> > 2σ(*F*<sup>2</sup>)).

Fe(CO)<sub>3</sub> units coordinated by selenolato ligands.<sup>12</sup> The three Fe–C (1.808(7), 1.783(8), 1.780(7) Å) and C–O (1.140(8), 1.131(8), 1.141(8) Å) bond lengths in **4b** are not significantly different from one another and are similar to the corresponding distances of the terminal CO ligands in [Fe<sub>2</sub>(CO)<sub>9</sub>].<sup>13</sup>

To summarize, we have synthesized the IrCo<sub>2</sub> and IrFe mixed-metal clusters **2a,b** and **4a,b** from [Cp\*Ir-E<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)] [E = S (**1a**), Se (**1b**)]. The resultant clusters **2a,b** contain an IrCo<sub>2</sub>(μ<sub>3</sub>-E)<sub>2</sub> (E = S, Se) core with Ir–Co and Co–Co metal–metal bonds. Similarly, IrFe clusters (**4a,b**) containing an Ir–Fe bond were synthesized using this methodology.

### Experimental Section

**General Comments.** All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried by refluxing over sodium/benzophenone ketyl (toluene, hexane, cyclohexane) and distilled just before use. Co<sub>2</sub>(CO)<sub>8</sub> and Fe(CO)<sub>5</sub> were used as purchased. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer, whereas <sup>1</sup>H (500 MHz), <sup>11</sup>B (160 MHz), and <sup>13</sup>C (125 MHz) NMR spectra were obtained on a Bruker DMX-500 spectrophotometer in CDCl<sub>3</sub> solution. Elemental analyses were performed on an Elementar III Vario EI analyzer.

**Preparation of [Cp\*IrE<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)]{Co<sub>2</sub>(CO)<sub>5</sub>} (E = S (**2a**); Se (**2b**)).** To a solution of either **1a** (53 mg, 0.1 mmol) or **1b** (62 mg, 0.1 mmol) in toluene (30 mL) was added Co<sub>2</sub>(CO)<sub>8</sub> (0.1 mmol, 34 mg). The color of the solution changed immediately from blue or green to dark red. After stirring for 3 h, the solvent was evaporated under reduced pressure. The residue was redissolved in 5 mL of toluene and chromatographed on silica gel. Elution with toluene–hexane (1:5) gave a dark red zone which contained **2a** (60 mg, 76%) and **3a** (3 mg, 5%) or **2b** (70 mg, 79%) and **3b** (4 mg, 6%), respectively. Crystals of **2a,b** were obtained from toluene–hexane (1:1). Complex **2a**: Anal. Calcd for C<sub>17</sub>H<sub>25</sub>B<sub>10</sub>Co<sub>2</sub>IrO<sub>5</sub>S<sub>2</sub> (%): C 25.79, H 3.18. Found: C, 25.36, H 3.09. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.87(s, C<sub>5</sub>Me<sub>5</sub>, 15H). <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ -2.2, -4.5, -6.8, -7.4, -8.4,

-10.4, -12.2. <sup>13</sup>C NMR (CD<sub>3</sub>Cl): δ 9.3(s, C<sub>5</sub>Me<sub>5</sub>(Me)), 97.7(s, C<sub>2</sub>-carborane), 102.8(s, C<sub>5</sub>Me<sub>5</sub> (C<sub>5</sub>)), 169.2(s, CO). IR (KBr disk): 2593 cm<sup>-1</sup> (ν<sub>B-H</sub>), 2054(vs), 2031(vs), 2015(vs), 1980(s), 1821(s) cm<sup>-1</sup> (ν<sub>CO</sub>). Complex **3a**: Anal. Calcd for C<sub>13</sub>H<sub>25</sub>B<sub>10</sub>OS<sub>2</sub>Ir (%): C, 27.79, H, 4.49. Found: C, 27.56, H, 4.35. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.89(s, 15H, C<sub>5</sub>Me<sub>5</sub>). IR (KBr disk): 2596 cm<sup>-1</sup> (ν<sub>B-H</sub>), 2036 cm<sup>-1</sup> (ν<sub>CO</sub>). Complex **2b**: Anal. Calcd for C<sub>17</sub>H<sub>25</sub>B<sub>10</sub>Co<sub>2</sub>IrO<sub>5</sub>Se<sub>2</sub> (%): C 23.06, H 2.85. Found: C, 22.95, H 2.82. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.91(s, C<sub>5</sub>Me<sub>5</sub>, 15H). <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ -4.0, -5.0, -6.8, -7.9, -8.6, -10.6, -11.3. IR (KBr disk): 2580 cm<sup>-1</sup> (ν<sub>B-H</sub>), 2044(vs), 2027(vs), 2011(vs), 1978(s), 1818(s) cm<sup>-1</sup> (ν<sub>CO</sub>). Complex **3b**: Anal. Calcd for C<sub>13</sub>H<sub>25</sub>B<sub>10</sub>OSe<sub>2</sub>Ir (%): C, 23.82; H, 3.84. Found: C 24.03; H 3.85. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.89(s, C<sub>5</sub>Me<sub>5</sub>, 15H). IR (KBr disk): 2585 cm<sup>-1</sup> (ν<sub>B-H</sub>), 2042 cm<sup>-1</sup> (ν<sub>CO</sub>).

**Preparation of [Cp\*IrE<sub>2</sub>C<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)]{Fe(CO)<sub>3</sub>} (E = S (**4a**); Se (**4b**)).** To a solution of either **1a** (53 mg, 0.1 mmol) or **1b** (62 mg, 0.1 mmol) in toluene (30 mL) were added Fe(CO)<sub>5</sub> (0.1 mmol, 13 mL) and Me<sub>3</sub>NO (0.2 mmol, 15 mg). The color of the solution changed gradually from blue or green to red. After stirring for 8 h, the solvent was evaporated under reduced pressure. The residue was redissolved in 5 mL of toluene and chromatographed on silica gel. Elution with toluene–hexane (1:5) gave a red band which contained **4a** (63%) or **4b** (56%), respectively. Crystals of **4a,b** were obtained from toluene–hexane (1:1). Complex **4a**: Anal. Calcd for C<sub>15</sub>H<sub>25</sub>B<sub>10</sub>FeIrO<sub>3</sub>S<sub>2</sub> (%): C 26.74, H 3.74. Found: C, 26.53, H 3.69. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.01(s, C<sub>5</sub>Me<sub>5</sub>, 15H). <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ -2.4, -4.6, -6.1, -7.4, -8.5, -10.6, 11.9. IR (KBr disk): 2579 cm<sup>-1</sup> (ν<sub>B-H</sub>), 2037(vs), 1963(vs) (ν<sub>CO</sub>). Complex **4b**: Anal. Calcd for C<sub>15</sub>H<sub>25</sub>B<sub>10</sub>FeIrO<sub>3</sub>Se<sub>2</sub> (%): C 23.48, H 3.28. Found: C, 23.18, H 3.21. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.99(s, C<sub>5</sub>Me<sub>5</sub>, 15H). <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ -3.8, -5.0, -6.5, -7.3, -8.8, -10.9, -12.2. <sup>13</sup>C NMR (CD<sub>3</sub>Cl): δ 9.6(s, C<sub>5</sub>Me<sub>5</sub>(Me)), 91.7(s, C<sub>2</sub>-carborane), 102.1(s, C<sub>5</sub>Me<sub>5</sub> (C<sub>5</sub>)). IR (KBr disk): 2578 cm<sup>-1</sup> (ν<sub>B-H</sub>), 2038 cm<sup>-1</sup>(vs), 1963(vs) cm<sup>-1</sup> (ν<sub>CO</sub>).

**Crystallographic Analysis.** Dark red crystal of **2a**, **2b**, and **4b** were grown by slow diffusion from toluene–hexane solution. The crystals of all compounds were mounted by gluing onto the end of a thin glass fiber. X-ray intensity data were collected on the CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). All data were collected at room temperature using the ω scan technique. The structures were solved by direct methods, using Fourier techniques, and refined on *F*<sup>2</sup> by a full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included but not refined. All the calculations

*Chem.* **1993**, *32*, 3277. (g) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198. (h) Vivic, D. A.; Jones, W. D. *Organometallics* **1997**, *16*, 1912. (i) Tang, Z.; Nomura, Y.; Kuwata, S.; Ishii, Y.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 4909.

(12) (a) Mathur, P.; Ghosh, S. *Organometallic* **1997**, *16*, 3536. (b) Mathur, P.; Ghosh, S.; Sarkar, A.; Rheingold, A. L.; Guzei, I. A. *Organometallic* **1998**, *17*, 770.

(13) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155.

were carried out using the SHELXTL program. Crystal data, data collection parameters, and the results of the analyses of compounds **2a**, **2b**, and **4b** are listed in Table 4.

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**Supporting Information Available:** The crystallographic data for **2a**, **2b**, and **4b** are available free of charge via the Internet at <http://pubs.acs.org>.

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