Formation of Cup-Shaped Metallic Clusters via B−H Activation at the B(3)/B(6) Site of an *ortho*-Carborane-1,2-dichalcogenolato Ligand

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Received May 3, 2006

Dimetallic complexes {Cp*Ir[$E_2C_2(B_9H_9)$][(cod)Ir(OCH_3)]} (E = S, **3a**; E = Se, **3b**) and {Cp*Ir[E_2C_2($B_{10}H_9$)][(cod)Ir]} (E = S, **4a**; E = Se, **4b**) were synthesized by the reaction of half-sandwich complexes Cp*Ir[$E_2C_2(B_{10}H_{10})$] (E = S, **1a**; Se, **1b**) with 2 equiv of [Ir(cod)(μ-OMe)]$_2$ (**2-Ir**). Analogous reactions of **1a** with [Rh(cod)(μ-OMe)]$_2$ (**2-Rh**) were investigated, and three complexes, {Cp*Ir[$S_2C_2(B_9H_9)$][(cod)Rh(OCH_3)]} (**5a**), {Cp*Ir[$S_2C_2(B_{10}H_{10})$][(cod)Rh]} (**6a**), and {Cp*Ir[$S_2C_2(B_{10}H_9)$][(cod)Rh]} (**7a**), were obtained. By comparing the two reactions, the routes of metal-induced B−H activation at B(3)/B(6) of the *ortho*-carborane-1,2-dichalcogenolato ligand were investigated. These *nido*-carborane complexes such as **3a**, **3b**, and **5a** contain intercluster metal−metal bonds. Moreover, the V-shaped trimetallic units {(cod)Ir[$E_2C_2(B_9H_8)$][(cod)Ir(OCH_3)][(C_8H_{13})Ir]} (E = S, **9a**; Se, **9b**) have been constructed through the M_2-*nido*-carborane complexes {(cod)Ir[$E_2C_2(B_9H_9)$][(cod)Ir(OCH_3)]} (E = S, **8a**; Se, **8b**). Complexes **3**−**10** were characterized by NMR spectroscopy (^{1}H, ^{11}B NMR), and X-ray structural analyses were reported for complexes **3a**, **3b**, **4a**, **5a**, **6a**, **8a**, **9b**, and **10b**.

Introduction

The carborane anion [*nido*-$C_2B_9H_{11}$]$^{2-}$ may be compared with the cyclopentadienide anion [C_5R_5]$^-$, in that both can be coordinated to transition metal centers as pentahapto, six-π-electron ligands.[1] Following the synthesis of the first metallacarborane by Hawthorne et al. in 1967,[2] *nido*-carboranes have proved to be excellent bulky and stable building blocks that allow the synthesis of a wide range of heterocarboranes, which, in addition to boron and carbon atoms, contain other elements in their skeleton.[3] Such molecules have recently been shown to have a variety of applications in material science,[4] catalysis,[5] or medicine,[6] which makes carborane chemistry an interesting area of growth. The synthesis of metallacarboranes obtained through *nido*-carboranes have attracted considerable attention in recent years.[7] Particularly interesting metallacarboranes are those containing intercluster metal−metal bonds, which effectively bridge the two best developed areas of inorganic cluster chemistry, polyhedral boranes and metal clusters.[8]

We have recently expanded our studies to build heterometallic clusters starting from iridium or rhodium complexes Cp*M-[$E_2C_2(B_{10}H_{10})$] (M = Ir, Rh; E = S, Se).[9] The distinguishing feature associated with the new di- and oligonuclear products is the presence of metal−metal bonds that are stabilized by an

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(1) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, England, 1982; pp 411−542, and references therein.

(2) (a) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642−1643. (b) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. *J. Am. Chem. Soc.* **1965**, *87*, 1818−1819. (c) Hawthorne, M. F.; Pilling, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 470−471. (d) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862−868.

(3) General reviews: (a) Hawthorne, M. F. *Acc. Chem. Res.* **1968**, *1*, 281−288. (b) Dunks, G. B.; Hawthorne, M. F. *Acc. Chem. Res.* **1973**, *6*, 124−131. (c) Hawthorne, M. F. *J. Organomet. Chem.* **1975**, *100*, 97−110. (d) Grimes, R. N. *J. Organomet. Chem.* **1999**, *581*, 1−12. (e) Hosmane, N. S. *J. Organomet. Chem.* **1999**, *581*, 13−27. (f) Hosmane, N. S.; Maguire, J. A. *Eur. J. Inorg. Chem.* **2003**, 3989−3999. (g) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1−9. (h) Jin, G.-X. *Coord. Chem. Rev.* **2004**, *248*, 587−602.

(4) (a) Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Lopez-de-Luzuriaga, J. M.; Monge, M.; Perez, J. L.; Ramon, M. A. *Inorg. Chem.* **2003**, *42*, 2061−2068. (b) Hawthorne, M. F.; Zink, J. I.; Skelton, J. M.; Bayer, M. J.; Liu, C.; Livshits, E.; Baer, R.; Neuhauser, D. *Science* **2004**, *303*, 1849−1851. (c) Matejicek, P.; Cigler, P.; Prochazka, K.; Kral, V. *Langmuir* **2006**, *22*, 575−581.

(5) (a) Grimes, R. N. *Coord. Chem. Rev.* **2000**, *200*−*202*, 773−811. (b) Crowther, D. J.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1995**, *117*, 10403−10404.

(6) (a) Cigler, P.; Kozisek, M.; Rezacova, P.; Brynda, J.; Otwinowski, Z.; Pokorna, J.; Plesek, J.; Gruener, B.; Doleckova, L.; Masa, M.; Sedlacek, J.; Bodem, J.; Kraeusslich, H.-G.; Kral, V.; Konvalinka, J. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 15394−15399. (b) Hao, E.; Vicente, M. G. H. *Chem. Commun.* **2005**, 1306−1308. (c) Vicente, M. G. H. *Curr. Med. Chem. Anti-Cancer Agents* **2001**, *1*, 175−194.

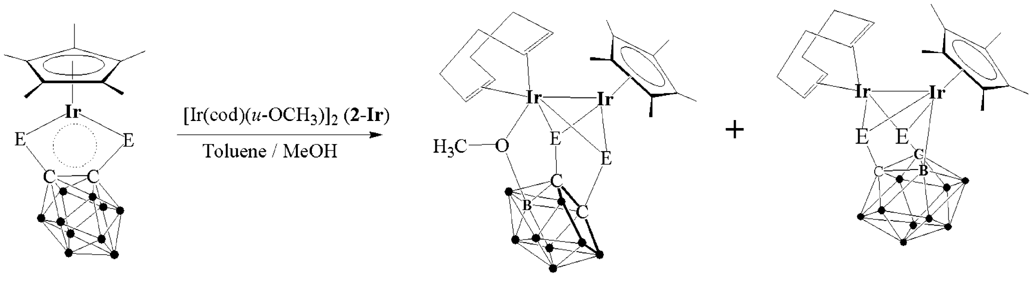
(7) Selected papers: (a) Teixidor, F.; Flores, M. A.; Vinas, C.; Sillanpaa, R.; Kivekas, R. *J. Am. Chem. Soc.* **2000**, *122*, 1963−1973. (b) Tutusaus, O.; Vinas, C.; Nunez, R.; Teixidor, F.; Demonceau, A.; Delfosse, S.; Noels, A. F.; Mata, I.; Molins, E. *J. Am. Chem. Soc.* **2003**, *125*, 11830−11831. (c) Tutusaus, O.; Vinas, C.; Kivekas, R.; Sillanpaa, R.; Teixidor, F. *Chem. Commun.* **2003**, 2458−2459. (d) Sogbein, O. O.; Merdy, P.; Morel, P.; Valliant, J. F. *Inorg. Chem.* **2004**, *43*, 3032−3034. (e) Vinas, C.; Llop, J.; Teixidor, F.; Kivekas, R.; Sillanpaa, R. *Chem. Eur. J.* **2005**, *11*, 1933−1941. (f) Nunez, R.; Tutusaus, O.; Teixidor, F.; Vinas, C.; Sillanpaa, R.; Kivekas, R. *Chem. Eur. J.* **2005**, *11*, 5637−5647. (g) Cheung, M.-S.; Chan, H. S.; Xie, Z. *Organometallics* **2005**, *24*, 4207−4215. (h) Lee, Y.-J.; Lee, J.-D.; Jeong, H.-J.; Son, K.-C.; Ko, J.; Cheong, M.; Kang, S. O. *Organometallics* **2005**, *24*, 3008−3019.

(8) (a) Collman, J. P.; Boulatov. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 3948−3961. (b) Sinfelt, J. H. In *Metal-Metal Bonds and Clusters in Chemistry and Catalysis*; Fackler, J. P., Jr., Ed.; Plenum Press: New York, 1990; pp 103−112.

(9) (a) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **1999**, *587*, 252−257. (b) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **1999**, 873−875. (c) Bae, J.-Y.; Park, Y.-I.; Ko, J.; Park, K.-I.; Cho, S.-I.; Kang, S. O. *Inorg. Chim. Acta* **1999**, *289*, 141−149.

10.1021/om060381a CCC: $33.50

Scheme 1. Reaction of 1a, 1b with 2-Ir



E = S(**1a**); E = Se(**1b**) E = S(**3a**); E = Se(**3b**) E = S(**4a**); Se(**4b**)

ancillary *ortho*-carborane-1,2-dichalcogenolato ligand.[10] It should be noted that some similar oligonuclear products contain metal−metal bonds built by mononuclear metalladichalcogenolenes.[11] However, to our knowledge, the construction of a metal cluster through *nido*-carborane ligands is rare. Herein we report the synthesis of a series of metal clusters containing *nido*-carborane and the first structural confirmation of a trinuclear metallic cluster that represents an unprecedented example of a metallacarborane complex featuring intercluster metal−metal bonds.

Results and Discussion

Synthesis of Dimetallic Iridium Complexes. Reaction of Cp*Ir[$E_2C_2(B_{10}H_{10})$] (E = S, **1a**; Se, **1b**) with 2 equiv of [Ir(cod)(μ-OMe)]$_2$ (**2-Ir**) in a refluxing toluene/methanol mixture yields one major product, **3** (in 39% (**3a**) and 52% (**3b**) yields), and a minor product, **4** (Scheme 1). The NMR spectra and crystal structure determination show that the cluster framework adopted by **3** is generated by incorporation of a *nido* C_2B_9 framework into an Ir_2 metal complex (Figures 1, 2). Selected bond lengths and angles of **3a** and **3b** are listed in Table 1. In **3a** and **3b**, the Cp*Ir and (cod)Ir fragments are bridged by two S or Se atoms that are linked to the open C_2B_3 face. The metal atoms are arranged at one side of the cup-shaped *nido*-carborane just like the handle of a cup. The Ir(1)−Ir(2) distances of 2.7250(9) Å (**3a**) and 2.8087(13) Å (**3b**) fall within the expected range of metal−metal single bonds;[12] consequently each iridium atom has 18 valence electrons and thus accounts for the diamagnetism observed for these complexes. The minor product **4a** was characterized by X-ray structure analysis (Figure 3), and selected bond lengths and angles of **4a** are listed in Table 2. The presences of a Ir−B bond indicates the activation of B−H, which is clearly induced by the metal atom. Complexes **3a** and **3b** can be obtained in higher yields when longer reaction times are applied. Hence it can be assumed that **4a** and **4b** are the precursor intermediates with reactive Ir−B bonds, generated after the iridium-induced B−H activation and then opening the cage with concomitant formation of **3**.

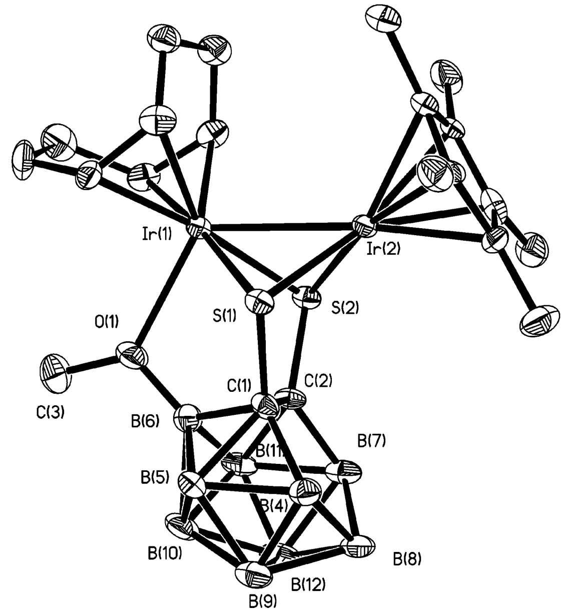


Figure 1. ORTEP drawing of **3a** with 30% probability ellipsoids and H atoms omitted.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 3a and 3b

	3a		
Ir(1)−Ir(2)	2.7250(9)	Ir(1)−S(1)	2.360(2)
Ir(1)−S(2)	2.363(2)	Ir(2)−S(1)	2.305(2)
Ir(2)−S(2)	2.309(2)	S(1)−C(1)	1.798(9)
C(1)−C(2)	1.558(11)	Ir(1)−O(1)	2.364(7)
O(1)−B(6)	1.382(13)	O(1)−C(3)	1.427(11)
Ir(1)−S(1)−Ir(2)	71.48(6)	Ir(1)−S(1)−C(1)	99.0(3)
Ir(2)−S(1)−C(1)	103.7(3)	Ir(1)−O(1)−C(3)	131.5(7)
Ir(1)−O(1)−B(6)	108.5(6)	C(3)−O(1)−B(6)	119.4(8)
	3b		
Ir(1)−Ir(2)	2.8087(13)	Ir(1)−Se(1)	2.4922(19)
Ir(1)−Se(2)	2.4910(17)	Ir(2)−Se(1)	2.4323(19)
Ir(2)−Se(2)	2.431(2)	Se(1)−C(1)	1.947(12)
C(1)−C(2)	1.598(18)	Ir(1)−O(1)	2.423(9)
O(1)−B(6)	1.366(16)	O(1)−C(3)	1.409(17)
Ir(1)−Se(1)−Ir(2)	69.54(4)	Ir(1)−Se(1)−C(1)	96.1(4)
Ir(2)−Se(1)−C(1)	102.0(4)	Ir(1)−O(1)−C(3)	128.1(10)
Ir(1)−O(1)−B(6)	112.7(8)	C(3)−O(1)−B(6)	118.1(13)

Synthesis of Mixed Rhodium−Iridium Complexes. To determine the function of metal-induced B−H activation in the

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(10) (a) Jin, G.-X.; Wang, J.-Q.; Zhang, Z.; Weng, L.; Herberhold, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 259−262. (b) Wang, J.-Q.; Weng, L. H.; Jin, G.-X. *J. Organomet. Chem.* **2005**, *690*, 249−252. (c) Wang, J.-Q.; Weng, L.; Jin, G.-X. *Rev. Inorg. Chem.* **2005**, *25*, 55−66. (d) Wang, J.-Q.; Hou, X.; Weng, L.; Jin, G.-X. *Organometallics* **2005**, *24*, 826−830. (e) Cai, S.; Wang, J.-Q.; Jin, G.-X. *Organometallics* **2005**, *24*, 4226−4231. (f) Wang, J.-Q.; Cai, S.; Weng, L.; Herberhold, M.; Jin, G.-X. *Chem. Eur. J.* **2005**, *24*, 7342−7350. (g) Cai, S.; Jin, G.-X. *Organometallics* **2005**, *24*, 5280−5286. (h) Liu, S.; Wang, X.; Jin, G.-X. *J. Organomet. Chem.* **2006**, *691*, 261−265. (i) Jin, G.-X.; Wang, J.-Q. *Dalton Trans.* **2006**, *1*, 86−90.

(11) (a) Nihei, M.; Nankawa, T.; Kurihara, M.; Nishihara, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1098−1100. (b) Mizutani, J.; Nihei, M.; Araki, S.; Yamada, T.; Nankawa, T.; Kurihara, M.; Kubo, K.; Nishihara, H. In *International Symposium on New Horizons of Coordination Chemistry towards the 21st Century*; Japan, 2000; p 111. (c) 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. (d) Nakagawa, N.; Yamada, T.; Murata, M.; Sugimoto, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 14−16. (e) Murata, M.; Habe, S.; Araki, S.; Namiki, K.; Yamada, T.; Nakagawa, N.; Nankawa, T.; Nihei, M. Mizutani, J.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 1108−1116.

(12) (a) Pinillos, M. T.; Elduque, A.; Oro, L. A.; Lahoz, F. J.; Bonati, F.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1990**, 989−994. (b) Nagao, S.; Seino, H.; Hidai, M.; Mizobe, Y. *J. Organomet. Chem.* **2003**, *669*, 124−134. (c) Casado, M. A.; Pérez-Torrente, J. J.; Ciriano, M. A.; Dobrinovitch, I. T.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **2003**, *42*, 3956−3964.

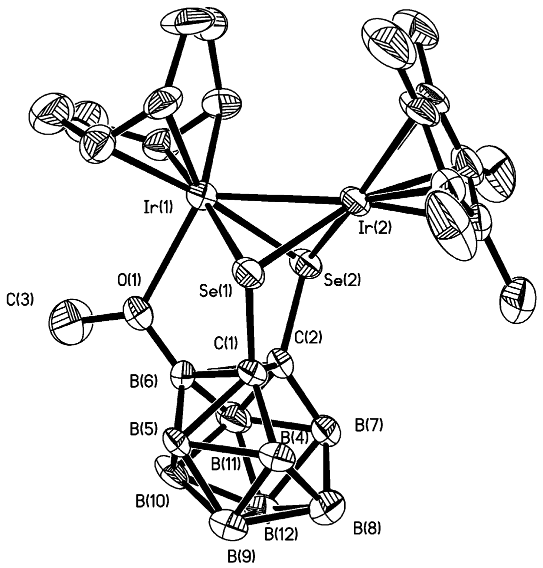

Figure 2. ORTEP drawing of **3b** with 30% probability ellipsoids and H atoms omitted.

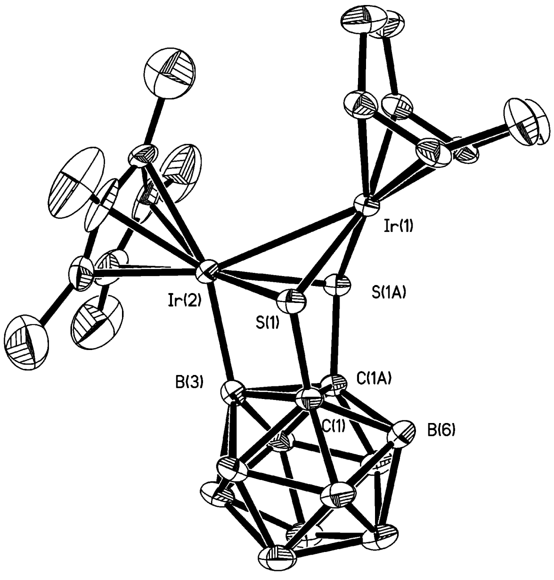

Figure 3. ORTEP drawing of **4a** with 30% probability ellipsoids and H atoms omitted.

Table 2. Selected Bond Lengths (Å) and Angels (deg) for 4a

Ir(1)−Ir(2)	2.9921(9)	Ir(1)−S(1)	2.3044(15)
Ir(2)−S(1)	2.4472(15)	Ir(2)−B(3)	2.103(11)
Se(1)−C(1)	1.808(6)	C(1)−C(1A)	1.649(11)
Ir(1)−Ir(2)−B(3)	100.4(2)	Ir(1)−Ir(2)−S(1)	48.88(3)
Ir(1)−S(1)−Ir(2)	77.99(5)	Ir(1)−S(1)−C(1)	107.63(18)
Ir(2)−B(3)−C(1)	98.4(5)	Ir(2)−S(1)−C(1)	85.41(18)

formation of *nido*-carboranes, similar reactions with rhodium complexes were investigated (Scheme 2). In the reaction of $Cp^*Ir[S_2C_2(B_{10}H_{10})]$ (**1a**) with 2 equiv of $[Rh(cod)(\mu\text{-}OCH_3)]_2$ (**2-Rh**), an analogous product, the dimetallic IrRh-*nido*-carborane **5a** was also obtained (Figure 4). More interesting is the isolation of **6a** and **7a**, two products that would be expected to arise from different B−H activation processes at the B(3)/B(6) sites of the carborane cage (Figure 5). Selected bond lengths and angles of **5a** and **6a** are listed in Table 3. The Ir−Rh distance in **6a** (2.7829(10) Å) should therefore be comparable with the Ir−Rh distance in the *nido* complex **5a** (2.7526(8) Å). In **6a**, the *o*-carborane group is close to the rhodium center (Rh(1)···B(3) 2.970 Å). An interesting phenomenon is that the B(3) atom appears to have the tendency to leave the cage. This tendency can also be deduced from the lengthening of the C(1)−B(3) and C(2)−B(3) bonds (1.78(4) and 1.84(4) Å, respectively), in contrast to 1.72 Å under normal conditions.[1a,13] It may be noted that the cyclometalation occurs at the iridium, not at the rhodium site. If the iridium atom approaches the B−H site, the result is the formation of **7a**, whereas the approach of the rhodium atom to the B−H site leads to **6a**. Complex **7a** is an analogous product of complexes **4a** and **4b**. (The molecular structure of **7a** was described previously in ref 10f.) All these differences can be ascribed to the formally different valence state of iridium and rhodium atoms before the reaction.

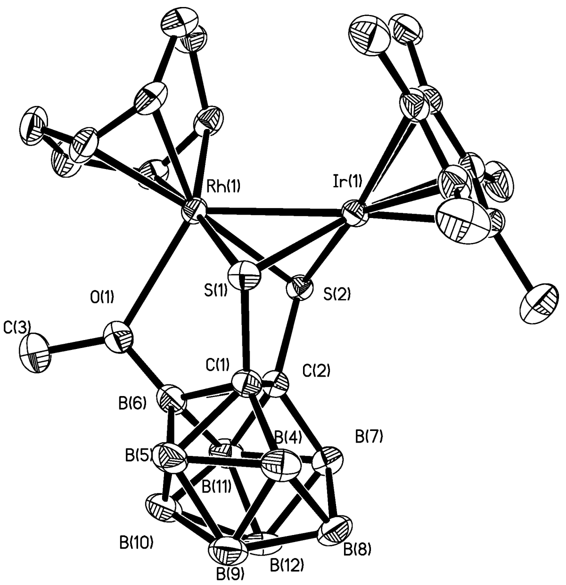

Figure 4. ORTEP drawing of **5a** with 30% probability ellipsoids and H atoms omitted.

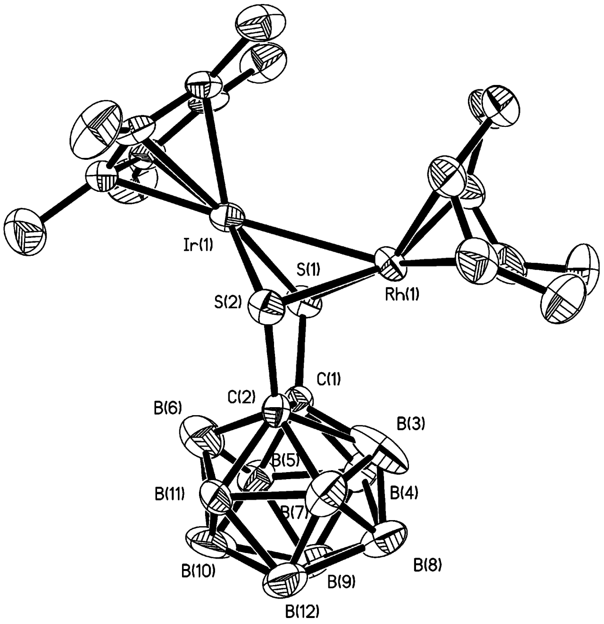

Figure 5. ORTEP drawing of **6a** with 30% probability ellipsoids and H atoms omitted.

Synthesis of Trimetallic Iridium Complexes. The 14-electron fragments Cp*Ir and (cod)IrCl are isolobal. Heating either **1a** or **1b** with 4 equiv of $[Ir(cod)(\mu\text{-}Cl)]_2$ generates *nido*-

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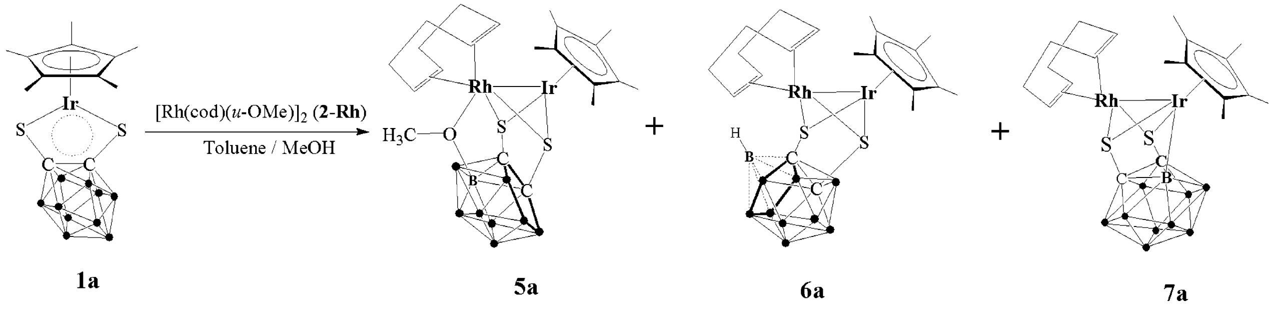
[13] Oliva, J. M.; Allan, N. L.; Schleyer, P. V. R.; Vinas, C.; Teixidor, F. *J. Am. Chem. Soc.* **2005**, *127*, 13538−13547.

Scheme 2. Reaction of 1a with 2-Rh



Scheme 3. Reaction of 1a with $[Ir(cod)(\mu\text{-}Cl)]_2$

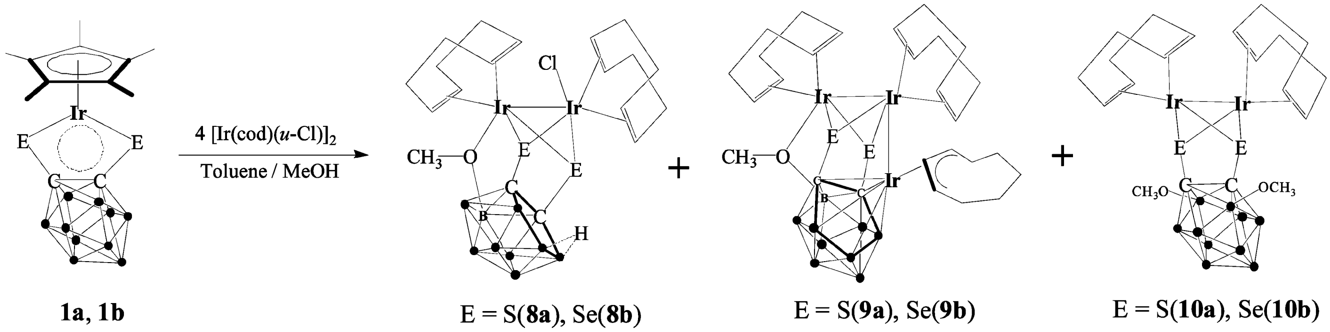


Table 3. Selected Bond Lengths (Å) and Angels (deg) for 5a and 6a

	5a		
Rh(1)−Ir(1)	2.7526(8)	Rh(1)−S(1)	2.3742(16)
Rh(1)−S(2)	2.3561(16)	Ir(1)−S(1)	2.3019(16)
Ir(1)−S(2)	2.3087(15)	S(1)−C(1)	1.810(6)
C(1)−C(2)	1.561(8)	Rh(1)−O(1)	2.459(4)
O(1)−B(6)	1.401(9)	O(1)−C(3)	1.407(8)
Rh(1)−S(1)−Ir(1)	72.10(5)	Rh(1)−S(1)−C(1)	98.3(2)
Ir(1)−S(1)−C(1)	103.2(2)	Rh(1)−O(1)−C(3)	131.8(5)
Rh(1)−O(1)−B(6)	104.9(4)	C(3)−O(1)−B(6)	120.2(6)
C(1)−B(6)−C(2)	53.0(3)		
	6a		
Ir(1)−Rh(1)	2.7829(10)	Ir(1)−S(1)	2.297(3)
Ir(1)−S(2)	2.277(2)	Rh(1)−S(1)	2.384(2)
Rh(1)−S(2)	2.374(3)	C(1)−C(2)	1.522(12)
C(1)−B(3)	1.78(4)	C(2)−B(3)	1.84(4)
B(3)−B(4)	1.53(4)	B(3)−B(7)	1.68(3)
B(3)−B(8)	1.42(4)	B(5)−B(6)	1.70(2)
B(6)−B(10)	1.72(2)	B(6)−B(11)	1.74(2)
S(1)−Ir(1)−S(2)	83.51(9)	S(1)−Rh(1)−S(2)	79.62(8)
Ir(1)−S(1)−Rh(1)	72.92(7)	Ir(1)−S(1)−C(1)	106.2(3)
Rh(1)−S(1)−C(1)	87.5(3)	C(1)−B(3)−C(2)	49.7(13)
C(1)−B(6)−C(2)	53.0(6)		

$[(cod)Ir(cod)IrCl][E_2C_2B_9H_9]$ (**8a**, **8b**) as the major product, as well as **9a**, **9b** and **10a**, **10b**, respectively, as minor products (Scheme 3). In refluxing toluene/methanol solution, the dimetallic clusters **8a** and **8b** are converted in more than 60% yield to the trimetallic complexes **9a**, **9b** when additional **2-Ir** is applied. An X-ray diffraction study of **8a** provided additional interesting features for this kind of *nido*-carborane complex (Figure 6). Both iridium centers are in a distorted octahedral environment. The difference between the two iridium atoms is that the Ir(1) center bears a bridging O−CH$_3$ ligand, whereas the Ir(2) center carries a terminal chloride ligand, in addition to the olefinic bonds of the cycloocta-1,5-diene ligands and the bridging sulfur atoms. More exciting is the isolation of **9a** and **9b**, the products with three metal atoms in a cluster, as confirmed by X-ray diffraction for **9b** (Figure 7). Selected bond length and angle of **8a** and **9b** are listed in Table 4. The Ir(3) atom is coordinated to the C$_2$B$_3$ pentagonal open face and to the three allylic carbon atoms of a cyclooctenyl ligand. In contrast to Ir(1)−Ir(2) (2.9473(10) Å), the Ir(2)−Ir(3) distance (3.0866 Å) is lengthened in **9b**. Interestingly, the C(1)−C(2) distance (1.81 Å) is longer than a normal bond between the two carbon atoms of carborane,[13] but shorter than those in the pesudocloso metallcarborane structure.[14] The lengthening of the C(1)−C(2) distance in **9b** produced a tetragonal open face Ir(3)−C(1)−C(2)−B(6), which is almost planar, with a dihedral angle along C(1)−C(2) of 163.7°. Complexes **10** are byproducts of the reaction, and **10b** has been characterized by X-ray diffraction methods (Figure 8). Selected bond lengths and angles of **10b** are listed in Table 5. Both the B(3)/B(6) sites of the carborane ligand are substituted with two methoxy groups.

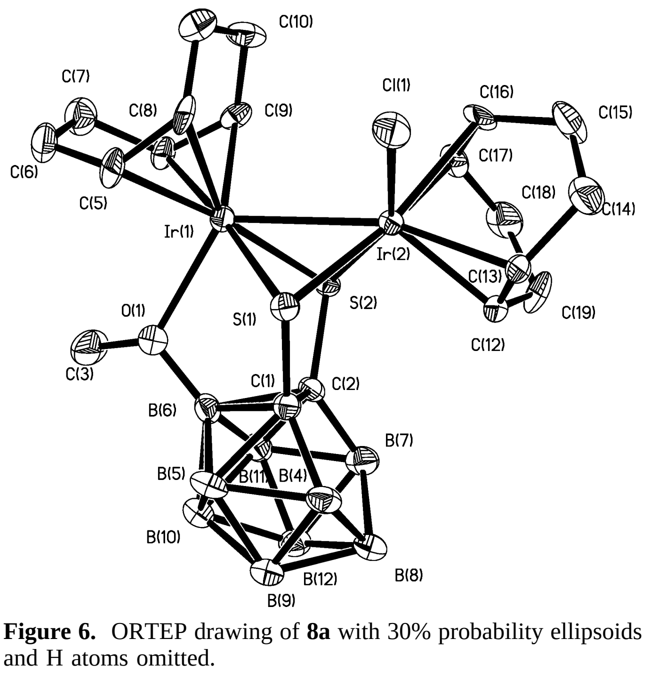


Figure 6. ORTEP drawing of **8a** with 30% probability ellipsoids and H atoms omitted.

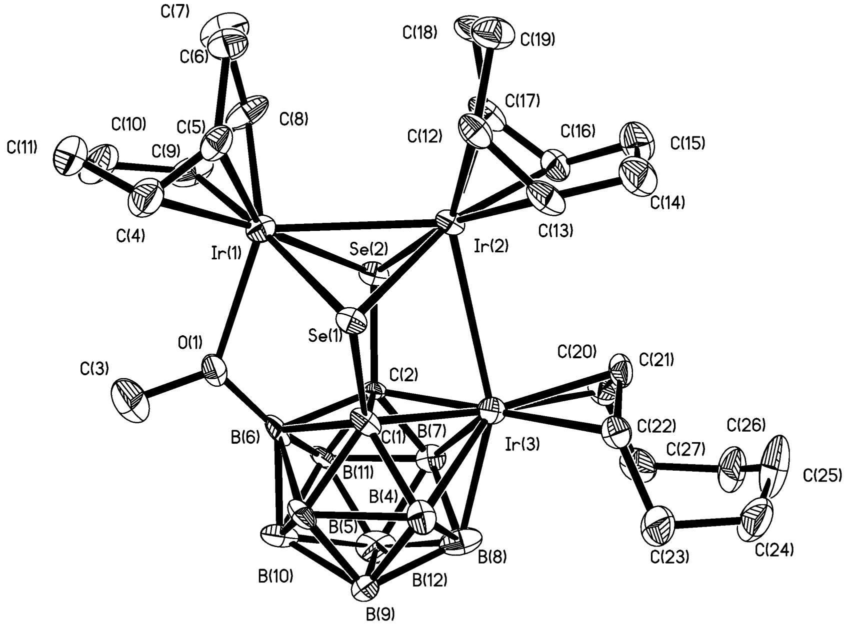


Figure 7. ORTEP drawing of **9b** with 30% probability ellipsoids and H atoms omitted.

Table 4. Selected Bond Lengths (Å) and Angels (deg) for 8a and 9b

	8a		
Ir(1)−Ir(2)	2.7379(8)	Ir(1)−S(1)	2.370(2)
Ir(1)−S(2)	2.357(2)	Ir(2)−S(1)	2.335(2)
Ir(2)−S(2)	2.318(2)	Ir(2)−Cl(1)	2.403(2)
S(1)−C(1)	1.806(8)	C(1)−C(2)	1.570(11)
Ir(1)−O(1)	2.323(6)	O(1)−B(6)	1.423(12)
O(1)−C(3)	1.433(11)	Ir(1)−S(1)−Ir(2)	71.17(6)
Ir(1)−S(1)−C(1)	99.5(3)	Ir(1)−Ir(2)−Cl(1)	97.80(7)
Ir(2)−S(1)−C(1)	104.7(3)	S(1)−Ir(2)−Cl(1)	84.06(8)
Ir(1)−O(1)−C(3)	127.6(5)	Ir(1)−O(1)−B(6)	109.4(5)
C(3)−O(1)−B(6)	116.2(7)	C(1)−B(6)−C(2)	53.4(5)
	9b		
Ir(1)−Ir(2)	2.9473(10)	Ir(2)−Ir(3)	3.0866(10)
Ir(1)−Se(1)	2.5274(17)	Ir(1)−Se(2)	2.5255(16)
Ir(2)−Se(1)	2.4433(15)	Ir(2)−Se(2)	2.4595(16)
Ir(1)−O(1)	2.413(9)	O(1)−C(3)	1.400(18)
O(1)−B(6)	1.389(19)	Ir(1)−C(4)	2.118(16)
Ir(1)−C(5)	2.115(14)	Ir(2)−C(12)	2.141(14)
Ir(2)−C(13)	2.173(16)	Ir(3)−C(20)	2.224(14)
Ir(3)−C(21)	2.120(14)	Ir(3)−C(22)	2.241(15)
Ir(3)−C(1)	2.116(13)	Ir(3)−C(2)	2.142(14)
Ir(3)−B(4)	2.225(17)	Ir(3)−B(7)	2.250(17)
Ir(3)−B(8)	2.240(17)	C(1)−C(2)	1.819(18)
C(20)−C(21)	1.43(2)	C(21)−C(22)	1.419(19)
C(22)−C(23)	1.55(2)	C(23)−C(24)	1.53(2)
Ir(1)−Ir(2)−Ir(3)	99.62(3)	Se(1)−Ir(1)−Se(2)	82.34(5)
Se(1)−Ir(2)−Se(2)	85.44(5)	Ir(1)−O(1)−C(3)	126.6(10)
Ir(1)−O(1)−B(6)	115.1(8)	C(1)−B(6)−C(2)	61.5(8)
C(1)−Ir(3)−C(2)	50.6(5)		

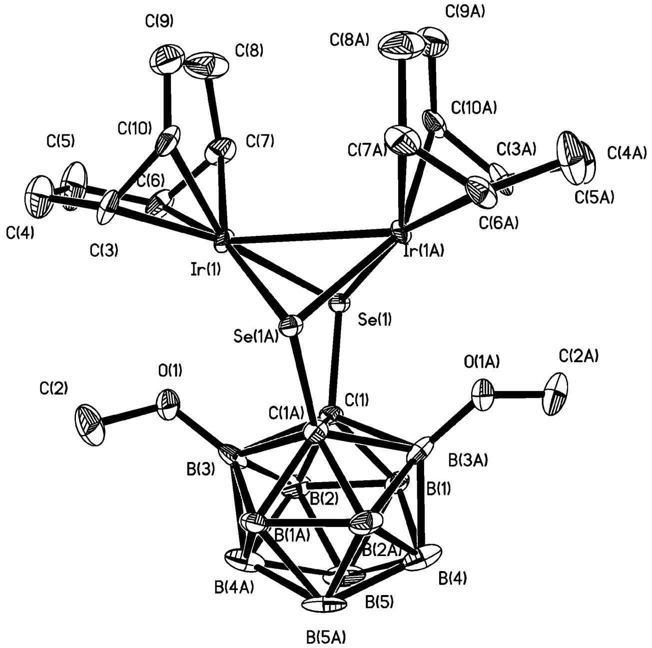


Figure 8. ORTEP drawing of **10b** with 30% probability ellipsoids and H atoms omitted.

Table 5. Selected Bond Lengths (Å) and Angels (deg) for 10b

Ir(1)−C(6)	2.113(13)	Ir(1)−C(7)	2.089(14)
Ir(1)−Ir(1A)	2.8939(15)	Ir(1)−Se(1)	2.5060(16)
S(1)−C(1)	1.950(12)	C(1)−C(1A)	1.65(3)
C(1)−B(1)	1.70(2)	C(1)−B(3)	1.78(2)
O(1)−B(3)	1.37(2)	O(1)−C(2)	1.38(2)
Ir(1)−Se(1)−Ir(1A)	70.16(5)	Ir(1)−Se(1)−C(1)	98.7(4)
Se(1)−Ir(1)−Se(1A)	81.77(6)	B(3)−O(1)−C(2)	118.5(14)

Conclusion

We have synthesized the cup-shaped *nido*-carborane complexes **3**, **5**, and **8**, which appear to provide useful structural information for further studies on the preparation of other *nido*-carborane and polymetallic species. Complexes of type **9** represent a novel class of cluster compounds in which a V-shaped trimetallic unit has been constructed through a new type of M_2-*nido*-carborane complex. Although some kinds of carborane-supported metallic clusters have been reported,[3,15] the development of a rational approach for the synthesis of bi- and trimetallic carborane clusters is still an important step forward in the synthesis of this class of compounds.

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(14) (a) Chizhevsky, I. T.; Lobanova, I. A.; Petrovskii, P. V.; Bregadze, V. I.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Y. T.; Chistyakov, A. L.; Stankevich, I. V.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1999**, *18*, 726−735. (b) Safronov, A. V.; Zinevich, T. V.; Dolgushin, F. M.; Tok, O. L.; Vornontsov, E. V.; Chizhevsky, I. T. *Organometallics* **2004**, *23*, 4970−4979.

(15) (a) Jelliss, P. A.; Stone, F. G. A. *J. Organomet. Chem.* **1995**, *500*, 307−323, and references therein. (b) Du, S.; Kautz, J. A.; McGrath, T. D.; Stone, F. G. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 5728−5730.

Table 6. Crystallographic Data and Structural Refinement Details of 3a, 3b, 4a, and 5a

	3a	**3b**	**4a**	**5a**
empirical formula	$C_{21}H_{39}B_9OS_2Ir_2$	$C_{33}H_{51}B_9OSe_2Ir_2$	$C_{20}H_{36}B_{10}S_2Ir_2$	$C_{21}H_{39}B_9OS_2IrRh$
fw	853.33	1103.35	833.11	764.04
cryst syst	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	*Pnma*	$P2_1/c$
a (Å)	10.992(5)	12.388(8)	17.969(5)	12.803(3)
b (Å)	11.339(5)	17.128(10)	12.700(4)	12.046(3)
c (Å)	13.260(6)	19.889(12)	12.078(3)	18.726(5)
α (deg)	107.244(4)			
β (deg)	96.233(5)	91.302(10)		96.323(4)
γ (deg)	115.175(5)			
V (Å^3)	1374.9(10)	4219(4)	2756.3(13)	2870.3(12)
Z	2	4	4	4
ρ_{calcd} (g/cm^3)	2.061	1.737	2.008	1.768
μ(Mo Kα) (mm^{-1})	9.837	8.051	9.808	5.367
no. of reflns obsd	5789	19 099	11 185	12 977
no. of params	334	382	175	334
goodness of fit	1.000	0.961	1.079	1.022
R_1 ($I > 2\sigma(I)$)	0.0396	0.0555	0.0241	0.0375
wR_2 (all data)	0.1051	0.1555	0.0675	0.0850
largest peak in diff map (e Å^{-3})	2.236/−3.184	1.401/−0.719	0.905/−0.892	1.859/−0.531

Table 7. Crystallographic Data and Structural Refinement Details of 6a, 8a, 9b, and 10b

	6a	**8a**	**9b**	**10b**
empirical formula	$C_{20}H_{36.50}B_{9.50}S_2IrRh$	$C_{20}H_{38}B_9Cl_3OS_2Ir_2$	$C_{27}H_{48}B_9OSe_2Ir_3$	$C_{20}H_{38}B_{10}O_2Se_2Ir_2$
fw	738.92	946.66	1220.46	960.92
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/n$	*P*bca	$P\bar{1}$	$P2/c$
a (Å)	10.542(3)	21.235(6)	11.587(3)	18.289(8)
b (Å)	14.967(4)	11.528(3)	12.647(3)	12.197(5)
c (Å)	17.522(5)	24.514(7)	12.776(3)	12.852(6)
α (deg)			86.511(4)	
β (deg)	93.321(5)		74.525(4)	107.713(6)
γ (deg)			68.482(4)	
V (Å^3)	2759.9(13)	6001(3)	1677.1(8)	2731(2)
Z	4	8	2	4
ρ_{calcd} (g/cm^3)	1.778	2.096	2.417	2.337
μ(Mo Kα) (mm^{-1})	5.576	9.285	14.066	12.421
no.of reflns obsd	11 420	24 000	7767	13 332
no. of params	317	342	387	334
goodness of fit	1.010	1.012	1.074	1.127
R_1 ($I > 2\sigma(I)$)	0.0473	0.0369	0.0609	0.0512
wR_2 (all data)	0.1024	0.0838	0.1109	0.1349
largest peak in diff map (e Å^{-3})	1.860/−0.677	1.146/−1.094	1.394/−1.758	3.337/−2.242

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques; all solvents were dried and deoxygenated before use. The starting materials Cp*Ir[$S_2C_2(B_{10}H_{10})$] (**1a**),[9] Cp*Ir[$Se_2C_2(B_{10}H_{10})$] (**1b**),[9] [Ir(cod)(μ-OCH_3)]$_2$ (**2-Ir**),[16] [Ir(cod)(μ-Cl)]$_2$ (**2**),[16] and [Rh(cod)(μ-OCH_3)]$_2$ (**2-Rh**)[16] were prepared according to literature methods. The ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS) and ^{11}B NMR spectra (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$) were obtained on a Bruker DMX500 spectrometer.

Synthesis of 3a and 4a. 2-Ir (66 mg, 0.1 mmol) was added to the green solution of **1a** (106 mg, 0.2 mmol) in toluene (15 mL) and methanol (15 mL). The mixture was refluxed for 12 h. Removal of the solvent and column chromatography (silica gel) gave **4a** (CH_2Cl_2/hexane (1:3)) and **3a** (CH_2Cl_2/THF (50:1)). **3a**: yield 39% (67 mg). Anal. Calcd for $C_{21}H_{39}B_9OS_2Ir_2$: C 29.56, H 4.61. Found: C 29.18, H 4.42. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.90 (s, 15H, C_5Me_5), 2.22 (m, 4H, CH_2), 2.51 (m, 4H, CH_2), 3.63 (s, 3H, OCH_3), 4.11 (br, 2H, $CH{=}$), 5.08 (m, 2H, $CH{=}$). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ 9.7, −11.7, −15.2, −17.3, −18.5, −20.6, −32.1, −38.5, −40.0 (in the ratio 1:1:1:1:1:1:1:1:1). IR (KBr disk): 2562, 2589 cm^{-1} (ν_{B-H}). **4a**: yield 15% (25 mg). Anal. Calcd for $C_{20}H_{36}B_{10}S_2Ir_2$: C 28.83, H 4.36. Found: C 28.61, H 4.35. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.91 (s, 15H, C_5Me_5), 2.23 (br, 8H, CH_2), 4.01 (m, 4H, $CH{=}$). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ −3.6, −6.2, −9.7, −10.6, −17.2, −21.3 (overlap). IR (KBr, disk): 2569 cm^{-1} (ν_{B-H}).

Synthesis of 3b and 4b. 2-Ir (66 mg, 0.1 mmol) was added to the green solution of **1b** (125 mg, 0.2 mmol) in toluene (15 mL) and methanol (15 mL). The mixture was refluxed for 12 h. Removal of the solvent and chromatographic separation on silica gel gave **4b** (CH_2Cl_2/hexane (1:3)) and **3b** (CH_2Cl_2/THF (50:1)). **3b**: yield 52% (98 mg). Anal. Calcd for $C_{21}H_{39}B_9OSe_2Ir_2$: C 26.63, H 4.15. Found: C 26.58, H 4.13. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.91 (s, 15H, C_5Me_5), 2.10 (m, 4H, CH_2), 2.57 (m, 4H, CH_2), 3.50 (s, 3H, OCH_3), 4.29 (m, 2H, $CH{=}$), 5.21 (m, 2H, $CH{=}$). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ 7.0, −9.9, −13.8, −18.5, −20.2, −22.3, −33.2, −37.5, −39.1 (in the ratio 1:1:1:1:1:1:1:1:1). IR (KBr disk): 2571, 2582 cm^{-1}(ν_{B-H}). **4b**: yield 10% (19 mg). Anal. Calcd for $C_{20}H_{36}B_{10}Se_2Ir_2$: C 25.91, H 3.91. Found: C 25.71, H 3.85. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.88 (s, 15H, C_5Me_5), 2.40 (m, 8H, CH_2), 4.11 (m, 4H, $CH{=}$). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ −2.9, −5.7, −9.1, −13.2, −15.28, −20.6 (1:2:2:2:2:1). IR (KBr disk): 2577 cm^{-1} (ν_{B-H}).

Synthesis of 5a−7a. 2-Rh (96 mg, 0.2 mmol) and **1a** (212 mg, 0.4 mmol) in toluene (15 mL) and methanol (15 mL) were refluxed

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(16) (a) Pannetier, G.; Fougeroux, P.; Bonnaire, R.; Platzer, N. *J. Less-Common Met.* **1971**, *24*, 83−92. (b) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126−130. (c) Green, L. M.; Meek, D. W. *Organometallics* **1989**, *8*, 659−666.

for 8 h. After removal of the solvent and column chromatography (silica gel) the products **7a** (CH_2Cl_2/hexane (1:3)), **6a** (CH_2Cl_2), and **5a** (CH_2Cl_2/THF (20:1)) were isolated. **5a**: yield 41% (70 mg). Anal. Calcd for $C_{21}H_{39}B_9OS_2Ir_2$: C 29.56, H 4.61. Found: C 29.23, H 4.51. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.88 (s, 15H, C_5Me_5), 1.97 (m, 4H, CH_2), 2.51 (m, 4H, CH_2), 3.32 (s, 3H, OCH_3), 4.12 (br, 2H, $CH{=}$), 5.38 (br, 2H, $CH{=}$). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ 5.2, −8.1, −13.8, −15.7, −18.9, −25.1, −31.6, −35.5, −37.2 (in the ratio 1:1:1:1:1:1:1:1:1). IR (KBr disk): 2561, 2579, 2588 cm^{-1}(ν_{B-H}). **6a**: yield 10% (15 mg). Anal. Calcd for $C_{20}H_{36.50}B_{9.50}S_2IrRh$: C 32.51, H 4.98. Found: C 32.62, H 5.01. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.86 (s, 15H, C_5Me_5), 2.21 (m, 4H, CH_2), 3.09 (m, 4H, CH_2), 4.26 (m, 2H, $CH{=}$), 4.72 (m, 2H, $CH{=}$). IR (KBr disk): 2571, 2583 cm^{-1}(ν_{B-H}). **7a**: yield 32% (55 mg). Anal. Calcd for $C_{20}H_{36}B_{10}S_2IrRh$: C 32.29, H 4.88. Found: C 32.22, H 4.86. Spectroscopic data as reported previously.[10f]

Synthesis of 8a−10a. $[Ir(cod)(\mu\text{-}Cl)]_2$ (132 mg, 0.2 mmol) and **1a** (106 mg, 0.2 mmol) in toluene (15 mL) and methanol (15 mL) were refluxed for 12 h. After removal of the solvent, column chromatography on silica gel gave sequentially **10a** (CH_2Cl_2/hexane (1:5)), **8a** (CH_2Cl_2), and **9a** (CH_2Cl_2/THF (20:1)). **8a**: yield 32% (55 mg). Anal. Calcd for $C_{19}H_{36}B_9ClOS_2Ir_2$: C 26.48, H 4.21. Found: C 26.22, H 4.03. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.77 (m, 8H, CH_2), 2.23 (m, 8H, CH_2), 3.52 (s, 3H, OCH_3), 4.01 (m, 4H, $CH{=}$), 4.52 (m, 4H, $CH{=}$). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ 9.2, −4.9, −12.1, −15.1, −18.2, −25.3, −27.2, −28.8, −36.7 (in the ratio 1:1:1:1:1:1:1:1:1). IR (KBr disk): 2569 cm^{-1} (ν_{B-H}). **9a**: yield 10% (23 mg). Anal. Calcd for $C_{27}H_{48}B_9OS_2Ir_3$: C 28.78, H 4.29. Found: C 28.42, H 4.13. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.97(m, 8H, CH_2), 3.96 (m, 4H, $CH{=}$), 2.17 (m, 8H, CH_2), 4.37 (br, 4H, $CH{=}$), 1.67 (m, 2H, CH_2), 1.81 (br, 4H, CH_2), 2.52 (m, 2H, CH_2), 4.81 (m, 2H, CH_2), 5.43−5.09 (m, 3H, CH), 3.36 (s, 3H, OCH_3). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ 5.6, −5.5, −10.1, −16.2, −22.8 (1: 2: 1: 3: 2). IR (KBr disk): 2568, 2578 cm^{-1} (ν_{B-H}). **10a**: yield 15% (26 mg). Anal. Calcd for $C_{20}H_{38}B_{10}O_2S_2Ir_2$: C 27.70, H 4.42. Found: C 27.32, H 4.23. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.66 (m, 8H, CH_2), 3.73 (s, 6H, OCH_3), 4.07 (m, 16H, CH_2). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ 3.2, −1.3, −13.8, −15.5 (2:3:3:2). IR (KBr disk): 2572 cm^{-1} (ν_{B-H}).

Synthesis of 8b−10b. $[Ir(cod)(\mu\text{-}Cl)]_2$ (132 mg, 0.2 mmol) and **1b** (125 mg, 0.2 mmol) in toluene (15 mL) and methanol (15 mL) were refluxed for 12 h. After removal of the solvent and chromatography (silica gel) the products **10b** (CH_2Cl_2/hexane (1:5)), **8b** (CH_2Cl_2), and **9b** (CH_2Cl_2/THF (20:1)) were obtained. **8b**: yield 39% (75 mg). Anal. Calcd for $C_{19}H_{36}B_9ClOSe_2Ir_2$: C 23.88, H 3.80. Found: C 23.82, H 3.80. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.81(m, 8H, CH_2), 2.21 (m, 8H, CH_2), 3.39 (s, 3H, OCH_3), 4.13 (m, 4H, $CH{=}$), 4.52 (m, 4H, $CH{=}$). ^{11}B NMR (160 MHz; $CDCl_3$, 25 °C): δ 7.2, −4.3, −11.6, −15.9, −18.2, −23.9, −26.6, −35.9 (1:1:1:1:1:1:2:1). IR (KBr disk): 2580 cm^{-1} (ν_{B-H}). **9b**: yield 12% (29 mg). Anal. Calcd for $C_{27}H_{48}B_9OSe_2Ir_3$: C 26.57, H 3.96. Found: C 26.42, H 4.01. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.95 (m, 8H, CH_2), 4.01 (m, 4H, $CH{=}$), 2.22 (m, 8H, CH_2), 4.51 (m, 4H, $CH{=}$), 1.58 (m, 2H, CH_2), 1.83 (m, 4H, CH_2), 2.56 (m, 2H, CH_2), 4.73 (m, 2H, CH_2), 5.38−5.11 (m, 3H, CH), 3.42 (s, 3H, OCH_3). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ 3.9, −4.6, −9.8, −15.9, −20.3 (1:2:1:3:2). IR (KBr disk): 2566, 2578, 2589 cm^{-1} (ν_{B-H}). **10b**: yield 7% (26 mg). Anal. Calcd for $C_{20}H_{38}B_{10}O_2Se_2Ir_2$: C 25.00, H 3.99. Found: C 24.72, H 3.83. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 1.86 (m, 8H, CH_2), 3.77 (s, 6H, OCH_3), 4.21 (m, 16H, CH_2). ^{11}B NMR (160 MHz, $CDCl_3$, 25 °C, $BF_3{\cdot}OEt_2$): δ 2.6, −3.3, −15.1, −17.2 (2:3:3:2). IR (KBr disk): 2570 cm^{-1} (ν_{B-H}).

X-ray Structure Determination. Suitable crystals of **3a**, **3b**, **4a**, **5a**, **6a**, **8a**, **9b**, and **10b** were grown by slow diffusion from dichloromethane/hexane or toluene/hexane solution. The crystals of all compounds were mounted by gluing them 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 the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were included but not refined. All the calculations were carried out the SHELXTL program. Crystal data, data collection parameters, and the results of the analyses of complexes **3a**, **3b**, **4a**, **5a**, **6a**, **8a**, **9b**, and **10b** are listed in Table 6 and Table 7.

Acknowledgment. Financial support by the National Science Foundation of China for Distinguished Young Scholars (29925101, 20274008) and by the Doctoral Fund of the Education Ministry of China (No. 20020246011) is gratefully acknowledged.

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OM060381A