DOI: 10.1002/ejic.201100159

Reactivity of a 16-Electron CpCo Half-Sandwich Complex Containing a Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-diselenolate Ligand towards FcC(O)C≡CH

Hongde Ye,[a,b] Wenjun Bai,[a] Mingshi Xie,[a] Yizhi Li,[a] and Hong Yan*[a]

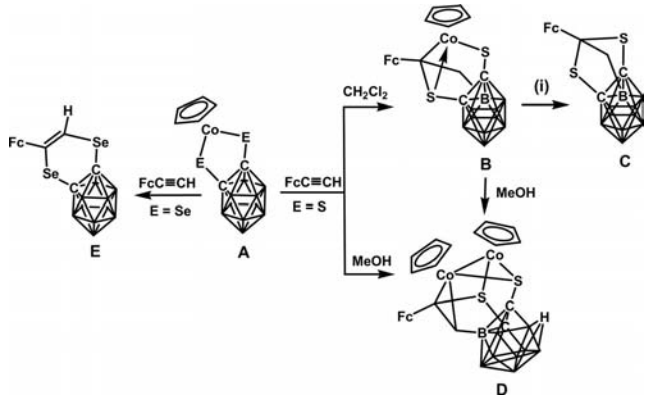
Keywords: Transition metals / Half-sandwich complexes / Cobalt / Chalcogens / Alkynes / Carboranes / B–H activation

The 16-electron half-sandwich complex $CpCo(Se_2C_2B_{10}H_{10})$ (**1**, Cp = cyclopentadienyl) reacts with FcC(O)C≡CH in CH_2Cl_2 at ambient temperature to give [{FcC(O)CCH}-$(Se_2C_2B_{10}H_{10})$] (**3**) and [$CpCo(Se_2C_2B_{10}H_9)${$CH_2CC(O)Fc$}] (**4**). Complex **3** is generated by the alkyne addition to the 1,2-dicarba-*closo*-dodecaborane-1,2-diselenolate ligand in **1** with the loss of the CpCo unit. In **4**, metal-induced B–H activation occurs in the B(3)/B(6) position of carborane followed by the formation of a C–B bond. In MeOH the reaction leads to an unexpected product, [{FcC(O)CHCH}CpCo-$(Se_2C_2B_9H_9)${$CH_2CC(O)Fc$}] (**5**), which contains two alkynes and a *nido*-C_2B_9 cage. In MeOH, **4** can further react with the alkyne to give **5**. In the presence of silica, **4** loses the CpCo unit to afford [{$FcC(O)CCH_2$}$(Se_2C_2B_{10}H_9)$] (**6**), which is a symmetrical molecule with the B–CH_2 unit retained. All of these complexes have been characterized by IR, NMR, elemental analysis, mass spectrum, and single-crystal X-ray diffraction analysis.

Introduction

Recently, a class of mononuclear 16-electron half-sandwich complexes of Ru, Os, Co, Rh, and Ir containing a chelating 1,2-dicarba-*closo*-dodecaborane-12-dichalcogenolate ligand have been prepared and studied extensively.[1–8] These sterically congested, coordinatively unsaturated compounds can be stored conveniently and used for the completion of various chemical transformations. For example, they are capable of combining metal fragments to afford new types of homometallic or heterometallic clusters containing one or more 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligands[1] and they can react with Lewis bases to generate their 18-electron congeners.[2–4] Furthermore, the combination of the electron deficiency at the metal center and the reactive metal–chalcogen bonds renders these 16-electron species interesting candidates for reactions with alkynes.[5–8]

Our previous studies on the reactivity of these 16-electron starting materials have shown that the metal center, the chalcogen, the substrate, and the ancillary ligand together with the reaction temperature, the solvent, and the ratio of the reactants play key roles in the types and structures of the products.[6–8] For instance, the reaction of $CpCo(S_2C_2B_{10}H_{10})$ with PhC≡CH leads to two 18-electron products: the alkyne double-inserted product at the Co–S bond and the product with the alkyne reduced to an alkane.[6a] Whereas, $CpCo(S_2C_2B_{10}H_{10})$ reacts with the activated alkyne PhC(O)C≡CH to give a new 17-electron product containing a bicyclo[2.2.1]heptene unit at the B(3)/B(6) site of carborane and a 16-electron half-sandwich complex containing a B-monosubstituted *o*-carborane-1,2-dithiolate ligand.[8] In the case of FcC≡CH, the reaction with $CpCo(S_2C_2B_{10}H_{10})$ in CH_2Cl_2 affords **B**, which can be converted to **C** and **D** as shown in Scheme 1. However, the selenium analogue, $CpCo(Se_2C_2B_{10}H_{10})$ (**1**), does not react with this alkyne under the same conditions, but in MeOH the alkyne addition product **E** was isolated (Scheme 1). Owing to the insolubility and low reactivity of **1**, its reaction chemistry has been scarcely described.[6b] Herein we report on its reaction with the less studied alkyne FcC(O)C≡CH.



Scheme 1. Previous results.[6b] (i) silica or toluene at 110 °C or MeOH at room temp.

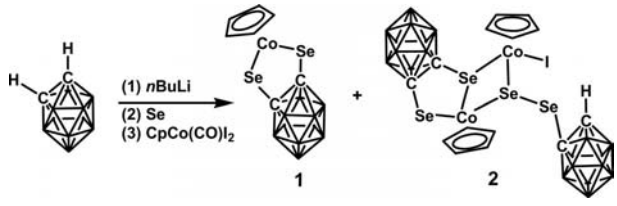
[a] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Jiangsu 210093, China
Fax: +86-25-83314502
E-mail: hyan1965@nju.edu.cn
[b] Department of Chemistry, Shangrao Normal University, Jiangxi 334001, China

Moreover, in the course of the preparation of **1**, the new binuclear cobalt complex **2** containing two carborane cages was isolated. Its structure and spectroscopic data are also discussed.

Results and Discussion

Synthesis and Structure of 2

In the preparation of **1** according to the literature,[2a,5a] **2** was obtained as a minor product as shown in Scheme 2. Its solid-state structure (Figure 1) shows a binuclear complex containing both $(Se_2C_2B_{10}H_{10})^{2-}$ and $(SeSeC_2B_{10}H_{11})^{-}$ units. The presence of a CH unit in one carborane cage indicates that *o*-carborane is not completely deprotonated by *n*-butyllithium. To confirm this, we used a little more *n*-butyllithium and as a result **2** was not generated. The NMR spectra demonstrate the nondeprotonated CH unit at the carborane with the broad ^1H singlet at 3.76 ppm and the ^{13}C signal at 66.4 ppm. As seen in Figure 1, the two selenium atoms bridge the two cobalt atoms to form a four-membered ring, Co(1)Se(2)Co(2)Se(3), which is nonplanar with a dihedral angle of 160.1° at the Se(2)···Se(3) vector. The five-membered ring Co(1)Se(1)C(1)C(2)Se(2) is no longer planar[5b] and has a dihedral angle of 157.1° at the Se(1)···Se(2) vector. The Se(3)–Se(4) bond length of 2.381 Å falls in the range typical of a Se–Se single bond.[9]



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

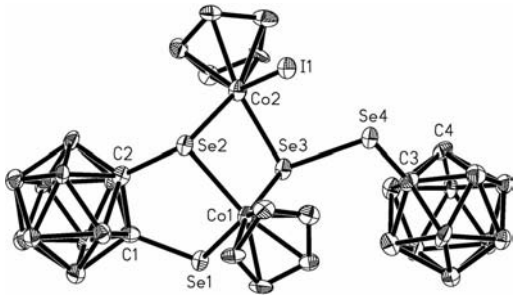
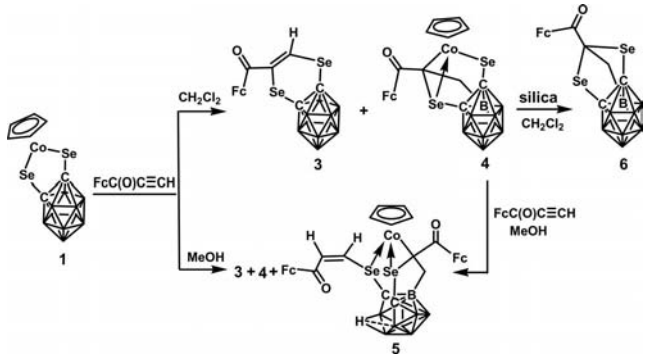


Figure 1. Molecular structure of **2**. Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): C(1)–C(2) 1.682(10), C(3)–C(4) 1.665(11), C(1)–Se(1) 1.919(7), C(2)–Se(2) 1.991(7), C(3)–Se(4) 1.907(8), Co(1)–Se(1) 2.3688(13), Co(1)–Se(2) 2.3784(12), Co(1)–Se(3) 2.3673(13), Co(2)–Se(2) 2.3951(12), Co(2)–Se(3) 2.3549(13), Co(2)–I(1) 2.5863(12), Se(3)–Se(4) 2.3807(10); C(1)–Se(1)–Co(1) 103.0(2), C(2)–Se(2)–Co(1) 103.4(2), C(3)–Se(4)–Se(3) 100.1(2), Co(1)–Se(2)–Co(2) 92.65(4), Co(1)–Se(3)–Co(2) 93.96(4), Co(2)–Se(3)–Se(4) 98.06(4), Se(1)–Co(1)–Se(2) 93.56(4), Se(2)–Co(1)–Se(3) 84.87(4), Se(2)–Co(2)–Se(3) 84.77(4).

Interestingly, an iodine atom is present at Co(2) which is further confirmed by the mass spectrometry. The retained iodine atom arises from the $CpCo(CO)I_2$ starting material. Thus **2** can be considered as a dimer of the two 16-electron species $CpCo(Se_2C_2B_{10}H_{10})$ (**1**) and $CpCoI(SeSeC_2B_{10}H_{11})$. The former can be present as a stable monomer, but the latter cannot. However, their combination leads to the stable product **2** as each metal center has an 18-electron configuration. An analogous structure of a sulfur complex $[CpCo(S_2C_2B_{10}H_{10})][\{CpCo(SC_2B_{10}H_{11})\}(n\text{-BuS})]$ has been previously reported by our group.[10]

Reaction of 1 with FcC(O)C≡CH

Compound **1** reacts with FcC(O)C≡CH in CH_2Cl_2 at ambient temperature to lead to **3** and **4** in 18% and 40% yield, respectively (Scheme 3). The X-ray crystal structure of **3** (Figure 2) shows an addition product of the alkyne directly connected to the *o*-carborane-diselenolate ligand with loss of the CpCo unit from **1**. The newly generated six-membered ring C(1)C(2)Se(2)C(4)C(3)Se(1) is bent at the Se(1)···Se(2) vector with a dihedral angle of 140.9°. The NMR spectra are in agreement with the solid-state structure. The ^1H NMR spectrum shows a singlet at 8.21 ppm, which is assigned to the C(3)*H* unit, and the ^{13}C signals are identified at 129.8 for *C*(3) and 141.6 ppm for *C*(4). FcC≡CH does not react with **1** in CH_2Cl_2 but in the protic solvent MeOH the sole product **E** (Scheme 1) is generated which is similar to **3** in structure. This demonstrates that FcC(O)C≡CH is more reactive than FcC≡CH. In contrast, the other two sulfur analogs were prepared through the reactions of the square-planar species $[(Cp_2Co)^+\{Co(S_2C_2B_{10}H_{10})_2\}^-]$ with the corresponding alkynes.[11]



Scheme 3. Synthesis of **3**–**6**.

Complex **4** was isolated as the major product and its solid-state structure (Figure 3) shows the presence of a B–CH_2 unit. One hydrogen atom at B(3)/B(6) has been transferred to the terminal carbon of the alkyne to form the B–CH_2 unit. As a result, the C≡C bond of the alkyne is reduced to a C–C single bond (1.531 Å). The NMR spectroscopic data support the solid-state structure. In the ^1H NMR spectrum the two broad doublets at 3.28 and 1.52 ppm are assigned to the newly generated alkyl group of the B–CH_2 unit, and the large value (16 Hz) of the geminal coupling

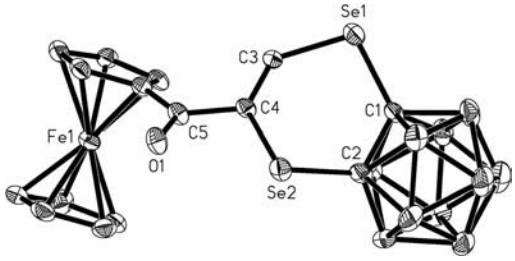


Figure 2. Molecular structure of **3**. Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): C(1)–C(2) 1.640(6), C(1)–Se(1) 1.929(5), C(2)–Se(2) 1.924(5), C(3)–C(4) 1.328(6), C(3)–Se(1) 1.882(4), C(4)–Se(2) 1.894(4); C(1)–C(2)–Se(2) 121.5(3), C(2)–C(1)–Se(1) 122.5(3), C(3)–C(4)–Se(2) 128.3(3), C(4)–C(3)–Se(1) 128.9(4), C(1)–Se(1)–C(3) 100.77(19), C(2)–Se(2)–C(4) 100.46(19).

constants ^2J (^{1}H, ^{1}H) is typical for diastereotopic ^{1}H nuclei of the B–CH_2 group.[6,7a,7b,8a] In the ^{13}C NMR spectroscopic data, the broad signal of *C*(3) at 32.6 ppm is attributed to ^{13}C–^{11}B coupling.[8a] The signal of *C*(4) is shifted to a lower field at 108.5 ppm owing to the metal effect on the ^{13}C nuclear shielding. In **4**, the ^{13}C data of the carborane cage at 84.4 and 70.8 ppm are significantly shifted to higher field in comparison with the range of 90–110 ppm of its sulfur analogs.[6a,6b,7a,8a] Analogous structures and mechanistic studies have been reported by our group.[6–8] The reaction takes place through a series of sequential steps such as an alkyne insertion into a M–E (E = S, Se) bond, metal induced B–H activation, the formation of M–B, and then the formation of C–B.

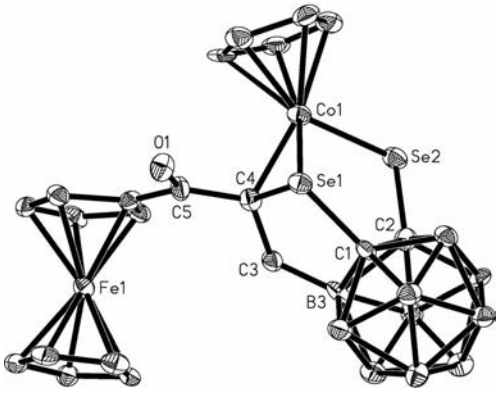


Figure 3. Molecular structure of **4**. Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): Co(1)–C(4) 1.995(5), Co(1)–Se(1) 2.3139(9), Co(1)–Se(2) 2.3479(9), C(1)–C(2) 1.627(7), C(1)–Se(1) 1.954(5), C(2)–Se(2) 1.927(5), C(3)–C(4) 1.531(7), C(3)–B(3) 1.578(8), C(4)–Se(1) 1.950(5); Co(1)–C(4)–Se(1) 71.82(16), Co(1)–Se(1)–C(4) 55.00(13), Co(1)–Se(2)–C(2) 101.25(15), Co(1)–Se(1)–C(1) 102.89(13), C(1)–Se(1)–C(4) 91.37(19), C(3)–C(4)–Se(1) 115.4(3), C(4)–C(3)–B(3) 112.4(4), C(4)–Co(1)–Se(1) 53.18(13), C(4)–Co(1)–Se(2) 97.36(14), Se(1)–Co(1)–Se(2) 96.41(3).

However, the reaction of **1** with FcC(O)C≡CH in MeOH at ambient temperature leads to **5** (Scheme 3, Figure 4). Its solid-state structure shows that two alkynes are involved. The existence of one alkyne is similar to that of **4**, indicating that B–H activation has occurred leading to a B–CH_2 unit. The other alkyne is added to the second selenium atom at its terminal carbon atom to form a vinyl unit in a Z configuration. Another remarkable feature of **5** is that one apex at the B(6) site of the carborane has been lost to generate a *nido*-C_2B_9 cage. Conversion of a neutral *closo*-$C_2B_{10}H_{10}$ cage to a negatively charged *nido*-$C_2B_9H_{10}^-$ cluster has been extensively reported if an alcohol or a nucleophilic reagent is present.[1a,6b,12] As confirmed in the solid-state structure, the unusual face-bridging hydrogen binding to the three B atoms at the open face is observed at –2.87 ppm in the ^{1}H NMR spectrum. The two typical doublets at 7.24 and 7.19 ppm with a coupling constant of J = 9 Hz are assigned to the two olefinic protons of C(6)*H* and C(7)*H*, respectively. The characteristic doublets at 3.19 and 1.25 ppm with J = 16 Hz are ascribed to the alkyl group of the B–CH_2 unit.[6,7a,7b,8a] In the ^{13}C NMR spectrum, two signals at 139.2 and 128.1 ppm are assigned to *C*(6) and *C*(7), respectively. The broad signal of *C*(3) at 29.7, *C*(4) at 106.1, and *C*(1)/*C*(2) at 62.9/59.4 ppm have been unquestionably designated and are in parallel with data observed for **4**.

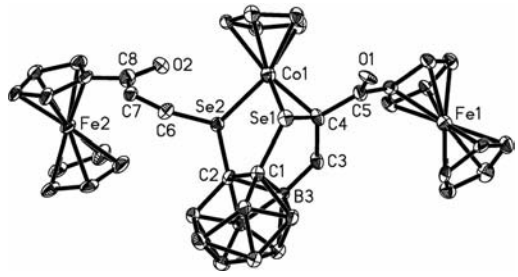


Figure 4. Molecular structure of **5**. Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): C(1)–C(2) 1.558(6), C(1)–Se(1) 1.933(4), C(2)–Se(2) 1.932(4), C(6)–Se(2) 1.922(5), C(6)–C(7) 1.309(6), C(3)–C(4) 1.521(6), C(3)–B(3) 1.585(7), C(4)–Se(1) 1.936(4), C(4)–Co(1) 2.000(5), Co(1)–Se(1) 2.3134(9), Co(1)–Se(2) 2.3435(8); C(1)–Se(1)–Co(1) 103.97(13), C(1)–Se(1)–C(4) 93.60(18), C(2)–Se(2)–Co(1) 102.92(14), C(3)–C(4)–Co(1) 121.6(3), C(3)–C(4)–Se(1) 113.9(3), C(4)–Co(1)–Se(1) 52.75(13), C(4)–Co(1)–Se(2) 96.19(12), C(4)–Se(1)–Co(1) 55.28(14), Se(1)–C(4)–Co(1) 71.97(16), Se(1)–Co(1)–Se(2) 94.05(3).

Transformations of 4

In the presence of silica in CH_2Cl_2, **4** is quantitatively converted to **6** in two days (Scheme 3). The solid-state structure shows that **6** is a symmetric molecule (Figure 5), thus the chemical environments of the two hydrogen atoms in the B–CH_2 unit and the two carbon atoms in the carborane cage are identical and both show only one NMR signal. In comparison to its sulfur analog **C**, generated from FcC≡CH (Scheme 1), the ^{13}C NMR signal of carborane is shifted to a higher field.[6b,6c] It is worth noting that **4** behaves significantly differently from its sulfur analog **B**. The latter undergoes immediate conversion to **C** as the sole product on silica (Scheme 1), and the conversion goes well in MeOH at ambient temperature or in boiling toluene.[6b] In contrast, **4** is hardly converted to **6** under the same conditions, demonstrating its higher stability. Con-

cerning the loss of the CpCo unit of **4** and **B** on silica, we assume that the acidity of silica might play a key role since both compounds are stable towards neutral alumina.

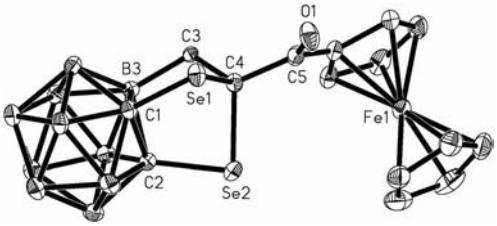


Figure 5. Molecular structure of **6**. Thermal ellipsoids are depicted at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles (°): C(1)–C(2) 1.696(4), C(1)–Se(1) 1.928(3), C(2)–Se(2) 1.936(3), C(3)–B(3) 1.584(4), C(3)–C(4) 1.572(4), C(4)–C(5) 1.521(4), C(4)–Se(1) 1.989(3), C(4)–Se(2) 2.002(3); C(1)–Se(1)–C(4) 84.34(13), C(2)–Se(2)–C(4) 84.26(13), C(3)–C(4)–C(5) 118.8(3), C(3)–C(4)–Se(1) 107.25(19), C(3)–C(4)–Se(2) 105.70(19), C(5)–C(4)–Se(1) 105.2(2), C(5)–C(4)–Se(2) 115.0(2), Se(1)–C(4)–Se(2) 103.56(14).

In MeOH and in the presence of FcC(O)C≡CH, **4** could be converted to **5**. It is suggested that the generation of **5** might be a synergetic process of loss of a BH apex of carborane of **4** under the attack of MeOH and the addition of one alkyne into the other Co–Se bond in **4** (Scheme 3).

Conclusion

$CpCo(Se_2C_2B_{10}H_{10})$ (**1**) is insoluble and less reactive than its sulfur analog $CpCo(S_2C_2B_{10}H_{10})$. Previous results show that only one reaction between **1** and FcC≡CH in MeOH could take place to produce the sole product $[(FcCCH)(Se_2C_2B_{10}H_{10})]$. In this study the reaction with FcC(O)C≡CH goes smoothly both in CH_2Cl_2 and MeOH at ambient temperature to lead to new products **3**, **4**, and **5**. Only in MeOH, was the new compound **5** generated. For the first time, we have observed that a stable 18-electron species such as **4** can further react with an alkyne to generate a new product. The protic solvent MeOH plays a key role in the formation of **5**. In addition, the selenium species **4** shows higher stability against such as silica, MeOH, and temperature than the sulfur analogue **B** generated from FcC≡CH, demonstrating the lower reactivity of selenium species vs. sulfur species. In general, this study shows that the reactivity of **1** towards the activated alkyne FcC(O)C≡CH is analogous to that of $CpCo(S_2C_2B_{10}H_{10})$ towards FcC≡CH. These results enrich the understanding of the reaction chemistry of the 16-electron half-sandwich transition metal complexes containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate with alkynes.

Experimental Section

General Procedures: All experiments were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried by heating to reflux with sodium (petroleum ether, ether, and THF) or calcium hydride (dichloromethane) under nitrogen and then distilled prior to use. $CpCo(CO)I_2$,[13] $CpCo(Se_2C_2B_{10}H_{10})$ (**1**)[2a,5a] and FcC(O)C≡CH[14] were prepared according to literature methods. Ferrocenecarbaldehyde (Alfa Aesar) and *n*-butyllithium (2.0 M in cyclohexane, Aldrich) were used without further purification. Elemental analysis was performed with an elementar vario EL III elemental analyzer. NMR spectroscopic data were recorded with a Bruker DRX-500 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were reported in ppm with respect to $CHCl_3/CDCl_3$ (^{1}H: δ = 7.24, ^{13}C: δ = 77.0) and ^{11}B NMR spectra were reported in ppm with respect to external $Et_2O{\cdot}BF_3$ (^{11}B: δ = 0). IR spectra were recorded with a Bruker Tensor 27 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. The mass spectra were recorded with a Micromass GC-TOF for EI-MS (70 ev) or Finnigan MAT TSQ7000 for ESI-MS.

Synthesis of 1 and 2: To a solution of *o*-carborane (0.144 g, 1.0 mmol) in diethyl ether (20 mL) was added *n*-butyllithium (1.1 mL, 2.2 mmol) and the solution was stirred at ambient temperature. After 0.5 h, selenium powder (2.2 mmol) was added and the solution was stirred for 1 h at ambient temperature. This solution was added to a solution of $CpCo(CO)I_2$ (0.39 g, 0.96 mmol) in THF (25 mL) at 0 °C. The mixture was allowed to react for 1 h at 0 °C and then stirred for another 2 h at ambient temperature. After removal of solvent, the residue was chromatographed on silica. Elution with petroleum ether/CH_2Cl_2 (1:2) gave **1** (161 mg, 38%) and **2** (19.5 mg, 4%) based on *o*-carborane. **2**: black solid, m.p. 225 °C (dec.) ^{1}H NMR ($CDCl_3$): δ = 5.35 (s, 5 H, Cp), 5.04 (s, 5 H, Cp), 3.76 [br. s, 1 H, C(4)*H*] ppm. ^{11}B NMR ($CDCl_3$): δ = –3.2 (6B), –6.2 (6B), –9.8 (4B), –13.8 (4B) ppm. ^{13}C NMR ($CDCl_3$): δ = 87.5 (Cp), 83.8 (Cp), 74.9 (carborane-*C*), 71.9 (carborane-*C*), 66.4 (carborane-*C*H), 59.5 (carborane-*C*) ppm. IR (KBr): $\tilde{\nu}$ = 2585 (B–H) cm^{-1}. ESI-MS (poitive ion mode): *m*/*z* (%) = 977.25 (12) [M + H]$^+$, 849.50 (25) [M – I]$^+$. $C_{14}H_{31}B_{20}Co_2ISe_4{\cdot}H_2O$ (994.20): calcd. C 16.91, H 3.35; found C 16.67, H 3.44.

Synthesis of 3 and 4: FcC(O)C≡CH (71.4 mg, 0.3 mmol) was added to the suspension of **1** (85.2 mg, 0.2 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 2 d at ambient temperature. After removal of solvent, the residue was chromatographed on silica. Elution with petroleum ether/CH_2Cl_2 (1:1) gave **3** and **4**. **3**: brown solid, yield 18% (19.4 mg), m.p. 233 °C (dec.) ^{1}H NMR ($CDCl_3$): δ = 8.21 [s, 1 H, C(3)*H*], 4.90 (m, 2 H, Fc-C*H*), 4.70 (m, 2 H, Fc-C*H*), 4.27 (s, 5 H, Fc-Cp) ppm. ^{11}B NMR ($CDCl_3$): δ = 0.1 (3B), –5.1 (7B) ppm. ^{13}C NMR ($CDCl_3$): δ = 193.0 [*C*(5)], 141.6 [*C*(4)], 129.8 [*C*(3)], 75.1 (Fc-*C*), 74.2 (Fc-*C*H), 70.9 (Fc-*C*H), 70.8 (Fc-Cp), 63.4 (carborane), 60.3 (carborane) ppm. IR (KBr): $\tilde{\nu}$ = 1606 (C=O), 2585 (B–H) cm^{-1}. EI-MS (70eV): *m*/*z* = 537.9 (M$^+$, 100). $C_{15}H_{20}B_{10}FeOSe_2$ (538.18): calcd. C 33.48, H 3.75; found C 33.19, H 3.66. **4**: brown solid, yield 40% (53.0 mg), m.p. 284 °C (dec.) ^{1}H NMR ($CDCl_3$): δ = 5.02 (m, 2 H, Fc-C*H*), 4.99 (m, 2 H, Fc-C*H*), 4.69 (s, 5 H, Cp), 4.37 (s, 5 H, Fc-Cp), 3.28 [d, *J* = 16 Hz, 1 H, C(3)H_2], 1.52 [d, *J* = 16 Hz, 1 H, C(3)H_2] ppm. ^{11}B NMR ($CDCl_3$): δ = 2.9 (1B, B-C), 2.7 (2B), –1.8 (2B), –5.6 (3B), –8.3 (2B) ppm. ^{13}C NMR ($CDCl_3$): δ = 208.0 [*C*(5)], 108.5 [*C*(4)], 84.5 (Cp), 84.4 (carborane), 70.8 (carborane), 77.3 (Fc-*C*), 73.5 (Fc-*C*H), 72.1 (Fc-*C*H), 71.4 (Fc-*C*H), 70.0 (Fc-*C*H), 70.3 (Fc-Cp), 32.6 [br., *C*(3)] ppm. EI-MS (70eV): *m*/*z* = 661.8 (14) [M$^+$]. IR (KBr): $\tilde{\nu}$ = 1581 (C=O), 2578 (B–H). $C_{20}H_{25}B_{10}CoFeOSe_2$ (662.20): calcd. C 36.27, H 3.81; found C 36.02, H 3.68.

Synthesis of 5. Method 1: FcC(O)C≡CH (71.4 mg, 0.3 mmol) was added to the suspension of **1** (85.2 mg, 0.2 mmol) in MeOH (20 mL), and the mixture was stirred for 2 d at ambient temperature. After removal of solvent, the residue was chromatographed on silica. Elution with petroleum ether/CH_2Cl_2 (1:1) gave in turn **3** (33.4 mg, 31%), **4** (30.5 mg, 23%) and **5** (8.9 mg, 5%).

Table 1. Crystallographic data for complexes **2**–**6**.

	2·H_2O	**3**	**4**	**5**·CH_2Cl_2	**6**
Chemical formula	$C_{14}H_{31}B_{20}Co_2ISe_4 \cdot H_2O$	$C_{15}H_{20}B_{10}FeOSe_2$	$C_{20}H_{25}B_{10}CoFeOSe_2$	$C_{33}H_{36}B_9CoFe_2O_2Se_2 \cdot CH_2Cl_2$	$C_{15}H_{20}B_{10}FeOSe_2$
Crystal size [mm]	0.28 × 0.26 × 0.24	0.28 × 0.24 × 0.22	0.29 × 0.26 × 0.23	0.28 × 0.24 × 0.22	0.28 × 0.24 × 0.22
Formula weight	994.20	538.18	662.20	975.38	538.18
Temperature [K]	291(2)	291(2)	291(2)	291(2)	291(2)
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Pbca$	$P2_1/c$
a [Å]	18.471(3)	14.630(2)	9.896(2)	14.176(3)	13.0164(18)
b [Å]	7.5318(11)	10.9098(19)	14.9005(15)	12.634(3)	11.653(2)
c [Å]	23.531(3)	14.630(2)	18.761(2)	42.071(10)	13.6683(19)
α [°]	90	90	110.908(2)	90	90
β [°]	93.976(2)	112.744(3)	103.538(2)	90	100.713(3)
γ [°]	90	90	90.076(3)	90	90
V [Å^3]	3265.7(8)	2153.6(6)	2501.5(7)	7535(3)	2037.0(6)
Z	4	4	4	8	4
ρ_{calc} [g cm^{-3}]	2.020	1.660	1.758	1.720	1.755
Absorption coeff. [mm^{-1}]	6.435	4.085	4.168	3.302	4.319
F(000)	1868	1048	1296	3872	1048
θ range [°]	1.74–26.00	2.40–25.99	2.13–26.00	1.73–26.00	2.31–26.00
Reflections collected	17152	11339	13553	38738	10797
	(Rint = 0.0491)	(Rint = 0.0445)	(Rint = 0.0271)	(Rint = 0.0666)	(Rint = 0.0418)
Independent reflections	6406	4218	9600	7406	3997
Obsd. reflections [$I > 2\sigma(I)$]	4764	3385	6450	5666	3204
Data/restraints/parameters	6406/0/379	4218/0/238	9600/0/631	7406/0/477	3997/0/262
GOF	1.075	1.050	1.020	1.051	1.047
$R_1/wR_2[I > 2\sigma(I)]$	0.0543/0.1152	0.0523/0.1265	0.0446/0.0872	0.0495/0.0990	0.0344/0.0878
R_1/wR_2 (all data)	0.0762/0.1210	0.0632/0.1299	0.0697/0.0911	0.0678/0.1032	0.0471/0.0932
Largest peak/hole [e Å^{-3}]	0.614/–0.798	0.412/–0.552	0.808/–0.536	0.824/–0.770	0.923/–0.740

Method 2: To a solution of **4** (53.0 mg, 0.08 mmol) in MeOH (20 mL) was added FcC(O)C≡CH (71.4 mg, 0.3 mmol), and the mixture was stirred for 2 d. After removal of solvent, the residue was chromatographed on silica, and elution with petroleum ether/CH_2Cl_2 (1:1) gave **5** (5.7 mg, 8%). Brown solid, m.p. 172 °C (dec.) ^{1}H NMR ($CDCl_3$): δ = 7.24 [d, J = 9 Hz, 1 H, C(6)*H*], 7.19 [d, J = 9 Hz, 1 H, C(7)*H*], 5.00 (m, 1 H, Fc-C*H*), 4.98 (m, 1 H, Fc-C*H*), 4.94 (m, 1 H, Fc-C*H*), 4.81 (m, 1 H, Fc-C*H*), 4.79 (s, 5 H, Cp), 4.78 (m, 1 H, Fc-C*H*), 4.71 (m, 1 H, Fc-C*H*), 4.69 (m, 1 H, Fc-C*H*), 4.68 (m, 1 H, Fc-C*H*), 4.38 (s, 5 H, Fc-Cp), 4.28 (s, 5 H, Fc-Cp), 3.19 [d, J = 16 Hz, 1 H, C(3)H_2], 1.25 [d, J = 16 Hz, 1 H, C(3)H_2], –2.87 (br. s, 1 H, B*H*B) ppm. ^{11}B NMR ($CDCl_3$): δ = 2.1 (1B, B-C), –3.0 (2B), –7.9 (2B), –14.8 (1B), –30.0 (3B) ppm. ^{13}C NMR ($CDCl_3$): δ = 206.8 (*C*O), 193.2 (*C*O), 139.2 [*C*(6)], 128.1 [*C*(7)], 106.1 [*C*(4)], 86.1 (Cp), 78.2 (Fc-*C*), 77.5 (Fc-*C*), 74.7 (Fc-*C*H), 74.4 (Fc-*C*H), 73.6 (Fc-*C*H), 72.2 (Fc-*C*H), 71.2 (Fc-*C*H), 70.8 (Fc-*C*H), 70.4 (Fc-*C*H), 69.3 (Fc-*C*H), 70.7 (Fc-Cp), 70.5 (Fc-Cp), 62.9 (carborane), 59.4 (carborane), 29.7 [br. *C*(3)] ppm. ESI-MS: m/z (%) = 891.92 (100) [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 1633 (C=O), 2538 (B–H). $C_{33}H_{36}B_9CoFe_2O_2Se_2 \cdot CH_2Cl_2$ (975.38): calcd. C 41.86, H 3.93; found C 41.67, H 3.80.

Synthesis of 6: To a solution of **4** (53.0 mg, 0.08 mmol) in CH_2Cl_2 (20 mL) was added silica, and the mixture was stirred for 2 d. Then silica was removed by filtration. After removal of solvent, the residue was chromatographed on silica, and elution with petroleum ether/CH_2Cl_2 (1:1) gave **6**. Brown solid, yield 96% (41.3 mg), m.p. 288 °C (dec.) ^{1}H NMR ($CDCl_3$): δ = 5.08 (m, 2 H, Fc-C*H*), 4.70 (m, 2 H, Fc-C*H*), 4.31 (s, Fc-Cp), 2.76 [s, 2 H, C(3)H_2] ppm. ^{11}B NMR ($CDCl_3$): δ = 0.8 (1B, B-C), 0.6 (2B), –2.3 (2B), –5.0 (2B), –9.2 (1B), –12.0 (2B) ppm. ^{13}C NMR ($CDCl_3$): δ = 196.2 [*C*(5)], 97.4 [*C*(4)], 79.7 (carborane), 73.8 (Fc-*C*H), 71.1 (Fc-*C*H), 73.4 (Fc-*C*), 70.6 (Fc-Cp), 42.2 [br. *C*(3)] ppm. EI-MS (70eV): m/z (%) = 538.1 (100) [M$^+$]. IR (KBr): $\tilde{\nu}$ = 1627 (C=O), 2593 (B–H) cm^{-1}. $C_{15}H_{20}B_{10}FeOSe_2$ (538.18): calcd. C 33.48, H 3.75; found C 33.21, H 3.83.

X-ray Crystallography: X-ray crystallographic data[15] were collected with a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. The intensities were corrected for Lorentz polarization effects and empirical absorption with the SADABS program. The structures were solved by direct methods using the SHELXL-97 program. Crystal data, data collection parameters, and the results of the analyses of **2**–**6** are listed in Table 1.

CCDC-793519 (for **2**), 793520 (for **3**), 793521 (for **4**), 793522 (for **5**), and 793523 (for **6**) 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.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (grant numbers 20925104 and 21021062), the National Basic Research Program of China (grant numbers 2007CB925101 and 2010CB923303), the Natural Science Foundation of Jiangsu Province (grant number BK2010052), and the Ministry of Education of China (grant number 20090091110015).

[1] a) X. Meng, F. Wang, G. X. Jin, *Coord. Chem. Rev.* **2010**, *254*, 1260–1272; b) J. Q. Wang, L. H. Weng, G.-X. Jin, *J. Organomet. Chem.* **2005**, *690*, 249–252; c) S. Liu, X. Wang, G. X. Jin, *J. Organomet. Chem.* **2006**, *691*, 261–265.

[2] a) M. Herberhold, G. X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **1999**, *587*, 252–257; b) M. Herberhold, H. Yan, W. Milius, *J. Organomet. Chem.* **2000**, *598*, 142–

149; c) M. Herberhold, G. X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *Eur. J. Inorg. Chem.* **1999**, 873–875.

[3] a) J. Y. Bae, Y. I. Park, J. Ko, K. I. Park, S. I. Cho, S. O. Kang, *Inorg. Chim. Acta* **1999**, *289*, 141–148; b) J. H. Won, H. G. Lim, B. Y. Kim, J. D. Lee, C. Lee, Y. J. Lee, S. Cho, J. Ko, S. O. Kang, *Organometallics* **2002**, *21*, 5703–5712; c) B. Y. Kim, C. Lee, S. W. Chung, Y. J. Lee, J. Y. Park, J. Ko, S. O. Kang, *J. Organomet. Chem.* **2003**, *688*, 236–245.

[4] a) J. Q. Wang, C. X. Ren, G.-X. Jin, *Chem. Commun.* **2005**, 4738–4740; b) J. Q. Wang, C. X. Ren, L. H. Weng, G. X. Jin, *Chem. Commun.* **2006**, 162–164; c) S. Liu, J. S. Zhang, X. Wang, G. X. Jin, *Dalton Trans.* **2006**, 5225–5230; d) J. Q. Wang, C. X. Ren, G. X. Jin, *Eur. J. Inorg. Chem.* **2006**, 3274–3282; e) Y. F. Han, J. S. Zhang, Y. J. Lin, J. Dai, G. X. Jin, *J. Organomet. Chem.* **2007**, *692*, 4545–4550; f) S. Liu, G. L. Wang, G. X. Jin, *Dalton Trans.* **2008**, 425–432.

[5] a) J. H. Won, D. H. Kim, B. Y. Kim, S. J. Kim, C. Lee, S. Cho, J. Ko, S. O. Kang, *Organometallics* **2002**, *21*, 1443–1453; b) D. H. Kim, J. Ko, K. Park, S. Cho, S. O. Kang, *Organometallics* **1999**, *18*, 2738–2740.

[6] a) B. H. Xu, D. H. Wu, Y. Z. Li, H. Yan, *Organometallics* **2007**, *26*, 4344–4349; b) B. H. Xu, X. Q. Peng, Y. Z. Li, H. Yan, *Chem. Eur. J.* **2008**, *14*, 9347–9356; c) B. H. Xu, J. C. Tao, Y. Z. Li, S. H. Li, H. Yan, *Organometallics* **2008**, *27*, 334–340.

[7] a) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **2000**, *604*, 170–177; b) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1627–1633; c) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Angew. Chem. Int. Ed.* **1999**, *38*, 3689–3691; d) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Chem. Eur. J.* **2000**, *6*, 3026–3032; e) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Chem. Eur. J.* **2002**, *8*, 388–395; f) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Organometallics* **2000**, *19*, 4289–4294; g) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *J. Chem. Soc., Dalton Trans.* **2001**, 1782–1789; h) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **2001**, *623*, 149–152.

[8] a) Y. G. Li, Q. B. Jiang, X. L. Zhang, Y. Z. Li, H. Yan, V. I. Bregadze, *Inorg. Chem.* **2010**, *49*, 3911–3917; b) Y. G. Li, Q. B. Jiang, Y. Z. Li, H. Yan, V. I. Bregadze, *Inorg. Chem.* **2010**, *49*, 4–6.

[9] a) H. U. Hummel, T. Fischer, D. Gruss, A. Franke, W. Dietzsch, *J. Chem. Soc., Dalton Trans.* **1992**, 2781–2785; b) S. Kumar, S. K. Tripathi, H. B. Singh, G. Wolmershaeuser, *J. Organomet. Chem.* **2004**, *689*, 3046–3055; c) S. S. Zade, S. Panda, H. B. Singh, R. B. Sunoj, R. J. Butcher, *J. Org. Chem.* **2005**, *70*, 3693–3704; d) S. M. Dibrov, B. Deng, D. E. Ellis, J. A. Ibers, *Inorg. Chem.* **2005**, *44*, 3441–3448; e) M. C. Hong, R. Cao, H. Kawaguchi, K. Tatsumi, *Inorg. Chem.* **2002**, *41*, 4824–4833.

[10] Y. G. Li, Q. B. Jiang, Y. Z. Li, X. J. Shen, H. Yan, V. I. Bregadze, *Inorg. Chem.* **2010**, *49*, 5584–5590.

[11] B. H. Xu, X. Q. Peng, Z. W. Xu, Y. Z. Li, H. Yan, *Inorg. Chem.* **2008**, *47*, 7928–7933.

[12] a) X. K. Huo, G. Su, G. X. Jin, *Dalton Trans.* **2010**, *39*, 1954–1961; b) J. S. Zhang, G. X. Jin, *J. Organomet. Chem.* **2007**, *692*, 3944–3948; c) J. S. Zhang, Y. J. Lin, G. X. Jin, *J. Organomet. Chem.* **2009**, *694*, 2069–2074; d) F. Teixidor, C. Vinas, J. Rius, C. Miravitlles, J. Casabo, *Inorg. Chem.* **1990**, *29*, 149–152; e) C. Vinas, W. M. Butler, F. Teixidor, R. W. Rudolph, *Inorg. Chem.* **1986**, *25*, 4369–4374; f) F. Teixidor, J. Casabo, C. Vinas, E. Sanchez, L. Escriche, R. Kivekas, *Inorg. Chem.* **1991**, *30*, 3053–3058; g) C. Vinas, W. M. Butler, F. Teixidor, R. W. Rudolph, *Organometallics* **1984**, *3*, 503–504.

[13] R. B. King, *Inorg. Chem.* **1966**, *5*, 82–87.

[14] S. Barriga, C. F. Marcos, O. Riant, T. Torroba, *Tetrahedron* **2002**, *58*, 9785–9792.

[15] *SMART*, version 5.0; *SAINT*, version 6; *SHELXTL*, version 6.1; *SADABS*, version 2.03, Bruker AXS Inc., Madison, WI, **2000**.

Received: February 18, 2011
Published Online: May 17, 2011

