

## 半夹芯 16 电子化合物 $\text{CpCo}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})$ 中 B(3,6) 位的选择性分步取代反应

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**摘要:** 16e 半夹芯化合物  $\text{CpCo}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})$  (Cp: cyclopentadienyl) (**1**) 与炔烃  $\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  (Fc: ferrocenyl) 在物质的量之比为 1:1 时反应生成化合物  $\text{CpCo}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_9)(\text{CH}=\text{CHC}(\text{O})\text{Fc})$  (**2**)。在化合物 **2** 中, 一分子  $\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  偶合到原料化合物 **1** 的碳硼烷笼子的 B(3) 位点, 导致 B(3) 位的氢原子迁移到炔烃的内部碳原子上形成烯炔取代基。**2** 能继续与另外一分子  $\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  反应, 生成 B-双取代产物  $\text{CpCo}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_8)(\text{CH}=\text{CHC}(\text{O})\text{Fc})_2$  (**3**)。**3** 仍然是 1 个 16e 化合物, 并且在 B(3,6) 位点有 2 个反式烯炔取代基  $\text{CH}=\text{CHC}(\text{O})\text{Fc}$ 。在过量炔烃存在情况下, 该反应生成化合物 **3** 及炔烃环三聚产物  $1,3,5\text{-}\{\text{HC}=\text{CC}(\text{O})\text{Fc}\}_3$  (**4**)。化合物 **2**、**3**、**4** 用红外, 核磁, 元素分析, 质谱和单晶 X-射线衍射分析等方法进行了表征。

**关键词:** 过渡金属; 碳硼烷; B-H 键活化; 晶体结构

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## Selective Stepwise Substitution in B(3,6) Positions of 16e Half-Sandwich Complex $\text{CpCo}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})$

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**Abstract:** The reaction of the 16e half-sandwich complex  $\text{CpCo}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})$  (Cp: cyclopentadienyl) (**1**) and the alkyne  $\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  (Fc: ferrocenyl) in a molar ratio of 1:1 leads to  $\text{CpCo}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_9)(\text{CH}=\text{CHC}(\text{O})\text{Fc})$  (**2**) in which the alkyne is coupled to the B(3) site of the carborane cage thus resulting in the transferring hydrogen of B(3)-H to the internal carbon of the alkyne to form a olefinic substituent  $\text{CH}=\text{CHC}(\text{O})\text{Fc}$ . **2** could further react with a second  $\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  to generate a B-disubstituted product  $\text{CpCo}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_8)(\text{CH}=\text{CHC}(\text{O})\text{Fc})_2$  (**3**). **3** is still a 16e compound with two  $\text{CH}=\text{CHC}(\text{O})\text{Fc}$  olefinic substituents in E/E configurations at the B(3,6) sites. In the presence of excess alkyne, the reaction leads to **3** and the alkyne cyclotrimerization product  $1,3,5\text{-}\{\text{HC}=\text{CC}(\text{O})\text{Fc}\}_3$  (**4**). Complexes **2**, **3**, **4** have been characterized by IR, NMR, elemental analysis, mass spectrometry and single-crystal X-ray diffraction analysis. CCDC: 813827, **2**; 813828, **3**; 802195, **4**.

**Key words:** transition metal; carborane; B-H activation; crystal structure

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## 0 Introduction

Over the past decade, a sort of mononuclear 16e half-sandwich complexes of Ru, Os, Co, Rh and Ir bearing a chelating 1,2-dicarba-closo-dodecaborane-1,2-dichalcogenolate ligand have been prepared and studied extensively<sup>[1-30]</sup>. These sterically congested, coordinatively unsaturated compounds have shown rich reaction chemistries towards metal fragments<sup>[5]</sup>, Lewis bases<sup>[6-13]</sup>, and alkynes<sup>[14-29]</sup>. Previous studies have shown that the types and structures of the products are dependant on the influencing factors such as metal center, chalcogen element, substrate, ancillary ligand on metal of the above mentioned 16e complexes, reaction temperature, solvent and the ratio of the reactants. For example, the 16e complexes Cp\*M (E<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) (Cp\* = pentamethylcyclopentadienyl; M = Rh, Ir; and E = S, Se) react with selected alkynes to generate activated B-H activated products in the B(3,6) positions of carborane<sup>[15-20]</sup>. However, the reactions of Cp\*Co(S<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) with alkynes lead almost to insertion products at one Co-S bond<sup>[28-29]</sup>. The treatment of CpCo(S<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) (**1**) with HC≡CC(O)Ph in a ratio of 2:1 produces a novel 17e product containing a functional group of bicyclo[2.2.1]heptene unit at the B(3,6) site of carborane<sup>[26]</sup>. In contrast, if less CpCo(S<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) is used, the reaction gives rise to 16e half-sandwich complexes containing one or two B-H functionalized vinyl groups in the B(3,6) positions of carborane<sup>[27]</sup>. As a continuation of this interesting chemistry, herein we report the stoichiometric reaction between CpCo(S<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) (**1**) with HC≡CC(O)Fc.

## 1 Experimental

### 1.1 Reagents and instruments

All experiments were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried by refluxing over sodium (petroleum ether, ether, and THF) or calcium hydride (CH<sub>2</sub>Cl<sub>2</sub>) under nitrogen and then distilled prior to use. CpCo(S<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>) (**1**)<sup>[1-2]</sup> and HC≡CC(O)Fc<sup>[31]</sup> were prepared according to the literature methods. Ferrocenecarbaldehyde (Alfa Aesar), and *n*-butyllithium (2.0 mol · L<sup>-1</sup> in cyclohexane, Sigma-

Aldrich) were used as commercial products without further purification. Elemental analyses were performed in an elemental vario EL III elemental analyzer. NMR data were recorded on a Bruker DRX-500 spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were reported in ppm with respect to CHCl<sub>3</sub>/CDCl<sub>3</sub> (δ(<sup>1</sup>H)=7.24, δ(<sup>13</sup>C)=77.0) and <sup>11</sup>B NMR spectra were reported in ppm with respect to external Et<sub>2</sub>O · BF<sub>3</sub> (δ(<sup>11</sup>B)=0). The IR spectra were recorded on a Bruker Tensor 27 spectrophotometer with KBr pellets in the 4 000 ~ 400 cm<sup>-1</sup> region. The mass spectra were recorded on Micromass GC-TOF for EI-MS (70 eV) or Finnigan MAT TSQ7000 for ESI-MS.

### 1.2 Synthesis of 2

HC≡CC(O)Fc (71.4 mg, 0.3 mmol) was added to the solution of **1** (99.0 mg, 0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and the mixture was stirred for 12 h at ambient temperature. After removal of solvent, the residue was chromatographed on TLC. Elution with CH<sub>2</sub>Cl<sub>2</sub>/ether (10:1, V/V) gave **2**. (brown-red solid). yield 37% (63.1 mg), mp 193 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 7.02 (d, 1H, *J*=18 Hz, B-CH=CH), 6.37 (d, 1H, *J*=18 Hz, B-CH=CH), 5.37 (s, 5H, Cp), 4.87 (m, 2H, Fc-CH), 4.61 (m, 2H, Fc-CH), 4.23 (s, 5H, Fc-Cp). <sup>11</sup>B NMR (CDCl<sub>3</sub>, ppm): δ -1.3 (1B), -3.6 (2B), -4.4 (2B), -6.7 (1B), -7.6 (4B). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): δ 192.69 (CO), 139.56 (B-CH=CH), 135.58 (br, B-CH=CH), 96.81 (carborane), 81.59 (Cp), 79.71 (Fc-C), 73.22 (Fc-CH), 69.94 (Fc-CH), 70.74 (Fc-Cp). IR (KBr): ν (cm<sup>-1</sup>): 1 642 (C=O), 2 585 (B-H). EI-MS (70 eV): *m/z* 568.0 (M<sup>+</sup>, 100%). Anal. calcd. for C<sub>20</sub>H<sub>25</sub>B<sub>10</sub>OS<sub>2</sub>FeCo (%): C, 42.26; H, 4.43. Found(%): C, 42.05; H, 4.54.

### 1.3 Synthesis of 3

HC≡CC(O)Fc (23.8 mg, 0.1 mmol) was added to the solution of **2** (56.8 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and the mixture was stirred for 12 h at ambient temperature. After removal of solvent, the residue was chromatographed on TLC. Elution with CH<sub>2</sub>Cl<sub>2</sub>/ether (10:1 of volume) gave **3**. Brown-red solid, yield 86% (69.3 mg), mp 217 °C dec. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): δ 7.05 (d, 2H, *J*=18 Hz, B-CH=CH), 6.26 (d, 2H, *J*=18 Hz, B-CH=CH), 5.43 (s, 5H, Cp), 4.87 (m, 4H, Fc-CH), 4.61 (m, 4H, Fc-CH), 4.24 (s, 10H, Fc-Cp). <sup>11</sup>B NMR (CDCl<sub>3</sub>, ppm): δ -2.0 (1B), -4.8 (4B), -8.1 (5B). <sup>13</sup>C NMR

( $\text{CDCl}_3$ , ppm):  $\delta$  192.63 (CO), 139.72 (B-CH=HH), 135.32 (br, B-CH=CH), 98.22 (carborane), 81.44 (Cp), 79.77 (Fc-C), 73.19 (Fc-CH), 70.40 (Fc-Cp), 69.97 (Fc-CH). IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ): 1 648 (C=O), 2 579 (B-H). ESI-MS (negative ion mode,  $m/z$ ): 805.7 ( $[\text{M-H}]^-$ , 63%). Anal. calcd. for  $\text{C}_{33}\text{H}_{35}\text{B}_{10}\text{O}_2\text{S}_2\text{Fe}_2\text{Co}$ (%): C, 49.15; H, 4.37. Found(%): C, 48.98; H, 4.29.

#### 1.4 Synthesis of 4

$\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  (119 mg, 0.5 mmol) was added to the solution of **1** (33 mg, 0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL), and the mixture was stirred for 12 h at ambient temperature. After removal of solvent, the residue was chromatographed on TLC. Elution with  $\text{CH}_2\text{Cl}_2$ /ether (10:1, V/V) gave **3** and **4**. **4**: brown-red solid, yield 5% (5.9 mg), mp 295 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  8.84 (s, 1H, Ph-CH), 4.94 (m, 2H, Fc-CH), 4.66 (m, 2H, Fc-CH), 4.30 (s, 5H, Fc-Cp).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$

197.91 (CO), 139.65 (Ph-CH), 131.20 (Ph-C), 77.75 (Fc-C), 73.07 (Fc-CH), 71.60 (Fc-CH), 70.48 (Fc-Cp). EI-MS (70 eV):  $m/z$  714.1 ( $\text{M}^+$ , 100%). IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ): 1 635 (CO). Anal. calcd. for  $\text{C}_{39}\text{H}_{30}\text{O}_3\text{Fe}_3\cdot\text{H}_2\text{O}$ (%): C, 63.97; H, 4.41. Found(%): C, 63.79; H, 4.35.

#### 1.5 X-ray crystal structure determination

X-ray crystallographic data<sup>[32]</sup> were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo  $K\alpha$  ( $\lambda=0.071\,073\text{ nm}$ ) 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**, **3** and **4** are listed in Table 1. Selected bond distances and bond angles are listed in Table 2.

CCDC: 813827, **2**; 813828, **3**; 802195, **4**.

Table 1 Crystal and structure refinement data for complexes **2**, **3** and **4**

|   | <b>2</b>   | <b>3</b>   | <b>4</b>   |
|---|--|--|--|
| Empirical formula                                     | $\text{C}_{20}\text{H}_{25}\text{B}_{10}\text{CoFeOS}_2$ | $\text{C}_{33}\text{H}_{35}\text{B}_{10}\text{CoFe}_2\text{O}_2\text{S}_2$ | $\text{C}_{39}\text{H}_3\text{Fe}_3\text{O}_3\cdot\text{H}_{20}$ |
| Crystal size / mm                                     | 0.28×0.24×0.22   | 0.28×0.24×0.22   | 0.28×0.24×0.22   |
| Formula weight  | 568.40   | 806.46   | 732.20   |
| Temperature / K                                       | 291(2)   | 291(2)   | 291(2)   |
| Crystal system  | Monoclinic   | Orthorhombic   | Triclinic  |
| Space group   | $P2_1/c$   | $Pnma$   | $P\bar{1}$   |
| $a$ / nm  | 1.579 91(15)   | 1.408 7(2)   | 1.161 82(16)   |
| $b$ / nm  | 1.196 69(11)   | 2.197 6(4)   | 1.205 64(17)   |
| $c$ / nm  | 1.391 76(13)   | 1.146 92(19)   | 1.464 2(2)   |
| $\alpha$ / (°)  |  |  | 103.998(2)   |
| $\beta$ / (°)   | 98.742 0(10)   |  | 102.540(3)   |
| $\gamma$ / (°)  |  |  | 113.812(2)   |
| $V$ / nm <sup>3</sup>                                 | 2.600 8(4)   | 3.550 5(10)  | 1.702 3(4)   |
| $Z$   | 4  | 4  | 2  |
| $D_c$ / ( $\text{g}\cdot\text{cm}^{-3}$ )             | 1.452  | 1.509  | 1.428  |
| Absorp. coeff. / $\text{mm}^{-1}$                     | 1.370  | 1.418  | 1.300  |
| $F(000)$  | 1 152  | 1 640  | 752  |
| $\theta$ range / (°)                                  | 2.14~26.00   | 1.85~26.00   | 1.99~26.00   |
| Reflns collected ( $R_{\text{int}}$ )                 | 13 983 (0.028 1)   | 18 227 (0.089 5)   | 9 383 (0.031 2)  |
| Indep. reflns   | 5 099  | 3 584  | 6 566  |
| Refns obs. ( $I>2\sigma(I)$ )                         | 4 251  | 2 278  | 4 534  |
| Data / restr. / paras                                 | 5 099 / 0 / 316  | 3 584 / 0 / 238  | 6 566 / 0 / 430  |
| GOF   | 1.090  | 1.021  | 1.091  |
| $R_1$ / $wR_2$ ( $I>2\sigma(I)$ )                     | 0.03 82 / 0.089 5  | 0.063 1 / 0.124 4  | 0.058 9 / 0.123 5  |
| $R_1$ / $wR_2$ (all data)                             | 0.047 9 / 0.091 7  | 0.098 7 / 0.130 4  | 0.079 0 / 0.127 5  |
| Larg. peak / hole / ( $\text{e}\cdot\text{nm}^{-3}$ ) | 231 / -312   | 357 / -515   | 449 / -606   |

**Table 2** Selected bond lengths (nm) and bond angles (°) for the complexes **2**, **3** and **4**

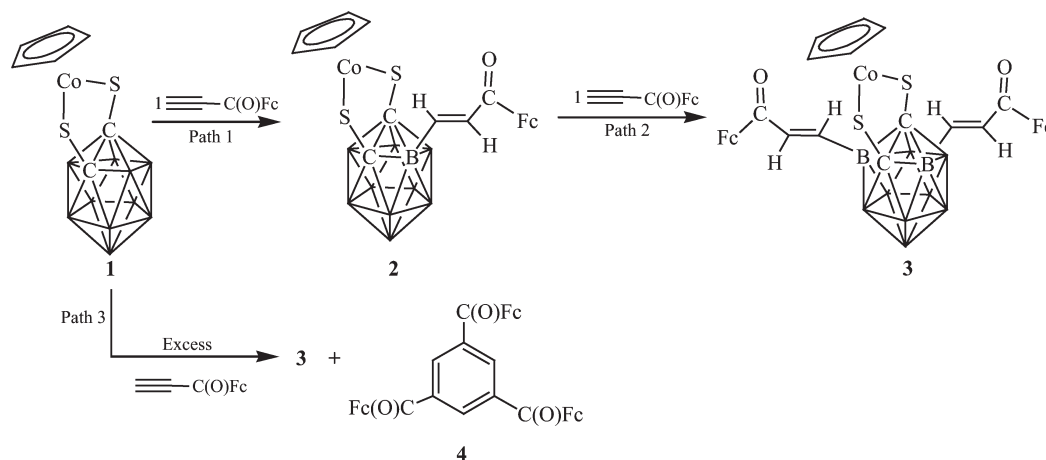
| <b>2</b>  |             |           |             |           |            |
|-----------|-------------|-----------|-------------|-----------|------------|
| B3-C3     | 0.153 8(4)  | B3-C2     | 0.174 7(3)  | B3-C1     | 0.175 0(3) |
| C1-C2     | 0.165 0(3)  | C1-S1     | 0.177 5(2)  | C2-S2     | 0.178 9(2) |
| C3-C4     | 0.130 1(4)  | C4-C5     | 0.148 5(3)  |           |            |
| Co1-S1    | 0.212 25(7) | Co1-S2    | 0.213 60(8) |           |            |
| C3-B3-C2  | 121.5(2)    | C3-B3-C1  | 120.6(2)    | C2-B3-C1  | 56.31(13)  |
| C2-C1-S1  | 116.51(15)  | B3-C1-S1  | 116.22(15)  | C1-C2-B3  | 61.95(14)  |
| C1-C2-S2  | 114.99(16)  | B3-C2-S2  | 115.96(16)  | C4-C3-B3  | 125.6(2)   |
| C3-C4-C5  | 123.0(2)    | S1-Co1-S2 | 97.35(3)    |           |            |
| C1-S1-Co1 | 105.44(8)   | C2-S2-Co1 | 105.44(8)   |           |            |
| <b>3</b>  |             |           |             |           |            |
| B3-C1     | 0.175 6(6)  | B3-C2     | 0.176 0(6)  | B3-C3     | 0.155 1(7) |
| C1-C2     | 0.162 6(9)  | C1-S1     | 0.178 6(6)  | C2-S2     | 0.178 5(7) |
| C3-C4     | 0.133 2(6)  | Co1-S1    | 0.212 6(2)  | Co1-S2    | 0.212 7(2) |
| C3-B3-C1  | 120.0(4)    | C3-B3-C2  | 118.0(4)    | C2-C1-B3  | 62.6(3)    |
| C2-C1-S1  | 116.3(4)    | C1-C2-B3  | 62.3(3)     | C1-C2-S2  | 115.7(4)   |
| B3-C2-S2  | 115.9(3)    | C3-C4-C5  | 124.9(5)    | S1-Co1-S2 | 97.30(7)   |
| C1-S1-Co  | 1105.2(2)   | C2-S2-Co  | 1105.5(2)   |           |            |
| <b>4</b>  |             |           |             |           |            |
| C1-C6     | 0.138 8(6)  | C1-C2     | 0.140 3(5)  | C2-C3     | 0.140 9(6) |
| C3-C4     | 0.139 6(6)  | C4-C5     | 0.142 6(6)  | C5-C6     | 0.139 5(5) |
| C6-C1-C2  | 118.9(4)    | C1-C2-C3  | 121.2(4)    | C4-C3-C2  | 119.1(4)   |
| C3-C4-C5  | 120.0(4)    | C6-C5-C4  | 119.1(4)    | C1-C6-C5  | 121.5(4)   |

## 2 Results and discussion

### 2.1 Synthesis of complexes

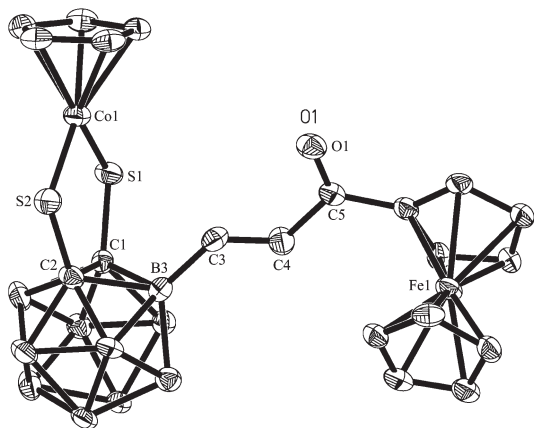
The reaction of **1** with  $\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  in a ratio of 1:1 in  $\text{CH}_2\text{Cl}_2$  at ambient temperature leads to **2** with a

yield of 37%. **2** could further react with the alkyne to generate **3** in a yield of 86%. Treatment of **1** with excess  $\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  under the same reaction conditions affords **3** along with the alkyne trimerized compound **4** as a minor product in a yield of 5% (Scheme 1).

Scheme 1 Synthesis of **2**–**4**

## 2.2 Structure of 2

The single-crystal X-ray diffraction analysis shows that **2** crystallizes in  $P2_1/c$  space group. The molecular structure, as seen in Fig.1, shows that  $\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  is added to the starting compound **1** at the B(3) site of the carborane cage. And the hydrogen atom of the BH bond has been transferred to the internal carbon of the alkyne to form the olefinic unit in an E configuration. As a result, the  $\text{C}\equiv\text{C}$  bond of the alkyne is reduced to a  $\text{C}=\text{C}$  bond (0.130 1 nm). The five-membered ring S(1)Co(1)S(2)C(2)C(1) is no longer planar which is slightly bent at the S(1)⋯S(2) vector with an angle of  $175.0^\circ$  owing to the alkyne addition. The  $^1\text{H}$  NMR data demonstrate a B-monosubstituted product as well as reflected by the integrals.

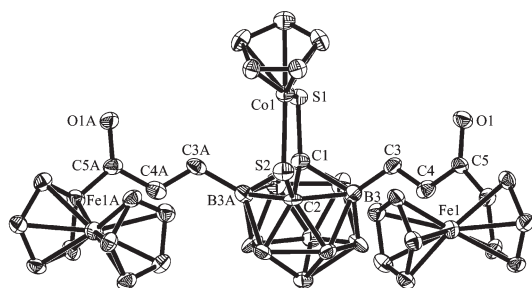


All hydrogen atoms are omitted for clarity

Fig.1 Molecular structure of **2** with thermal ellipsoids at 30% probability

## 2.3 Structure of 3

The single-crystal X-ray diffraction analysis shows that **3** crystallizes in  $Pnma$  space group. As shown in Fig.2, the second  $\text{HC}\equiv\text{CC}(\text{O})\text{Fc}$  molecule is added to **2**



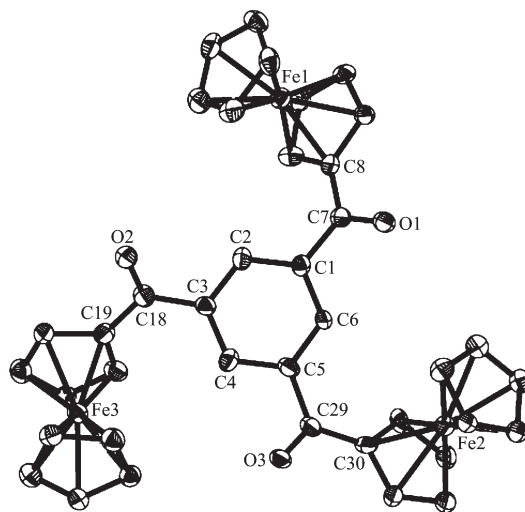
All hydrogen atoms are omitted for clarity

Fig.2 Molecular structure of **3** with thermal ellipsoids at 30% probability

at the B(6) site of carborane. The resulting two olefinic units take *E/E* configurations. **3** is a symmetrical molecule, thus the five-membered ring S(1)Co(1)S(2)C(2)C(1) is planar. The  $^1\text{H}$  NMR data show a B-disubstituted product as well, and both  $^1\text{H}$  and  $^{13}\text{C}$  data are parallel to those of the B-monosubstituted product **2**.

## 2.4 Structure of 4

The single-crystal X-ray diffraction analysis indicates that **4** crystallizes in  $P\bar{1}$  space group. The molecular structure (Fig.3) shows that **2** is a 1,3,5-trisubstituted benzene derivative generated from the alkyne cyclotrimerization. Since **2** is symmetric, its  $^1\text{H}$  NMR spectrum displays only one singlet at 8.84 ppm for the CH units in the benzene ring as well as one set of peaks from the ferrocenyl groups. The EI-MS measurement gives the  $\text{M}^+$  peak at 714.1 with an abundance of 100%.



All hydrogen atoms are omitted for clarity

Fig.3 Molecular structure of **4** with thermal ellipsoids at 30% probability

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