钴(Ⅲ)催化 CpCoS₂C₂B₁₀H₁₀ 分子内 B(3)/B(6)位和 Cp 配体偶联

叶红德*,1,2　徐宝华¹　胡久荣²　燕　红*,1

(¹ 南京大学化学化工学院,配位化学国家重点实验室,南京　210093)

(² 上饶师范学院化学化工学院,上饶　334001)

摘要：半夹芯 16e 化合物 CpCoS₂C₂B₁₀H₁₀(Cp:cyclopentadienyl) (**1**)与 HC≡CCO₂Me 在 2-甲基二硫代丙酸存在下反应生成化合物 {(C₅H₄CoS₂C₂B₉H₉)(CH=CHCO₂Me)(Me₂C=CS₂H)} (**2**)和(Me₂C=CS₂H)₃Co (**3**)。在化合物 **2** 中,原料化合物 **1** 中的一个 S-Co 键断裂,该 S 原子与一分子 HC≡CCO₂Me 末端炔基碳原子连接。Co 原子与 2-甲基二硫代丙酸的 S 原子连接成键,2-甲基二硫代丙酸分子中的 SH 基团与 Co 原子通过配位键相连;同时,Cp 环的一个碳原子与碳硼烷笼体的 B(3)/B(6)位相连,该 B(3)/B(6)位的氢原子迁移到炔烃 HC≡CCO₂Me 的内部炔基碳原子上形成反式烯键。3 个 2-甲基二硫代丙酸分子中的 3 个 S 原子分别与 **1** 中的 Co 原子通过共价键连接,3 个 SH 基团与 Co 原子通过配位键相连,从而形成化合物 **3**。化合物 **2** 和 **3** 分别用红外、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：钴；碳硼烷；配体；偶联

Cobalt(Ⅲ)-Mediated Intramolecular Coupling of B(3)/B(6) in CpCoS₂C₂B₁₀H₁₀ with Cp Ligand

YE Hong-De*,1,2　XU Bao-Hua¹　HU Jiu-Rong²　YAN Hong*,1

(¹*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*)

(²*School of Chemistry and Chemical Engineering, Shangrao Normal University, Shangrao, Jiangxi 334001, China*)

Abstract: Half-sandwich 16e complex CpCoS₂C₂B₁₀H₁₀ (Cp: cyclopentadienyl) (**1**) reacted with HC≡CCO₂Me in the presence of 2-methylpropanedithioic acid to generate compounds {(C₅H₄CoS₂C₂B₉H₉)(CH=CHCO₂Me)(Me₂C=CS₂H)} (**2**) and (Me₂C=CS₂H)₃Co (**3**). In **2**, one S-Co bond of **1** was broken, and the S atom linked with the terminal acetylenyl carbon atom of the HC≡CCO₂Me. Meanwhile, the Co atom in **1** linked to the S atom in 2-methylpropanedithioic acid with covalent bond while linked to the SH unit with coordinative bond. One carbon atom of Cp ring linked to the B(3)/B(6) cite of the carborane cage. The H atom of the B(3)/B(6) cite migrated to the internal acetylenyl carbon atom to form a trans-ethylenic bond. The Co atom of **1** linked to three S atoms of three 2-methylpropanedithioic acid molecules with covalent bond, while linked to the other three SH units with coordinative bond. As a result, product **3** formed. Complexes **2** and **3** have been characterized by IR, NMR, elemental analysis, mass spectrum and single-crystal X-ray diffraction analysis. CCDC: 1053736, **2**; 1053737, **3**.

Key words: cobalt; carborane; ligand; couple

0　Introduction

The 16e half-sandwich complexes $Cp*ME_2C_2B_{10}H_{10}$ (M=Co, Rh, Ir; E=S, Se) and $(p\text{-cymene})MS_2C_2B_{10}H_{10}$ (M =Ru, Os) are stabilized as monomers by the voluminous pentamethylcyclopentadienyl (Cp*) and 1,2-dicarba-closo-dodecarborane-1,2-dichalcogenolato ligands[1-3]. The combination of electron deficiency at the coordinatively unsaturated metal centre and reactivity of metal-chalcogen bonds renders these complexes promising precursors for synthesis of mixed-metal clusters[4]. Besides, they could serve as interesting candidates for reactions with unsaturated substrates such as alkynes. The range of reactions turned out to be rather wide from catalytic cyclotri-merization or dimerization of the alkyne[5-6] to stepwise B(3)/(6)-substitution at the carborane cage, and numerous intermediates have been isolated[6-13].

Our previous work has indicated that the cobalt complexes $CpCoS_2C_2B_{10}H_{10}$ and $CpCoSe_2C_2B_{10}H_{10}$ are more reactive than their rhodium and iridium analo-gues[6-7]. Their reactivity with methyl acetylene carbo-xylate leads to new complexes as the result of consecutive steps, in which the metal center and the metal-chalcogen bonds are involved as well as the B-H activation at the B(3)/B(6) cite of the o-carborane cage (Scheme 1)[7]. Recently, we have carried out the three-component reaction of $CpCoS_2C_2B_{10}H_{10}$ (1), $HC \equiv CCO_2Me$ and pyrrolidine-1-carbodithioic acid[14], which afforded selective B-functionalization at the carborane cage with Cp as a functional group. Herein, we report the three-component reaction of 1, $HC \equiv CCO_2Me$ and 2-methylpropanedithioic acid. One cobalt-promoted B-H and C-H activation product and one carborane-free cobalt(Ⅲ) complex have been isolated.
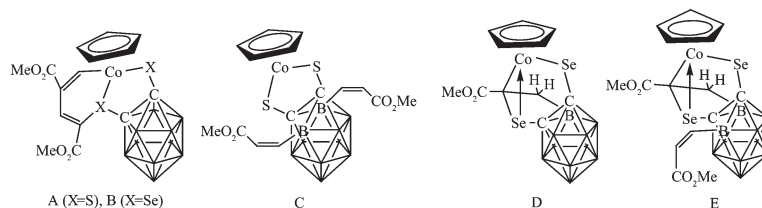
Scheme 1　Some examples of complexes from the reactions of $CpCoS_2C_2B_{10}H_{10}$ (or $CpCoSe_2C_2B_{10}H_{10}$) with $HC \equiv CCO_2Me$[7]

1　Experimental

1.1　Reagents and instruments

All reactions and manipulations 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_2Cl_2) under nitrogen and then distilled prior to use. $CpCo(CO)I_2$[15] and $CpCoS_2C_2B_{10}H_{10}$ (1)[16] were prepared according to the reported procedures. Elemental analyses were performed in an Elementar Corporation Vario EL Ⅲ elemental analyzer. NMR data were recorded on a Bruker DRX-500 spectro-meter. ^1H NMR and ^{13}C NMR spectra were reported with respect to $CHCl_3/CDCl_3$ (δ ^1H=7.24, δ ^{13}C=77.0) and ^{11}B NMR spectra were reported with respect to external $Et_2O \cdot BF_3$ (δ ^{11}B =0). The IR spectra were recorded on a Bruker Tensor 27 spectrophotometer

with KBr pellets in the 4 000~400 cm^{-1} region. The mass spectra were recorded on Micromass GC-TOF for EI-MS (70 eV).

1.2　Synthesis of 2 and 3

$HC \equiv CCO_2Me$ (210.2 mg, 2.5 mmol) and 2-methylpropanedithioic acid (120.2 mg, 1.0 mmol) were added to the solution of 1 (165.2 mg, 0.5 mmol) in CH_2Cl_2 (25 mL), and the mixture was stirred for 24 h at room temperature to give a deep green solution. After removing the solvent, the residue was purified on the thin layer chromatography gel and elution with petroleum ether/CH_2Cl_2 (2:1) gave 2 and 3 (Scheme 2). Recrystallization from CH_2Cl_2/petrol ether afforded crystals of 2 and 3.

2: blue solid, yield 165.1 mg (62% based on 1), m.p. 202 ℃ dec. ^1H NMR $(CDCl_3)$: δ 3.12 (s, 3H, Me), 3.14 (s, 3H, Me), 3.80 (s, 3H, OMe), 4.85 (s, 1H, Cp-CH), 5.28 (s, 1H, Cp-CH), 5.81 (s, 1H, Cp-CH),
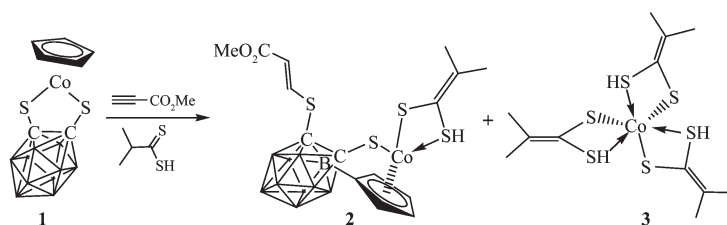
Scheme 2　Synthesis of **2** and **3**

5.97 (s, 1H, Cp-CH), 6.30 (d, J=16 Hz, 1H, S-CH=), 7.95 (d, J=16 Hz, 1H, =CH-C(O)). ^{13}C NMR: δ 38.06 (Me), 51.98 (OMe), 83.30 (Cp-CH), 83.97 (Cp-CH), 84.36 (Cp-CH), 92.28 (Cp-CH), 89.71 (carborane), 117.04 (carborane), 120.48 (S-CH), 126.25 (br, Cp-C), 128.20 (Me$_2C$ =), 143.09 (=CH-C (O)), 164.55 (C =O), 203.05 (=CS$_2$). ^{11}B NMR (CDCl$_3$): δ −12.7 (1B), −9.3 (4B), −5.3 (2B), −1.7 (3B). EI-MS: m/z 533.1 (M$^+$, 26%). IR (KBr, ν / cm^{-1}): 1 670 (C=O), 1 717 (S-C-S), 2 582 (B-H). Elemental analysis: Calcd. for C$_{15}$H$_{25}$B$_{10}$CoO$_2$S$_4$ (%): C, 33.82; H, 4.73. Found(%): C, 34.05; H, 4.57.

3: green solid, yield 16.6 mg (8% based on **1**), m.p. 223 ℃ dec. ^{1}H NMR (CDCl$_3$): δ 3.27 (s, 18H, Me). ^{13}C NMR: δ 37.66 (Me), 134.58 (Me$_2C$=), 205.41 (=CS$_2$). EI-MS (70 eV): m/z 416.2 (M$^+$, 6%). IR (KBr, ν / cm^{-1}): 1 729 (S-C-S), 1 523 (C=C). Elemental analysis: Calcd. for C$_{12}$H$_{21}$CoS$_6$(%): C 34.59, H 5.08. Found(%): C 34.82, H 4.87.

1.3　X-ray crystal structure determination

　　X-ray crystallographic data were collected on a Bruker SMART Apex Ⅱ CCD diffractometer using graphite-monochromated Mo $K\alpha$ (λ =0.071 073 nm) radiation. The intensities were corrected for Lorentz polarization effects and empirical absorption with the SADABS program[17]. The structures were solved by direct methods using the SHELXS-97 program[18] and refined by full-matrix least-squares techniques on F^2 with the SHELXL-97 program[19]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically and refined isotropically using the riding model. Crystal data, data collection parameters and the results of the analyses of **2** and **3** are listed in Table 1. Selected bond lengths and bond angles are listed in Table 2.

　　CCDC: 1053736, **2**; 1053737, **3**.

Table 1　Crystal and structure refinement data for 2 and 3

Compound	**2**	**3**
Formula	C$_{15}$H$_{25}$B$_{10}$CoO$_2$S$_4$	C$_{13}$H$_{21}$CoS$_6$Cl$_2$
Crystal size / mm	0.26×0.22×0.20	0.26×0.24×0.20
Formula weight	532.62	499.48
Temperature / K	291(2)	291(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	0.763 97(15)	0.917 40(13)
b / nm	1.257 0(2)	0.947 92(14)
c / nm	1.320 2(3)	1.268 96(18)
α / (°)	95.905(2)	75.226(2)
β / (°)	104.690(2)	88.107(2)
γ / (°)	90.226(2)	82.341(2)
V / nm^3	1.219 3(4)	1.057 5(3)
Z	2	8
D_c / (g·cm^{-3})	1.451	1.569
Absorption coefficient / mm^{-1}	1.059	1.649
F(000)	544	512

Continued Table 1

θ range / (°)	2.16~27.00	2.24~26.00
Reflns collected	7 115 (R_{int}=0.003 6)	5 804 (R_{int}=0.093 3)
Independent reflns	5 118	4 070
Reflns observation ($I>2\sigma(I)$)	3 705	3 229
Data / restrained / paras	5 118 / 0 / 292	4 070 / 6 / 205
GOF	1.088	1.052
Final R indices ($I>2\sigma(I)$)	R_1=0.049 1, wR_2=0.122 7	R_1=0.061 7, wR_2=0.171 5
R indices (all data)	R_1=0.055 2, wR_2=0.123 4	R_1=0.071 9, wR_2=0.184 7
Largest diff. peak and hole / (e·nm⁻³)	446 and −393	932 and −889

Table 2　Selected bond lengths (nm) and bond angles (°) for 2 and 3

2					
C1-C2	0.169 3(5)	C1-S1	0.179 3(4)	C2-S2	0.178 3(4)
C3-S1	0.173 7(4)	C3-C4	0.131 3(5)	B3-C11	0.156 9(6)
Co1-S2	0.228 71(12)	Co1-S3	0.225 06(12)	Co1-S4	0.225 93(11)
S3-C7	0.170 1(4)	S4-C7	0.170 9(4)	C7-C8	0.132 0(5)
C1-S1-C3	101.56(18)	S1-C3-C4	122.1(3)	C2-C1-S1	113.5(2)
C1-C2-S2	116.3(2)	C2-S2-Co1	104.30(13)	B3-C11-Co1	118.2(3)
C2-B3-C11	112.9(3)	S2-Co1-S3	91.69(4)	S2-Co1-S4	97.06(4)
Co1-S3-C7	86.77(13)	Co1-S4-C7	86.29(13)	S3-C7-S4	110.1(2)
3					
C1-C2	0.131 6(6)	C3-C4	0.130 8(6)	C5-C6	0.131 2(6)
Co1-S1	0.227 69(13)	Co1-S2	0.226 81(12)	Co1-S3	0.226 76(13)
Co1-S4	0.226 72(12)	Co1-S5	0.227 64(13)	Co1-S6	0.226 71(12)
S1-C1-S2	110.1(2)	S3-C3-S4	110.0(3)	S5-C5-S6	110.4(3)
S1-Co1-S2	76.23(5)	S3-Co1-S4	76.44(5)	S5-Co1-S6	76.30(4)

2　Results and discussion

2.1　Structure of 2

The X-ray structure of **2** (Fig.1) displays a B-C bond bridging the carborane cage and the Cp ligand. The B-C bond distance (0.156 9(6) nm) is much the same as the B-C length in trimethylborane (0.157 8 nm)[20]. S(2) has disconnected from cobalt center and then connected with the S-CH=CHCO₂Me unit. The newly generated five-membered ring (Co(1)S(2)C(2)B(3)C(11)) is almost perpendicular to the Cp ring and fused with CpCo unit at Co(1)-C(11) bond resulting in a relative rigid Cp ring. On the other hand, the solid-state structure bears an auxiliary ligand, 2-methylprop-1-ene-1,1-dithiol anion, rearranged from 2-methylpropanedithioic acid in a bidentate κ^2-S,S′ mode. An important change is that the C(7)-C(8) bond (0.132 0(5)

nm) has been shortened, which indicates that it's a C=C bond. Furthermore, the hydrogen atom at the B(3)
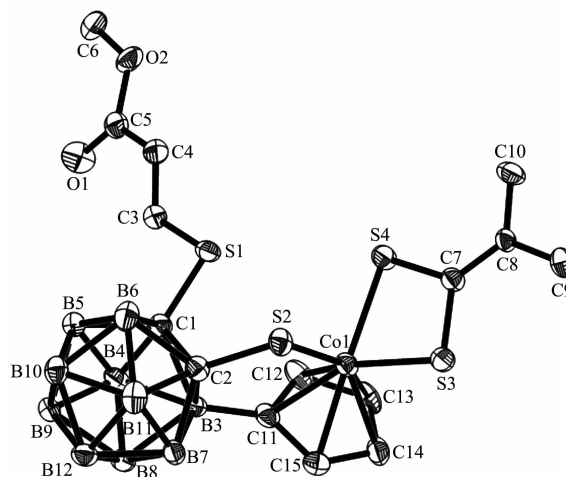

Fig.1　Molecular structure of **2** with 30% thermal ellipsoids

position of the carborane cage has been transferred to the terminal carbon of the alkyne to generate an olefinic substituent in a trans arrangement at the S(1) atom[14]. The torsion angle of S(1)C(1)C(2)S(2) (8.7°) doesn't change too much as compared with 9.7° in **1**[12].

Considering the charge compensation in the environment of cobalt center, the hydrogen atom bounded to the S(4) atom was located by constrained method. Thus, the S(4)→Co coordinative bond and two other S-Co covalent bond, together with a η^5-C_5H_5 ligand allow the metal to attain 18-electron configuration. This is consistent with the observed properties of **2**. **2** is a neutral compound and exhibits normal NMR spectra with no evidence of paramagnetism. However, spectroscopic data are not consistent with the structure in Fig.1, since there is no signature for the S-H functional group in ¹H NMR spectra. This implies the presence of an "extra" hydrogen atom in the vicinity of Co(1), probably bridging between the metal and one or more nearby sulfur atoms and completing an 18-electron metal configuration. The possibility of these extra hydrogens variably adopting M-H-S bridging (η^2), H-MS$_2$ face-bridging (η^3), or M-H$_{terminal}$ (η^3) modes is convinced since instead of sulfur such bonding types for boron atoms are a well-known feature in small metallaborane and metallacarborane clusters (especially those Co, Fe and Ru clusters)[21-25].

With above comprehensible exception, spectroscopic and analytical data of **2** are consistent with its solid-state structure. In the ¹H NMR data, four distinguishable signals assigned to the hydrogen atoms of the substituted Cp ring could be attributed to their inequivalent chemical environment. The ¹H NMR spectrum also shows three singlets assigned to OMe (3.80) and Me₂C (3.14, 3.12) groups as well as two doublets (6.30, 7.95) owing to ^3J(¹H, ¹H) across the C=C bond. The large coupling constant (*J*=16 Hz) corresponds to an *E* configuration as confirmed by the solid-state structure. Characteristic resonances for CH units of the substituted Cp ring at about 83.30, 83.97, 84.36 and 92.28 were found in the ¹³C NMR spectra.

2.2　Structure of 3

The single-crystal X-ray diffraction (Fig.2) shows

that **3** is a neutral complex. The cobalt atom is located at the apparent intersection of D_3 symmetry and surrounded by six sulfur atoms in a distorted octahedral environment. Despite the apparent presence of the rotational axes, all of the atoms in the structure were found to be unique; there are no symmetry-related atoms. The average distance of three carbon-carbon bonds (C(1)-C(2), C(3)-C(4) and C(5)-C(6)) is 0.131 nm, showing that they are double bonds[7]. Recently, a similar compound has been synthesized in the two-component reaction of **1** with 2-methylpropanedithioic acid[26]. However, three carbon-carbon bonds are single bonds rather than double bonds.
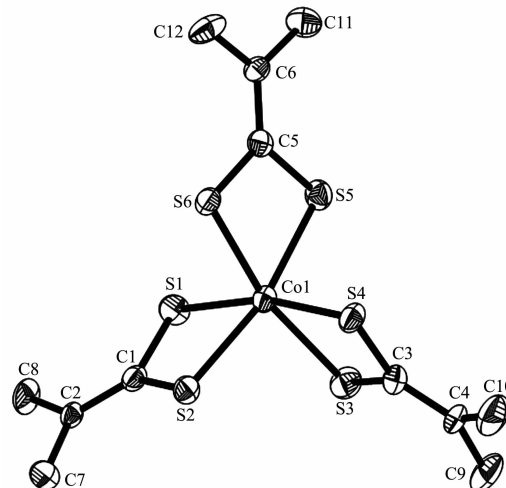

Fig.2　Molecular structure of **3** with 30% thermal ellipsoids

For the same reason explained for the structure of the complex **2**, three hydrogen were constrainedly located at S(2), S(4) and S(5), respectively, and there were no signals in ¹H NMR spectra. However, the spectroscopic and analytical data support its principal part in the solid-state structure. The singlet at 3.27 was assigned to the alkyl group of the Me₂C unit as expected for a symmetrical structure.

The work described here sheds light on a relatively unexplored facet of *o*-carborane chemistry. Further experimental and theoretical work is underway.

References:

[1] Herberhold M, Jin G X, Yan H, et al. *Eur. J. Inorg. Chem.*,

1999,**5**:873-875

[2] Herberhold M, Jin G X, Yan H, et al. *J. Organomet. Chem.*, **1999**,**587**:252-257

[3] Bae J Y, Park Y L, Ko J, et al. *Inorg. Chim. Acta*, **1999**,**289**: 141-148

[4] Liu S, Han Y F, Jin G X. *Chem. Soc. Rev.*, **2007**,**36**:1543-1560

[5] Herberhold M, Yan H, Milius W, et al. *Organometallics*, **2000**,**19**:4289-4294

[6] Xu B H, Wu D H, Li Y Z, et al. *Organometallics*, **2007**,**26**: 4344-4349

[7] Xu B H, Tao J C, Li Y Z, et al. *Organometallics*, **2008**,**27**: 334-340

[8] Herberhold M, Yan H, Milius W, et al. *Chem. Eur. J.*, **2000**, **6**:3026-3032

[9] Herberhold M, Yan H, Milius W, et al. *J. Chem. Soc., Dalton Trans.*, **2001**:1782-1789

[10]Herberhold M, Yan H, Milius W, et al. *Angew. Chem. Int. Ed.*, **1999**,**38**:3689-3691

[11]Herberhold M, Yan H, Milius W, et al. *Z. Anorg. Allg. Chem.*, **2000**,**626**:1627-1633

[12]Kim D H, Ko J, Park K, et al. *Organometallics*, **1999**,**18**: 2738-2740

[13]Won J H, Kim D H, Kim B Y, et al. *Organometallics*, **2002**, **21**:1443-1453

[14]Zhang R, Zhu L, Liu G F, et al. *J. Am. Chem. Soc.*, **2012**,

134:10341-10344

[15]Frith S A, Spencer J L. *Inorg. Synth.*, **1990**,**28**:273-280

[16]Hou X F, Wang X, Wang J Q, et al. *J. Organomet. Chem.*, **2004**,**689**:2228-2235

[17]Sheldrick G M. *SADABS, An Empirical Absorption Correction Program*, Bruker Analytical X-ray Systems, Madison, WI, **1996**.

[18]Sheldrick G M. *SHELXS*-97, *Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**.

[19]Sheldrick G M. *SHELXL*-97, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.

[20]Boese R, Blaser D, Niederprum N, et al. *Angew. Chem. Int. Ed.*, **1992**,**31**:314-316

[21]Yao H J, Grimes R N. *Organometallics*, **2003**,**22**:4539-4546

[22]Russell J M, Sabat H, Grimes R N. *Organometallics*, **2002**, **21**:5613-5621

[23]Yan H, Beatty A M, Fehlner T P. *Angew. Chem. Int. Ed.*, **2001**,**40**:4498-4501

[24]Yan H, Beatty A M, Fehlner T P. *Angew. Chem. Int. Ed.*, **2002**,**41**:2578-2581

[25]Yan H, Beatty A M, Fehlner T P. *J. Am. Chem. Soc.*, **2002**, **124**:10280-10281

[26]Zhang R, Zhu L, Lu Z Z, et al. *Dalton Trans.*, **2012**,**41**: 12054-12063