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一个含呋喃环顺磁性碳硼烷衍生物的合成及其生成机理

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摘要: 半夹芯 16e 化合物 $CpCoS_2C_2B_{10}H_{10}$(Cp: cyclopentadienyl)(**1**)与 2-呋喃炔酮在物质的量比为 1:1.5 时反应分离得到 1 个顺磁性化合物 $CpCoS_2C_2B_{10}H_9(C_{12}H_{10}O_2)$(**2**)。在化合物 **2** 的合成过程中,一分子 **1** 中的 Cp 环与另一分子 **1**中的 B(3)/B(6)位连接;同时,该 Cp 环与 1 个 2-呋喃炔酮分子发生 Diels-Alder 反应,生成 1 个双环[2.2.1]-2-庚烯基结构单元。此外,呋喃炔酮分子中的末端炔基碳原子与原料 **1** 中的 1 个硫原子相连,从而使得产物 **2** 中的钴中心离子是个 17e 中心。化合物 **2** 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。晶体属三斜晶系,空间群 $P\bar{1}$,晶胞参数:a=0.966 57(11) nm,b=1.544 23(15) nm,c=1.756 50(18) nm,α=114.080 0(10)°,β=105.433(2)°,γ=98.639 0(10)°。

关键词: 钴; 碳硼烷; B-H 键活化; 表征

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Synthesis of A Paramagnetic Carborane Derivative Containing A Furyl Ring and Its Formation Mechanism

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Abstract: The reaction of the 16e half-sandwich complex $CpCoS_2C_2B_{10}H_{10}$ (Cp: cyclopentadienyl) (**1**) with 2-furylpropynone in a molar ratio of 1:1.5 affords a paramagnetic derivative $CpCoS_2C_2B_{10}H_9(C_{12}H_{10}O_2)$ (**2**). In the synthesis process of compound **2**, a Cp ring of one **1** molecule is connected with the B(3)/B(6) cite of the carborane cage of another **1** molecule. At the same time, the Cp ring and a 2-furylpropynone molecule take part in the Diels-Alder reaction to give a bicyclo [2.2.1]hept-2-enyl unit. Additionally, the terminal alkynyl carbon atom of 2-furylpropynone is connected with a sulpher atom of the reactant **1**. As a result, the cobalt of the compound **2** is a 17e center. Complex **2** has been characterized by IR, NMR, elemental analysis, mass spectrum and single-crystal X-ray diffraction analysis. It crystallizes in triclinic system with space group $P\bar{1}$. The crystal data are: a=0.966 57(11) nm, b=1.544 23(15) nm, c=1.756 50(18) nm, α=114.080 0(10)°, β=105.433(2)°, γ=98.639 0(10)°. CCDC: 967543.

Key words: cobalt; carborane; B-H activation; characterization

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Carboranes are a kind of carbon-containing polyhedral boron-cluster compounds. They have been studied since 1960s[1]. For example, carboranes and their derivatives have been used in increased applications[2] such as catalysis[3], boron neutron capture therapy (BNCT)[4], polymers[5], solvent extraction of radionuclides[6], ceramics[7] and so on. Of all the known carboranes, the icosahedral *o*-carborane (*o*-$C_2B_{10}H_{12}$) has been studied extensively because of its easy preparation[8]. The stability of the carborane cage is shown under many reaction conditions used to synthesize a large number of C- and B-substituted carborane derivatives[9].

Recently, a sort of mononuclear 16e half-sandwich carborane complexes have been synthesized[10-11]. As the central metal ions of these 16e half-sandwich carborane complexes are coordinatively unsaturated, they can react with donor Ligands such as metal fragments[12], Lewis bases[13] and alkynes[14]. According to the reaction results, alkynones are more active than their corresponding alkynes in regard to their reactivity with the 16e half-sandwich carborane complexes. For example, $CpCo(S_2C_2B_{10}H_{10})$ (**1**) reacts with PhC(O)C≡CH[15] and FcC(O)C≡CH[16] to give both B-H activation and Cp-involved Diels-Alder reaction products. While the reactions of **1** with PhC≡CH[17] or FcC≡CH[18] dont afford these corresponding complexes. To the best of our knowledge, there is no reports about the reaction system of **1** with 2-furylpropynone. As a continuation of our systematic study, herein we report on the reaction chemistry of **1** with 2-furylpropynone.

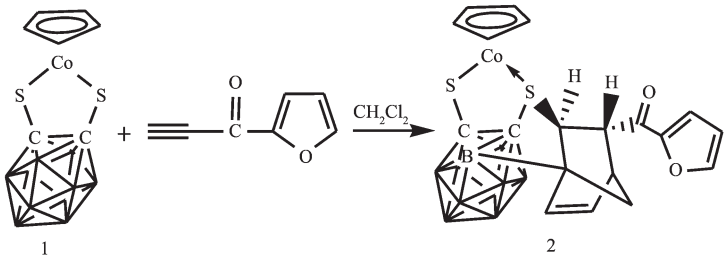
1 Experimental

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_2Cl_2) under nitrogen and then distilled prior to use. CpCo ($S_2C_2B_{10}H_{10}$) (**1**)[10] and 2-furylpropynone [19] were prepared according to the literature methods. Elemental analyses were performed in an elementar vario EL III elemental analyzer. NMR data were recorded on a Bruker DRX-500 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were reported in ppm with respect to $CHCl_3$/$CDCl_3$ (δ ^{1}H=7.24, δ ^{13}C=77.0) and ^{11}B NMR spectra were reported in ppm 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

2-Furylpropynone (36.0 mg, 0.3 mmol) and **1** (66.0 mg, 0.2 mmol) were solved in CH_2Cl_2 (25 mL), and the mixture was stirred for 12 h at ambient temperature. After removal of solvent, the residue was chromatographed on silica gel. Elution with petroleum ether/CH_2Cl_2 (1∶2, *V*/*V*) gave **2** (Scheme 1). Yellow solid, yield 44.0% (22.7 mg), m.p. 210 ℃ dec. ^{1}H NMR ($CDCl_3$): 10.43 (br), 9.75, 8.53, 7.93 (br), 7.67 (br), 7.63 (br), 7.60, 7.55, 7.19 (br), 7.15, 7.05, 7.03, 6.91, 6.79 (br), 6.58 (br), 6.57 (br), 6.55, 6.52, 6.51, 6.26 (br), 6.17 (br), 6.07, 5.24, 4.84 (br), 4.61, 4.59, 4.48 (br), 4.03, 3.81 (br), 3.77 (br), 3.67(br), 3.61 (br), 3.57, 2.26, 2.03, 1.96, 1.94, 1.72, 1.41, −2.80 (br), −3.01 (br), −3.59 (br), −4.06 (br). ^{11}B NMR ($CDCl_3$): δ 10.93 (1B), 1.05 (1B), −2.69 (1B), −5.99 (2B), −6.55 (1B), −9.13 (1B), −13.48 (1B), −17.67 (1B), −22.31 (1B). IR (KBr): (cm^{-1}):1671 (C=O), 2586 (B-H). EI-MS (70 eV): *m*/*z* 515.2 (M^+, 31.42%). Anal. Calcd. for



1 2

Scheme 1 Synthesis of **2**

$C_{19}H_{24}B_{10}O_2S_2Co$ (%): C, 44.26; H, 4.69. Found (%): C, 44.11; H, 4.85.

1.3 X-ray crystal structure determination

X-ray crystallographic data[20] 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. The structure was solved by direct methods using the SHELXS-97 program[21] and refined by full-matrix least-squares techniques on F^2 with the SHELXL-97 program [22]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were assigned with commonly isotropic displacement factors and included in the final refinement by use of geometrical restrains. Crystal data, data collection parameters and the results of the analyses of **2** are listed in Table 1. Selected bond lengths and bond angles are listed in Table 2.

CCDC: 967543.

Table 1　Crystal and structure refinement data for 2

Chemical formula	$C_{19}H_{24}B_{10}CoO_2S_2$	Z	4
Crystal size / mm	0.28×0.24×0.22	D_c / (g·cm^{-3})	1.46
Formula weight	515.53	Absorp. coeff. / mm^{-1}	0.928
Temperature / K	291(2)	F(000)	1 052
Crystal system	Triclinic	θ range / (°)	2.15~26.00
Space group	$P\bar{1}$	Reflns collected	12 924 (R_{int}=0.026 3)
a / nm	0.966 57(11)	Indep. Reflns	9 030
b / nm	1.544 23(15)	Refns obs. ($I>2\sigma(I)$)	6 325
c / nm	1.756 50(18)	Data /restr./paras	9 030/0/613
α / (°)	114.080 0(10)	GOF	1.078
β / (°)	93.475(2)	Final R indices ($I>2\sigma(I)$)	R_1=0.050 9, wR_2=0.106 3
γ / (°)	98.639 0(10)	R indices (all data)	R_1=0.070 4, wR_2=0.110 6
V / nm^3	2 344.8(4)	Largest diff. peak and hole / (e·nm^{-3})	319 and −361

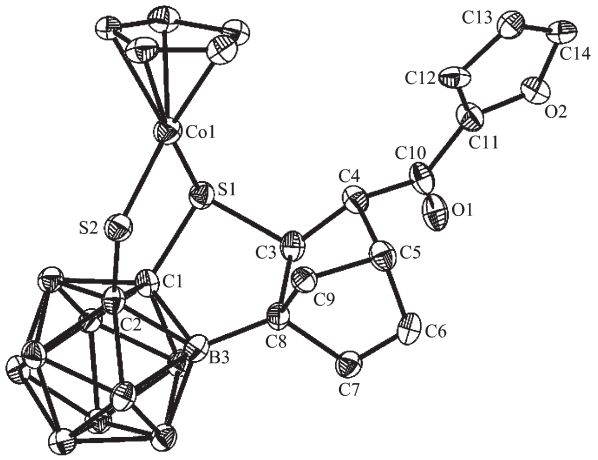
Table 2　Selected bond lengths (nm) and bond angles (°) for 2

B3-C1	0.173 2(5)	B3-C2	0.177 0(5)	C1-C2	0. 166 4(4)
C1-S1	0.181 7(3)	C2-S2	0.177 5(3)	C3-C4	0.152 2(4)
C3-C8	0.159 2(5)	C3-S1	0.185 8(3)	C4-C10	0.152 3(4)
C4-C5	0.160 1(5)	C5-C6	0.151 2(5)	C5-C9	0.152 8(5)
C6-C7	0.132 3(5)	C7-C8	0.152 9(4)	C8-C9	0.155 6(4)
Co1-S2	0.216 69(11)	Co1-S1	0.219 05(10)		
C8-B3-C1	108.7(3)	C8-B3-C2	121.6(3)	C1-B3-C2	56.72(19)
C2-C1-B3	62.8(2)	C2-C1-S1	111.6(2)	B3-C1-S1	108.2(2)
C1-C2-B3	60.5(2)	C1-C2-S2	119.5(2)	B3-C2-S2	121.2(2)
C4-C3-S1	116.2(2)	C8-C3-S1	110.0(2)	C3-C4-C10	115.6(3)
C3-C4-C5	101.7(3)	C10-C4-C5	110.8(3)	C6-C5-C9	101.0(3)
C6-C5-C4	107.0(3)	C9-C5-C4	98.1(3)	C7-C6-C5	107.9(3)
C6-C7-C8	108.6(3)	C7-C8-C9	99.1(2)	C7-C8-B3	120.5(3)
C9-C8-B3	124.7(3)	C7-C8-C3	100.1(2)	C9-C8-C3	100.1(2)
B3-C8-C3	108.1(3)	C5-C9-C8	95.2(2)	S2-Co1-S1	95.54(4)
C1-S1-C3	92.35(14)	C1-S1-Co1	105.46(10)	C3-S1-Co1	109.77(10)
C2-S2-Co1	104.28(10)				

2 Results and discussion

2.1 Structure of 2

The single-crystal X-ray diffraction analysis shows that **2** crystallizes in $P\bar{1}$ space group. The molecular structure (Fig.1) shows that a Cp ring, which is from another CpCo ($S_2C_2B_{10}H_{10}$) molecule, is connected with the starting compound **1** at the B(3)/B(6) site of the carborane cage. At the same time, the Cp ring and 2-furylpropynone take part in the Diles-Alder reaction to give a norbornenyl unit. Additionally, the terminal carbon atom of 2-furylpropynone is linked to one sulpher atom of **1**. As a result, **2** is a 17e cobalt complex and possesses magnetism. The Cp ring is no longer planar and is bent at the C(5)···C(8) vector with a dihedral angle of 129.4°. The newly generated six-membered ring C(3)C(4)C(5)C(6)C(7)C(8) is bent at the C(5)···C(8) vector with a dihedral angle of 109.6°. The C-C bond of the alkyne is reduced to a single bond (0.152 2 nm).



All hydrogen atoms are omitted for clarity

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

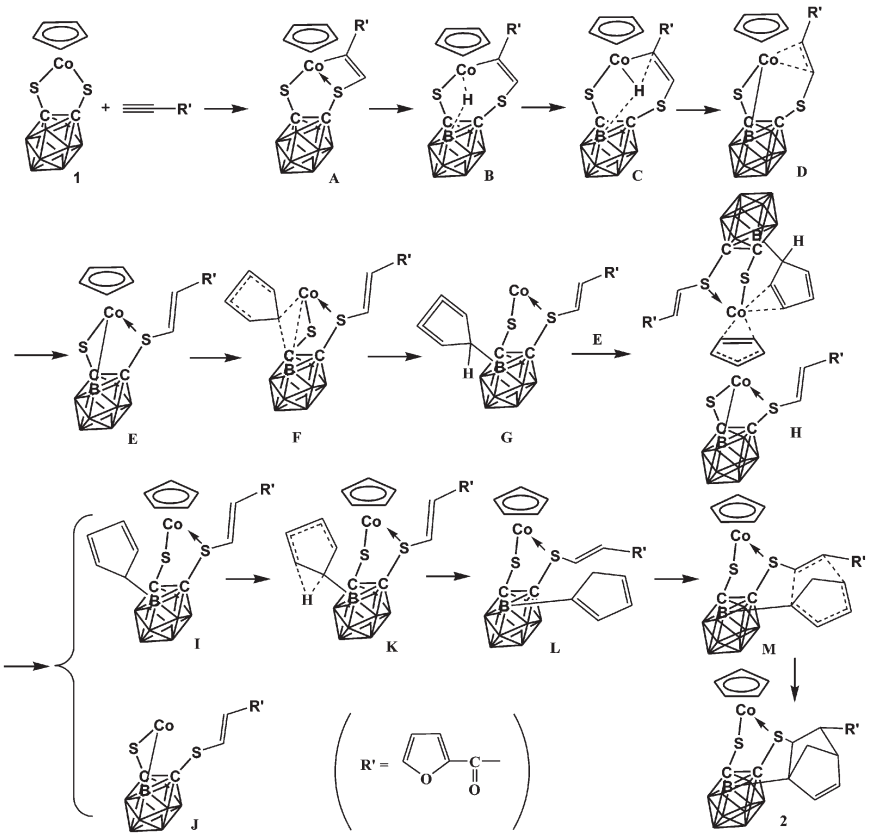
As discussed above, **2** is a paramagnetic compound. ^{1}H NMR spectra further support the viewpoint. ^{1}H NMR signals exceed normal ranges and cant be accurately assigned.

2.2 Formation mechanism of 2

As complex **2** is unique, it is necessary for us to deduce its formation process. However, **2** is a paramagnetic compound. Elucidation of formation mechanism by routine analytical means such as NMR and MS is not realistic. By combining experimental evidence along with theoretical calcutations[16], we give the possible mechanistic process of **2** (Scheme 2).

At first, the acetenyl group of 2-furylpropynone is inserted into a Co-S bond of **1** to lead to intermediate A. In the following step, the H atom at the B(3) cite of the carborane cage was activated (B) and transfered to vinyl (C) to give D. There are two notable features in D, *i.e.*, a Co-B bond is formed and the vunyl is coordinated to cobalt atom. D is easily converted to E by vinyl stretch. In the optimized stucture of E, the shortest distance between C(η^5-Cp) and B(3)/B(6) is inclined to form a bond [16] and allow B-Cp formation (G). Within G, cobalt is coordinated by Cp (neutral) in η^4-mode with +1 valence state. When G and E is jointed, intermediate H is formed. Note that in H, E and G share one Cp ligand.

The Cp ligand combines to Co(Ⅲ)/Co(Ⅰ) in η^3/η^2 modes simutaneously, and esch cobalt in H possesses 16 electrons. Thereafter, through η^3-Cp dissocation and electron transfer, two Co(Ⅱ) intermediates I and J is formed. In I, [1,5]-H shift is occured and L is formed. The η^4-Cp and vinyl unit in L take part in intramolecular Diels-Alder reaction to give the product **2**.



Scheme 2　Possible formation process of **2**

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