Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 689 (2004) 2228–2235

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Sulfur and oxygen functionalized cyclopentadienyl half-sandwich cobalt complexes with 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligands ☆

Xiu-Feng Hou, Xiao-Chuan Wang, Jian-Qiang Wang, Guo-Xin Jin *

Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Handan Road 220, Shanghai 200433, China

Received 8 February 2004; accepted 8 April 2004

Abstract

Sulfur and oxygen functionalized cyclopentandienyl half-sandwich cobalt dicarbonyl complexes [η^5-$C_5H_4(CH_2)_2$-SCH_2CH_3]$Co(CO)_2$ (**3**) and [η^5-$C_5H_4(CH_2)_2OCH_3$]$Co(CO)_2$ (**7**) were prepared. Oxidation of **3** or **7** with I_2 led to formation of 18-electron complexes [η^5-$C_5H_4(CH_2)_2SCH_2CH_3$]CoI_2 (**4**) and [η^5-$C_5H_4(CH_2)_2OCH_3$]$Co(CO)I_2$ (**8**). The reactions of diiodide complex (**4**) with dilithium 1,2-dicarba-*closo*-dodecaborane(12)-1,2-dichalcogenolates [$(THF)_3LiE_2C_2B_{10}H_{10}Li(THF)$]$_2$ [E = S (**1a**), Se (**1b**)] afforded 18-electron mononuclear complexes [η^5-$C_5H_4(CH_2)_2SCH_2CH_3$]$Co(E_2C_2B_{10}H_{10})$ [E = S (**5a**), Se (**5b**)] in which sulfur atoms of side-chain were attached via an intramolecular coordination. Complex **7** reacted with **1a** and **1b** to give the binuclear complexes {[η^5-$C_5H_4(CH_2)_2OCH_3$]$Co(E_2C_2B_{10}H_{10})$}$_2$ [E = S (**10a**), Se (**10b**)]. The molecular structures of **5a** and **10b** were determined by X-ray crystallographic analysis. According to the X-ray structure analyses, **10b** contains two *o*-carborane diselenolate bridges, and each Cp′Co fragment is attached to one terminal and two bridging selenolato ligands. The central Co_2Se_2 four-membered ring is planar, and the direct metal–metal interaction is absent.

Keywords: Half-sandwich complexes; Cobalt; Fuctionalized cyclopentadienyl ligands; Carborane; X-ray structure

1. Introduction

Up to date intensive studies on half-sandwich transition metal complexes of Fe [1], Ru [1], Co [2], Rh [3], Ir [4] and Zr [5] containing the chelating 1,2-dicarba-*closo*-dodecabarane-1,2-dichalcogenolate ligands have illustrated that these complexes serve as excellent precursors to study the insertion of alkynes into one of the metal–chalcogen bonds; this may lead to the formation of a metal-to-boron bond and/or substitution of the carborane cage in the position B(3)/B(6) [6,7]. The coordination chemistry of appended cyclopentadienyl ligands has attracted a great deal of interest to take the advantage of stabilized molecular structure of complexes in recent years [8].

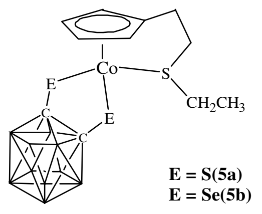
In previous paper [9], we have described the synthesis and characterization of dilithium dichalcogenolate carboranes. The molecular structure analysis indicated that dilithium dichalcogenolate carboranes are dimers with formula [$(THF)_3LiE_2C_2B_{10}H_{10}Li(THF)$]$_2$ [E = S (**1a**), Se (**1b**)]. They can be used as chelate ligands with transition metals or lanthanide to give mono-nuclear or oligo-nuclear complexes [1]. In this paper, several half-sandwich mono- and binuclear cobalt complexes containing dichalcogenolate *o*-carboranyl ligands were obtained from the reactions of dilithium dichalcogenolate *o*-carborane with *S*- and *O*-functionalized cyclopentadienyl half-sandwich cobalt complexes. Among them two complexes (**5a**, **10b**) were crystallographically studied.

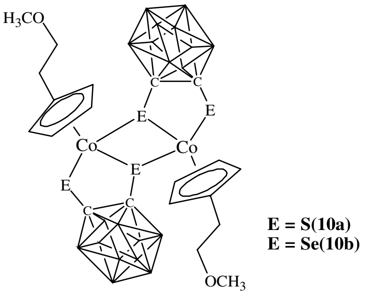
☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.04.013.

* Corresponding author. Tel.: +86-21-65643776; fax: +86-21-65641740.

E-mail address: gxjin@fudan.edu.cn (G.-X. Jin).

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.04.013





2. Results and discussion

2.1. Syntheses

The synthetic approach to the half-sandwich cobalt dichalcogenolate carborane complex (**5a** or **5b**) is outlined in Scheme 1.

The dithium 1,2-dichalcogenolate carboranes were obtained by insertion of elemental chalcogens into the two carbon–lithium bonds of the dilithiated carborane in diethyl ether solution [9]. The dilithium 1,2-dichalcogenolate carboranes are dimers [9] $[(THF)_3LiE_2C_2B_{10}H_{10}Li(THF)]_2$ [E = S (**1a**), Se (**1b**)] and can be used for further reactions.

The *S*-functionalized cyclopentadiene (**2**) was prepared by the reaction of sodium cyclopentadienide with 2-chloroethyl ethyl sulfide in THF. The formula of **2** was confirmed by ^{1}H NMR spectroscopy and elemental analysis.

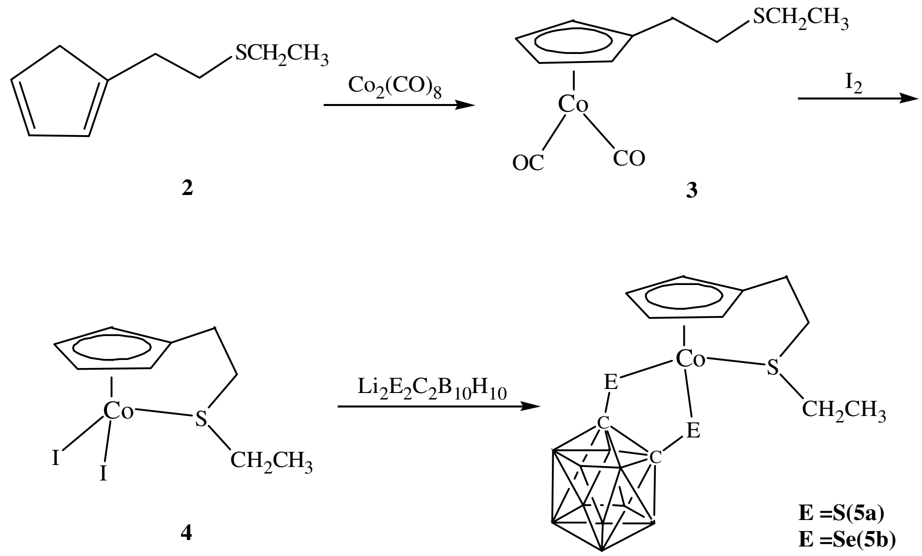
Complex **2** reacts with $Co_2(CO)_8$ in a refluxing CH_2Cl_2 solution to give dicarbonyl complex $[\eta^5\text{-}C_5H_4(CH_2)_2SCH_2CH_3]Co(CO)_2$ (**3**). Complex **3** is an air and light sensitive orange oil. Its infrared spectrum (film) shows two typical strong terminal carbonyl absorptions at 2022 and 1959 cm^{-1} which is consistent with the previously reported complex, $[\eta^5\text{-}C_5H_4(CH_2)_2\text{-}N(CH_3)_2]\text{-}Co(CO)_2$ [10]. In the ^{1}H NMR spectrum of **3** in $CDCl_3$, the cyclopentadienyl proton signals are observed at 4.98 and 4.88 ppm.

Complex **3** can be easily oxidized with elemental iodine in diethyl ether solutions to give the air-stable diiodocobalt(III) complexes $[\eta^5\text{-}C_5H_4(CH_2)_2S\text{-}CH_2\text{-}CH_3]CoI_2$ (**4**). Complex **4** is a black-purple crystalline solid. In IR spectrum, the carbonyl absorption is absent. The reaction of **4** with dilithium dichalcogenolate carboranes $[(THF)_3LiE_2C_2B_{10}H_{10}Li(THF)]_2$ [E = S (**1a**), Se (**1b**)] affords dark-green, 18-electron mononuclear complexes $[\eta^5\text{-}C_5H_4(CH_2)_2SCH_2CH_3]Co(S_2C_2B_{10}H_{10})$ (**5a**) and $[\eta^5\text{-}C_5H_4(CH_2)_2SCH_2CH_3]Co(Se_2C_2B_{10}H_{10})$ (**5b**).

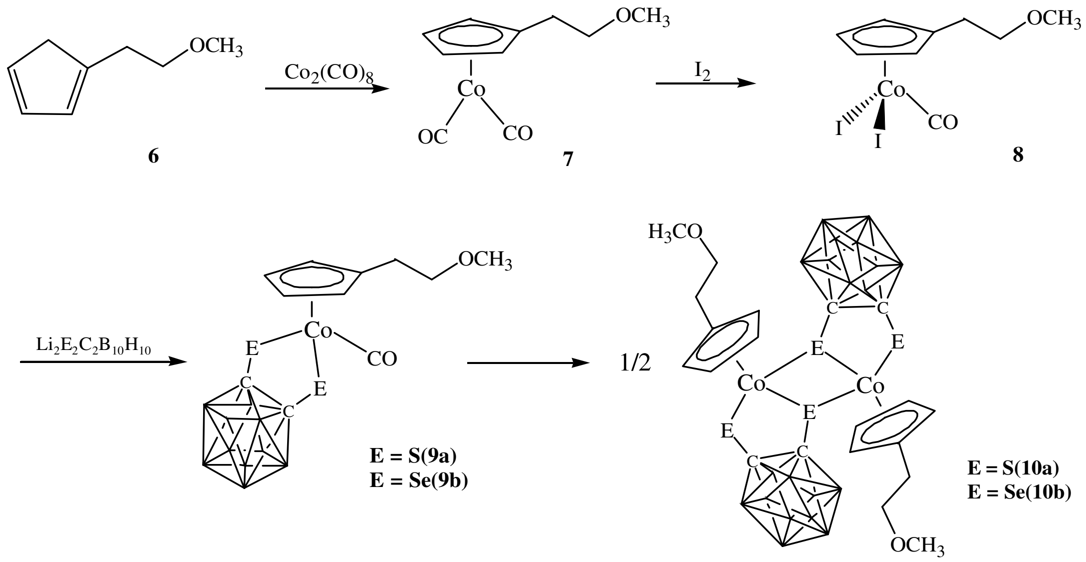
In the IR spectra of **5a**, **b**, the skeletal vibrations of the cyclopentadienyl ring are observed [11,12] at 3075, 1461, 1071, 1010 cm^{-1} and 3070, 1463, 1062, 1012 cm^{-1}, respectively. The bands at 2571 and 2575 cm^{-1} are, respectively, assigned to B–H characteristic absorptions of carboranes in **5a**, **b**. In the ^{1}H NMR spectra of **5a**, **b**, a couple of signals at 5.26, 5.24 and 5.27, 5.22 ppm were found, respectively, due to the cyclopentadienyl protons. The splitting of the ^{1}H NMR signals is about 0.04–0.05 ppm close to the value for **4**.

The *O*-functionalized cyclopentadiene (**6**) was prepared by the reaction of sodium cyclopentadienide with 2-chloroethyl methyl ether in THF by using method similar to the synthesis of **2** (Scheme 2). The ^{1}H NMR spectrum of **6** showed a typical singlet at 3.36 ppm corresponding to methyl resonance.

Reaction of $Co_2(CO)_8$ with **6** in a dichloromethane solution leads to the formation of the dicarbonyl complex $[\eta^5\text{-}C_5H_4(CH_2)_2OCH_3]Co(CO)_2$ (**7**) as an air-



Scheme 1. Synthesis of complexes **5a** and **5b**.



Scheme 2. Synthesis of complexes **10a** and **10b**.

sensitive orange oil. The infrared spectrum (film) of **7** shows two strong typical absorptions of terminal carbonyl group at 2018 and 1953 cm^{-1}. In the ^1H NMR spectrum of **7**, the cyclopentadienyl proton signals are observed at 5.04 and 4.91 ppm.

The mononuclear mono-carbonyl diiodo complex $[\eta^5\text{-}C_5H_4(CH_2)_2OCH_3]Co(CO)I_2$ (**8**) can be easily obtained by oxidative decarbonylation of half-sandwich dicarbonyl complex **7** using elemental iodine. The IR spectrum of **8** shows a strong carbonyl absorption at 2061 cm^{-1}.

The reactions of **8** with dilithium dichalcogenolate carboranes **1a** and **1b** yield dinuclear dithiolate and diselenolate carborane complexes $\{[\eta^5\text{-}C_5H_4(CH_2)_2OCH_3]Co(S_2C_2B_{10}H_{10})\}_2$ (**10a**) and $\{[\eta^5\text{-}C_5H_4(CH_2)_2OCH_3]Co(Se_2C_2B_{10}H_{10})\}_2$ (**10b**) as red-brown crystals. The mono-carbonyl complexes **9a** and **9b** can be observed by monitoring IR spectra at ca. 2057 cm^{-1}. However, complexes **9a**, **b** cannot be isolated since they convert easily to stable carbonyl-free dimers **10a**, **b**. The analogous half-sandwich iridium mono-carbonyl complexes $Cp^*Ir(CO)(E_2C_2B_{10}H_{10})$ ($E = S$, Se) have been synthesized by the addition of $Cp^*Ir\ (E_2C_2B_{10}H_{10})$ with carbon monoxide [3,4].

In the IR spectra of **10a** and **10b**, typical bands for the cyclopentadienyl ring were observed at 3108, 1462, 1064, 995 cm^{-1} and 3119, 1478, 1064, 1004 cm^{-1}, respectively. The bands at 2556 and 2560 cm^{-1} are, respectively, assigned to characteristic absorptions of B–H of **10a** and **10b**.

3. Molecular structures

The molecular structures of **5a** and **10b** were depicted in Figs. 1 and 2, and the relevant bond distances and angles are collected in Tables 2 and 3, respectively.

Complex **5a** possesses basically a tri-legged half-sandwich CpCo structure, in which the sulfur atom of side-chain of cyclopentadienyl ring was attached via an intramolecular coordination with cobalt to form the 18-electron complex. The C(9) position in side-chain is disordered. The five-membered metallacycle CoS_2C_2 has a distorted envelop conformation (the dihydral angle along the S···S vector is 159.2°) similar to $RhSe_2C_2$ ring found in $Cp^*Rh(PMe_3)(Se_2C_2B_{10}H_{10})$ [3a] and RhS_2C_2 ring in $Cp^{tt}Rh(CN^tBu)(S_2C_2B_{10}H_{10})$ [2b]. The bond angle (S(1)–Co–S(2)) of complex **5a** is 92.98°, which is typical for half-sandwich cobalt complexes [2,3]. In complex **5a**, the bond length of Co–S(3) is 2.2601 Å, that is close to 2.2395 Å for Co–S(1) and 2.2391 Å for Co–S(2).

The molecule of **10b** is dimer that has a central symmetry at the midpoint of two cobalt atoms. Complex **10b** is composed of two $\{[\eta^5\text{-}C_5H_4(CH_2)_2OCH_3]Co(Se_2C_2B_{10}H_{10})\}$ units. In each unit, the Co atom is η^5-bound to cyclopentadienyl ring and σ-bound to two bridging-selenium atoms of two diselenolate-carboranes and to one terminal-selenium atom of diselenolate-carborane in a distorted pentagonal arrangement. The oxygen atom of side-chain is free of coordination with cobalt. The bridging selenium atom is bonded to the carbon atom of the carborane ligand and two cobalt metals in a slightly distorted trigonal manner. Two cobalt atoms and two bridging selenium atoms are coplanar. In complex **10b**, the bond distances between the cobalt atoms and the bridging selenium atom are 2.3834(6) and 2.3860(6) Å, respectively, slightly longer than the Co(1)–Se(1) bond distance (2.3581(6) Å) between the cobalt atom and the non-bridging selenium atom [1a]. The Se(1)–C(1) band length of 1.921(3) Å is slightly shorter than the Se(2)–C(2) band length of

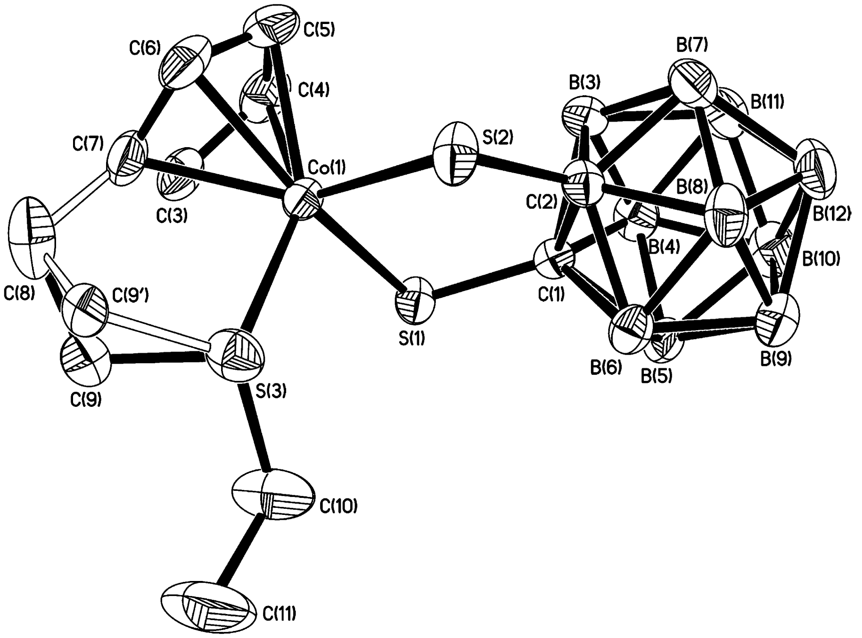


Fig. 1. Molecular structure of **5a**.

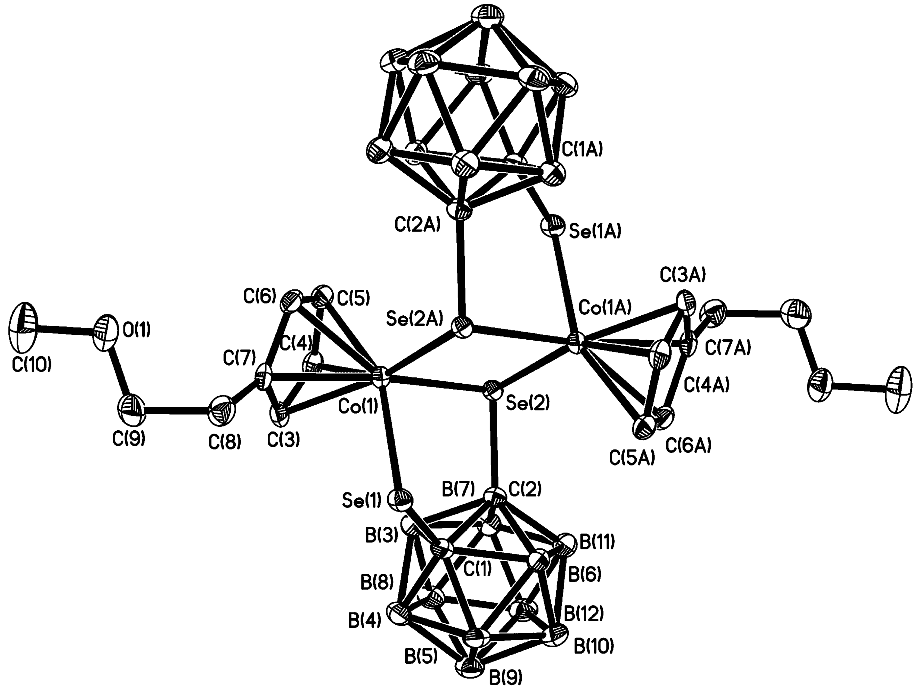


Fig. 2. Molecular structure of **10b**.

1.993(3) Å. The distance between Co(1) and Co(1A) atoms is 3.5060(9) Å and the bite angle of Se(2)–Co–Se(2A) is 85.367(17)°. This can be taken as an indication that direct cobalt–cobalt bonding interaction is absent in complex **10b**. The five-membered metallacycle $CoSe_2C_2$ in **10b** is not planar, the dihedral angle (Se–Co–Se/Se–C–C–Se) is 142.1°. The corresponding five-membered ring CoE_2C_2 (E = S, Se) in 16-electron half-sandwich CpCo complexes $CpCo(S_2C_2B_{10}H_{10})$ [2a] and $Cp^{tt}Co(Se_2C_2B_{10}H_{10})$ [2b] are planar.

4. Conclusion

The sulfur and oxygen functionalized cyclopentadienyl mononuclear and binuclear half-sandwich

Table 1
X-ray crystallographic data and processing parameters for **5a** and **10b**

	5a	**10b**
Empirical formula	$C_{11}H_{23}B_{10}CoS_3$	$C_{20}H_{42}B_{20}Co_2O_2Se_4$
Formula weight	418.50	964.44
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
a (Å)	12.336(2)	7.1696(10)
b (Å)	11.640(2)	10.9478(15)
c (Å)	14.031(2)	12.4115(17)
α (°)	90	70.3550(10)
β (°)	95.838(3)	87.223(2)
γ (°)	90	77.470(2)
V (Å^3)	2004.2(6)	895.3(2)
Z	4	2
μ (mm^{-1})	1.160	5.016
Crystal size (mm)	0.1 × 0.2 × 0.3	0.1 × 0.2 × 0.3
D_{calcd} (g/cm^3)	1.387	1.789
$F(000)$	856	468
θ range (°)	2.10–26.01	1.74–25.01
h, k, l collected	−14, 15; ±14; −14, 17	±8; ±13; ±14
Reflections collected/unique	9025/3938	5624/3107
Data/restraints/parameters	3938/10/277	3107/0/218
Goodness-of-fit on F^2	0.823	0.967
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0392$, $wR_2 = 0.0767$	$R_1 = 0.0285$, $wR_2 = 0.0668$
R indices (all data)	$R_1 = 0.0699$, $wR_2 = 0.0833$	$R_1 = 0.0342$, $wR_2 = 0.0683$
Largest difference peak and hole (e Å^{-3})	0.674 and −0.673	0.733 and −0.431

Table 2
Selected bond distances (Å) for **5a** and **10b**

5a		**10b**	
Co(1)–S(2)	2.2391(10)	Co(1)–Se(1)	2.3581(6)
Co(1)–S(1)	2.2395(10)	Co(1)–Se(2)#1	2.3834(6)
Co(1)–S(3)	2.2601(10)	Co(1)–Se(2)	2.3860(6)
Co(1)–C(7)	2.053(3)	Co(1)–C(7)	2.088(3)
Co(1)–C(6)	2.051(3)	Co(1)–C(6)	2.064(3)
Co(1)–C(5)	2.062(4)	Co(1)–C(5)	2.066(3)
Co(1)–C(4)	2.067(3)	Co(1)–C(4)	2.079(3)
Co(1)–C(3)	2.047(3)	Co(1)–C(3)	2.069(3)
S(1)–C(1)	1.774(3)	Se(1)–C(1)	1.921(3)
S(2)–C(2)	1.779(3)	Se(2)–C(2)	1.993(3)
C(1)–C(2)	1.655(4)	C(1)–C(2)	1.661(4)
C(1)–B(5)	1.702(5)	C(1)–B(5)	1.703(5)
C(1)–B(4)	1.711(5)	C(1)–B(4)	1.714(5)
C(1)–B(3)	1.729(5)	C(1)–B(3)	1.725(5)
C(1)–B(6)	1.732(5)	C(1)–B(6)	1.726(5)
C(2)–B(8)	1.693(5)	C(2)–B(7)	1.695(5)
C(2)–B(7)	1.700(5)	C(2)–B(11)	1.705(5)
C(2)–B(3)	1.730(5)	C(2)–B(6)	1.717(5)
C(2)–B(6)	1.733(5)	C(2)–B(3)	1.719(5)
C(3)–C(7)	1.400(5)	C(3)–C(4)	1.400(5)
C(3)–C(4)	1.410(5)	C(3)–C(7)	1.420(5)
C(4)–C(5)	1.382(5)	C(4)–C(5)	1.393(5)
C(5)–C(6)	1.393(5)	C(5)–C(6)	1.407(5)
C(6)–C(7)	1.399(5)	C(6)–C(7)	1.416(5)
C(7)–C(8)	1.495(5)	C(7)–C(8)	1.485(5)
C(8)–C(9)	1.468(4)	C(8)–C(9)	1.506(5)
C(10)–C(11)	1.507(5)	C(9)–O(1)	1.379(5)
S(3)–C(9)	1.756(4)	C(10)–O(1)	1.416(5)
S(3)–C(10)	1.767(4)	Cp'_{cent}–Co(1)	1.693
Cp'_{cent}–Co(1)	1.678		

Table 3
Selected bond angles (°) for **5a** and **10b**

5a		**10b**	
S(2)–Co(1)–S(1)	92.98(4)	Se(1)–Co(1)–Se(2)	90.007(18)
S(2)–Co(1)–S(3)	91.30(4)	Se(2)#1–Co(1)–Se(2)	85.367(17)
S(1)–Co(1)–S(3)	97.23(4)	Se(1)–Co(1)–Se(2)#1	86.07(2)
C(1)–S(1)–Co(1)	104.29(10)	C(1)–Se(1)–Co(1)	100.85(9)
C(2)–S(2)–Co(1)	104.63(11)	C(2)–Se(2)–Co(1)#1	116.06(9)
C(1)–C(2)–S(2)	116.0(2)	C(2)–Se(2)–Co(1)	101.39(10)
C(2)–C(1)–S(1)	117.3(2)	C(1)–C(2)–Se(2)	114.5(2)
C(9)–S(3)–Co(1)	98.8(2)	C(2)–C(1)–Se(1)	116.2(2)
C(10)–S(3)–Co(1)	113.09(14)	O(1)–C(9)–C(8)	109.2(3)
C(8)–C(9)–S(3)	112.5(4)	C(9)–O(1)–C(10)	112.3(3)
C(11)–C(10)–S(3)	113.0(3)		
C(9)–S(3)–C(10)	93.3(3)		
C(9)–S(3)–Co(1)	98.8(2)		
C(10)–S(3)–Co(1)	113.09(14)		

complexes (**5a**, **b**) and (**10a**, **b**) have been synthesized. Apparently, the cyclopentadienyl ligands bearing a sulfur or oxygen donor arm shield the outer hemisphere of cobalt atom effectively and facilitate the incorporation of two chalcogen atoms of dichalcogenolate carborane ligands into cobalt metal with terminal or bridging coordination. The corresponding half-sandwich rhodium and iridium complexes with dichalcogenolate carborane are under investigation.

5. Experimental

All reactions were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Tetrahydrofuran (THF), hexane and diethyl ether were distilled from sodium benzophenone; dichloromethane (CH_2Cl_2) was distilled from CaH_2. Separation of product mixtures and purification of the components was accomplished by column chromatography over silica which had been activated at 400 °C over night and kept under argon before use. $[(THF)_3LiE_2C_2B_{10}H_{10}Li(THF)]_2$ (E = S (**1a**), Se (**1b**)) were synthesized according to the procedures described in the literature [9]. The element analyses were performed on a Rapid CHN-O 240C Analyzer. Infrared spectra were recorded on Nicolet-FT-IR-50X spectrophotometer, only characteristic frequencies were listed. ^{1}H NMR and ^{11}B NMR spectra were obtained using a Bruker DMX-500 and DMX-300 spectrophotometer in $CDCl_3$, respectively.

5.1. *$HC_5H_4CH_2CH_2SCH_2CH_3$ (**2**)*

2-Chloroethyl ethyl sulfide (12.2 g, 97.9 mmol) was added to a solution of sodium cyclopentadienide (2.7 M, 70 ml, 0.191 mol) in 20 ml THF at −20 °C and then reaction was allowed to warm to room temperature. The resulting mixture was refluxed for 4 h. Water (80 ml) was added to the mixture which was then extracted with hexane (2× 50 ml). The solvent was removed under reduced pressure, and residue distilled, using a dry ice cooling device at 60–62 °C (6 mmHg). **2** (10.2 g, 68%) was collected as colorless oil. Anal. Calc. for $C_9H_{14}S$ (154.27 g/mol): C, 70.06; H, 9.15. Found: C, 70.35; H, 9.28%. IR (film): 728 cm^{-1} (ν_{CSC}). EI-MS (70 eV, m/e, rel): 154 (M^+, 100%). ^{1}H NMR (500 MHz, $CHCl_3$, ppm): δ 6.46–6.07 (m, 3H, Cp), 2.97–2.92 (m, 2H, Cp), 2.74–2.70 (m, 2H, CH_2), 2.66–2.65 (m, 2H, CH_2), 1.30–1.25 (m, 3H, CH_3).

5.2. *$[\eta^5\text{-}C_5H_4(CH_2)_2SCH_2CH_3]Co(CO)_2$ (**3**)*

A solution containing $Co_2(CO)_8$ (1.36 g, 3.98 mmol), **2** (1.54 g, 9.98 mmol) in CH_2Cl_2 (30 ml) was refluxed for 7 h and then solvent was removed in vacuo. The residue was chromatographed on silica gel column and eluted with ether/hexane (1/4). The red band was collected. The solvent was evaporated under vaccum and afforded **3** (1.07 g, 50%) as red liquid. Anal. Calc. for $C_{11}H_{13}CoO_2S$ (268.21 g/mol): C, 49.26; H, 4.88. Found: C, 49.08; H, 4.74%. IR (film): ν(CO) 2022, 1959 cm^{-1}, ν(CSC) 820 cm^{-1}. ^{1}H NMR (500 MHz, $CHCl_3$, ppm): 4.98 (t, 2H, Cp), 4.85 (t, 2H, Cp), 2.81 (t, 2H, SCH_2), 2.25 (t, 2H, CH_2), 2.44 (q, 2H, SCH_2), 1.19 (t, 3H, CH_3).

5.3. *$[\eta^5\text{-}C_5H_4(CH_2)_2SCH_2CH_3]CoI_2$ (**4**)*

A solution containing iodine (538 mg, 2.12 mmol) in ether (30 ml) was added dropwise to a solution of **3** (464 mg, 1.73 mmol) in ether (15 ml) at 0 °C. The color of the solution changed from red-brown to dark purple and the black-purple precipitate was formed. The solution was allowed to warm to room temperature and then stirred for 2 h. When the reaction mixture was filtered, its color changed to black, leaving black-purple microcrystals. The microcrystals were washed with 15 ml of ether and then dried in vacuo, air-stable **4** (580 mg, 72%)

was obtained. Anal. Calc. for $C_9H_{13}CoSI_2$ (465.99 g/mol): C, 23.20; H, 2.81. Found: C, 23.38; H, 2.48%. IR (film): ν(CSC) 831 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$, ppm): δ 5.22 (t, 2H, Cp), 5.08 (t, 2H, Cp), 3.99 (t, 2H, SCH_2), 2.49 (t, 2H, CH_2), 2.96 (q, 2H, SCH_2), 1.34 (t, 3H, CH_3, $^3J_{HH} = 7.3$ Hz).

5.4. [η^5-$C_5H_4(CH_2)_2SCH_2CH_3$]Co($S_2C_2B_{10}H_{10}$) (5a)

A solution of $Li_2S_2C_2B_{10}H_{10}$ (0.360 mmol in 10 ml of Et_2O) was added to the solution of **4** (165.0 mg, 0.354 mmol) in 20 ml of THF. The reaction mixture was stirred over night at room temperature, the solvent was removed under reduced pressure. The residue was redissolved in CH_2Cl_2 and the product purified by column chromatography on silica. Elution with CH_2Cl_2/hexane (2/1) gave a dark-red zone of **5a**. Recrystallization of **5a** from CH_2Cl_2/hexane afforded dark-red crystals of **5a** (91.8 mg, 62%). Anal. Calc. for $C_{11}H_{23}CoS_3B_{10}$ (418.50 g/mol): C, 31.57; H, 5.54. Found: C, 31.25; H, 5.42%. IR (KBr): ν(B–H) 2572 cm^{-1}, ν(CSC) 722 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$, ppm): δ 5.26 (t, 2H, Cp), 5.24 (t, 2H, Cp), 3.49 (t, 2H, SCH_2, $J_{HH} = 6.7$ Hz), 2.45 (t, 2H, CH_2, $J_{HH} = 6.8$ Hz), 2.75 (q, 2H, SCH_2, $J_{HH} = 7.4$ Hz), 1.41 (t, 3H, CH_3, $J_{HH} = 7.4$ Hz). ^{11}B NMR ($CDCl_3$, ppm): δ −1.44, −5.91, −6.81, −9.22.

5.5. [η^5-$C_5H_4(CH_2)_2SCH_2CH_3$]Co($Se_2C_2B_{10}H_{10}$) (5b)

Complex **5b** (96.4 mg, 49%) was obtained as dark green crystals from the reaction of $Li_2Se_2C_2B_{10}H_{10}$ (0.389 mmol in 10 ml of Et_2O) with **4** (178.9 mg, 0.384 mmol) in THF (20 ml) in a manner similar to that for **5a**. Anal. Calc. for $C_{11}H_{23}CoSe_2SB_{10}$ (512.30 g/mol): C, 25.79; H, 4.52. Found: C, 25.53; H, 4.40%. IR (KBr): ν(B–H) 2570 cm^{-1}, ν(CSC) 834 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$, ppm): δ 5.27 (t, 2H, Cp), 5.22 (t, 2H, Cp), 3.54 (t, 2H, SCH_2, $J_{HH} = 6.4$ Hz), 2.40 (t, 2H, CH_2, $J_{HH} = 6.4$ Hz), 2.76 (q, 2H, SCH_2, $J_{HH} = 7.2$ Hz), 1.38 (t, 3H, CH_3, $J_{HH} = 7.3$ Hz). ^{11}B NMR ($CDCl_3$, ppm): δ −1.68, −4.78, −7.01.

5.6. $HC_5H_4CH_2CH_2OCH_3$ (6)

Complex **6** was prepared from 2-chloroethyl methyl ether (12.1 g, 0.128 mol) with sodium cyclopentadienide (2.7 M, 70 ml, 0.191 mol) in THF (20 ml) by using procedure similar to those used in the synthesis of **2**. Collected temperature: 30–32 °C (6 mmHg). Yield: 11.1 g (70%). Anal. Calc. for $C_8H_{12}O$ (124.17 g/mol): C, 77.38; H, 9.74. Found: C, 77.13; H, 9.55%. MS (70 eV, *m/e*, rel): 124 (M^+, 100%). IR (film): 1118 cm^{-1} (COC). ^1H NMR (500 MHz, $CHCl_3$, ppm): δ 6.46–6.09 (m, 3H, Cp), 2.97–2.92 (m, 2H, Cp), 3.56 (m, 2H, OCH_2), 2.50 (m, 2H, CH_2), 3.36 (s, 3H, OCH_3).

5.7. [η^5-$C_5H_4(CH_2)_2OCH_3$]Co$(CO)_2$ (7)

Complex **7** was prepared as red liquid from $Co_2(CO)_8$ (1.54 g, 4.50 mmol) with **6** (1.40 g, 9.0 mmol) in CH_2Cl_2 (30 ml) by using procedure similar to those used in the synthesis of **3**. Yield: 1.07 g (50%). Anal. Calc. for $C_{10}H_{11}CoO_3$ (238.12 g/mol): C, 50.44; H, 4.66. Found: C, 50.24; H, 4.48%. IR (film): ν(CO) 2018, 1953 cm^{-1}; ν(CSC) 1118 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$, ppm): δ 5.04 (t, 2H, Cp), 4.91 (t, 2H, Cp), 3.52 (t, 2H, OCH_2), 2.50 (t, 2H, CH_2), 3.36 (s, 3H, OCH_3).

5.8. [η^5-$C_5H_4(CH_2)_2OCH_3$]Co(CO)I_2 (8)

Complex **8** (407.4 mg, 72%) was prepared as black crystals from **7** (290 mg, 1.22 mmol) with I_2 (309 mg, 1.22 mmol) in ether (15 ml) by using procedure similar to those used in the synthesis of **4**. Anal. Calc. for $C_9H_{11}CoO_2I_2$ (463.9 g/mol): C, 23.30; H, 2.39. Found: C, 23.15; H, 2.40%. IR (KBr): 2061 cm^{-1} (ν_{CO}); 1109 cm^{-1} (ν_{COC}). ^1H NMR (500 MHz, $CHCl_3$, ppm): δ 5.56 (t, 2H, Cp), 5.47 (t, 2H, Cp), 3.73 (t, 2H, OCH_2), 2.98 (t, 2H, CH_2), 3.40 (s, 3H, OCH_3).

5.9. {[η^5-$C_5H_4(CH_2)_2OCH_3$]Co($S_2C_2B_{10}H_{10}$)}$_2$ (10a)

A solution of $Li_2S_2C_2B_{10}H_{10}$ (0.565 mmol in 10 ml of Et_2O) was added to the solution of 260.8 mg (0.562 mmol) **8** in 30 ml of THF and gas evolution occurred immediately. The reaction mixture was stirred over night at room temperature, then the solvent was evaporated under reduced pressure. The residue was chromatographed on silica. Elution with CH_2Cl_2/hexane (2/1) gave a dark-red zone of **10a**. Recrystallization from CH_2Cl_2/hexane afforded dark-red crystals of **10a** (113.5 mg, 52%). Anal. Calc. for $C_{20}H_{42}Co_2O_2S_4B_{20}$ (388.46 g/mol): C, 30.92; H, 5.45. Found: C, 30.65; H, 5.40%. IR (KBr): ν(B–H) 2556 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$, ppm): δ 5.40 (t, 2H, Cp), 5.22 (t, 2H, Cp), 3.72 (t, 2H, OCH_2), 2.14 (t, 2H, CH_2), 3.40 (s, 3H, OCH_3). ^{11}B NMR ($CDCl_3$, ppm): δ −5.77, −7.74, −8.92, −11.16.

5.10. {[η^5-$C_5H_4CH_2CH_2OCH_3$]Co($Se_2C_2B_{10}H_{10}$)}$_2$ (10b)

Complex **10b** (162.9 mg, 60%) was obtained as red-brown crystals from the reaction of $Li_2Se_2C_2B_{10}H_{10}$ (0.565 mmol in 10 ml of Et_2O) with **8** (261.0 mg, 0.563 mmol) in 30 ml of THF in a manner similar to that for **5a**. Anal. Calc. for $C_{20}H_{42}Co_2O_2Se_4B_{20}$ (482.22 g/mol): C, 24.90; H, 4.39. Found: C, 24.75; H, 4.40%. IR (KBr): ν(B–H) 2575 cm^{-1}. ^1H NMR (500 MHz, $CHCl_3$, ppm): δ 5.29 (t, 2H, Cp), 5.00 (t, 2H, Cp), 3.57 (t, 2H, OCH_2, $J_{HH} = 9.4$ Hz), 2.65 (t, 2H, CH_2, $J_{HH} = 9.4$ Hz), 3.35 (s, 3H, OCH_3). ^{11}B NMR ($CDCl_3$, ppm): δ −5.17, −6.10, 7.09.

6. Structure solution and refinement for complexes **5a** and **10b**

Crystals of **5a**, **10b** suitable for X-ray crystallography were grown by slow diffusion of hexane into CH_2Cl_2 solution. The single crystals of **5a** and **10b** for X-ray were, respectively, sealed in glass capillaries, and were sequentially mounted on CCD-Bruker Smart diffractometer. All the determinations of unit cell and intensity data were performed with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature using the ω scan technique. These structures were solved by the direct methods, expanded using Fourier techniques and refined on F^2 by a full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. All the calculations were carried out with Siemens SHELXTL PLUS program. Details of crystal data for complexes **5a** and **10b** are summarized in Table 1.

7. Supplementary material

Crystallographic data for the structures of complexes **5a** and **10b** reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-221779 and 221780. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44-1233/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

Financial support by the National Nature Science Foundation of China for Distinguished Young Scholars (29925101) and by the special Funds for Major State Basic Research Projects (G 1999064800) and Youth Funds of Fudan University is gratefully acknowledged.

References

[1] (a) S. Lu, G.-X. Jin, S. Eibl, M. Herberhold, Y. Xin, Organometallics 21 (2002) 2533;
(b) G.-X. Jin, in: C.G. Screttas, B.R. Steele (Eds.), Perspectives in Organometallic Chemistry, RSC Cambridge Press, Cambridge, 2003, pp. 47–63.

[2] (a) D.H. Kim, J. Ko, K. Park, S. Cho, S.O. Kang, Organometallics 18 (1999) 2738;
(b) Q.A. Kong, G.-X. Jin, S.Y. Cai, L.H. Weng, Chin. Sci. Bull. 48 (2003) 783.

[3] (a) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, J. Organomet. Chem. 587 (1999) 252;
(b) Q.A. Kong, G.-X. Jin, Y.H. Lin, Chem. J. Chin. Univ. 23 (2002) 410;
(c) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, Angew. Chem., Int. Ed. Engl. 38 (1999) 3689;
(d) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, J. Organomet. Chem. 623 (2001) 149.

[4] (a) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, Eur. J. Inorg. Chem. (1999) 873;
(b) Y. Bae, Y.I. Park, J. Ko, K.I. Park, S.I. Cho, S.O. Kang, Inorg. Chim. Acta 289 (1999) 141.

[5] X.Y. Yu, G.-X. Jin, L.H. Weng, Chin. J. Chem. 20 (2002) 1256.

[6] (a) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, Chem. Eur. J. 8 (2002) 388;
(b) M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, Chem. Eur. J. 6 (2000) 3026.

[7] M.F. Hawthorne, Z. Zheng, Acc. Chem. Res. 30 (1997) 267.

[8] U. Siemeling, Chem. Rev. 100 (2000) 1495.

[9] X.Y. Yu, G.-X. Jin, N.H. Hu, L.H. Weng, Organometallics 21 (2002) 5540.

[10] A.I. Philippopoulos, R. Bau, R. Poiblanc, N. Hadjiliadis, Inorg. Chem. 37 (1998) 4822.

[11] H.P. Fritz, Adv. Organomet. Chem. 1 (1964) 239.

[12] O. Koch, F. Edelmann, U. Behrens, Chem. Ber. 115 (1982) 1305.