

Synthesis and structures of *binuclear half-sandwich cobalt (III) ortho-carboranedithiolato complexes with silyl-bridged bis(cyclopentadienyl) ligands*

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Dedicated to the memory of Professor Al Cotton.

Abstract

Five binuclear half-sandwich cobalt complexes, $[(\eta^5\text{-C}_5\text{H}_4)\text{Co}(\text{CO})\text{I}_2]_2\text{SiMe}_2$ (**3**), $[(\eta^5\text{-C}_5\text{H}_4)\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})]_2\text{SiMe}_2$ (**4**), $[(\eta^5\text{-C}_5\text{H}_4)_2\text{Co}_2(\mu_2\text{-S}_2\text{C}_2\text{B}_{10}\text{H}_{10})\text{SiMe}_2$ (**5**), $[(\eta^5\text{-C}_5\text{H}_3)\text{CoI}_2](\mu\text{-I})[(\eta^5\text{-C}_5\text{H}_3)\text{Co}(\text{CO})\text{I}](\text{SiMe}_2)_2$ (**8**), $[(\eta^5\text{-C}_5\text{H}_3)\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})]_2(\text{SiMe}_2)_2$ (**9**), were successfully synthesized in moderate yield by the reactions of corresponding ligands, $(\text{C}_5\text{H}_5)_2\text{SiMe}_2$ (**1**) and $(\text{C}_5\text{H}_4)_2(\text{SiMe}_2)_2$ (**6**), respectively. The molecular structures of **3**, **5**, **6**, **8** and **9** was determined by X-ray crystallographic analysis, which distinctly depict various molecular structures containing the Cp rings and the metal centers with halide or 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolato ligands. For the $(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2$ complexes, coordination of the fragments CpCo favors a *exo* conformation. With the rigid structure of the di-bridged ligand $(\text{C}_5\text{H}_4)_2(\text{SiMe}_2)_2$, only *cis* isomers of the corresponding $(\eta^5\text{-C}_5\text{H}_3)_2(\text{Si}_2\text{Me}_2)_2$ complexes are formed. All the complexes have been well characterized by elemental analysis, NMR and IR spectra.

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1. Introduction

During the past few years, metal complexes containing chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligands have attracted significant attentions for their advanced molecular structure [1]. A variety of the 16-electron “*pseudo*-aromatic” half-sandwich carborane complexes, such as $\text{Cp}^*\text{M}(\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10})$ ($\text{M} = \text{Co}$ [2], Rh [3], Ir [4]; $\text{E} = \text{S}, \text{Se}$), have been synthesized and described. Furthermore, these complexes can be used as precursors to the study of heterometallic clusters [5] and discrete supramolecular complexes [6].

In our previous work, we synthesized several half-sandwich *ortho*-carboranedichalcogenolato metal complexes with S- and O-functionalized cyclopentadienyl ligand to study the geometric chemistry of these compounds [7].

Recently, we have reported some binuclear half-sandwich *ortho*-carboranedichalcogenolato cobalt and rhodium complexes with flexible ether chain-bridged bis(cyclopentadienyl) group, and found that intermolecular channels were formed due to the chain-bridged Cp panels [8].

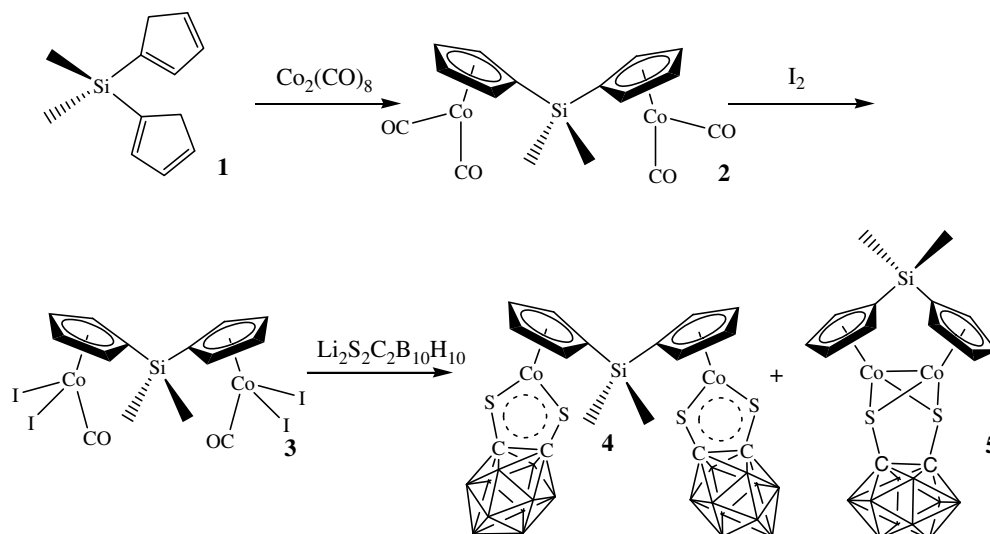
With the aim of extending the chemistry of binuclear *ortho*-carboranedichalcogenolato metal complexes, herein we explored the synthesis of $(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2$ and $(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2$ bridged cobalt derivatives, among which several crystal structures were crystallographically studied.

2. Results and discussion

2.1. Synthesis of the $(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2$ complexes

The synthetic approach to the binuclear half-sandwich cobalt dithiolate carborane complex **4** and **5** is outlined in Scheme 1.

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Scheme 1. Synthesis of the $(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2$ complexes.

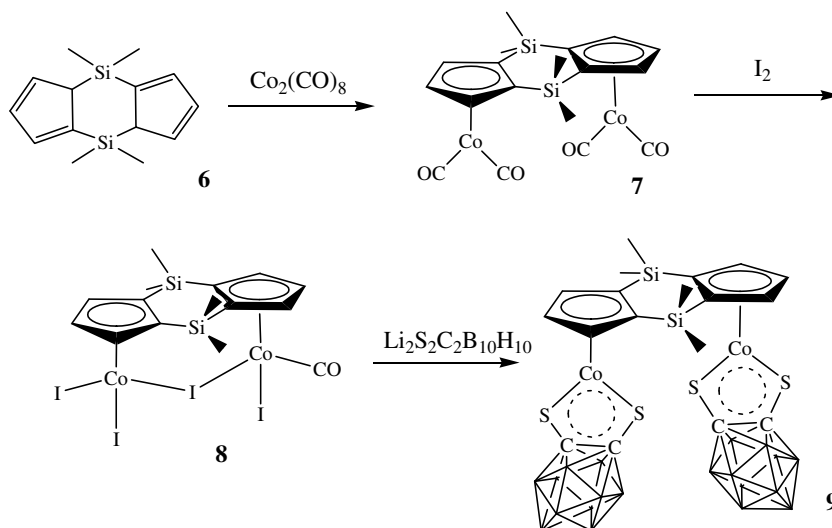
Dicyclopentadienyldimethylsilane **1** was synthesized by the reaction of excessive sodium cyclopentadienide with Me_2SiCl_2 in THF according to the similar procedure in the literatures [9]. The formula of **1** was confirmed by the IR and ^1H NMR spectra.

After refluxing for 5 h, **1** reacted with $\text{Co}_2(\text{CO})_8$ in CH_2Cl_2 solution to give the dicarbonyl complex **2** as red oil in moderate yield. Complex **2** showed two strong carbonyl stretching frequencies at 2002 and 1959 cm^{-1} , which have been identified as the terminal carbonyl groups in the typical region [7,8]. The black-purple air-sensitive complex **3** was obtained by the oxidative addition to the metal centers of **2** within the iodine solution. The IR spectrum showed a carbonyl absorption at 2064 cm^{-1} , in agreement with the molecular structure. In the ^1H NMR spectrum, the cyclopentadienyl signals of **3** appeared at 5.87 and 5.69 ppm, while the protons in the silyl bridge were observed at 1.06 ppm.

Treatment of complex **3** with dilithium dithiolate carborane gave two binuclear complexes **4** and **5**. The symmetric methyl deformations of the bridge between two cyclopentadienyl rings were observed at 1250 cm^{-1} and 1251 cm^{-1} in the IR spectra of the two products, respectively. The bands at 2575 cm^{-1} and 2560 cm^{-1} were assigned to the B–H characteristic absorptions of carborane. Beside the signals of silyl group at 0.86 ppm, a couple of signals were found in both of the ^1H NMR spectra, identified as the protons in the Cp rings of **4** and **5**.

2.2. Synthesis of the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{Si}_2\text{Me}_2)_2$ complexes

For comparison with the *mono*-bridged binuclear cobalt complexes, we have also investigated both the synthesis and structures of the cobalt analogues derived from the dibridged cyclopentadienyl ligand $(\text{C}_5\text{H}_4)_2(\text{Si}_2\text{Me}_2)_2$ (**6**), as depicted in Scheme 2.

Scheme 2. Synthesis of the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{Si}_2\text{Me}_2)_2$ complexes.

The ligand **6** can be easily prepared in 75% yield by the reaction of the Me_2SiCl_2 with the sodium salt of **1**, following a slightly modified literature method [10].

Binuclear cobalt complex **7** was obtained through the similar literature procedure. The IR spectrum was in good agreement with molecular structure which has been reported before [11].

Complex **8** was obtained by the oxidation decarbonylation of **7** as a black-purple solid. Owing to its solubility in Et_2O , complex **8** was purified by hexane, which was a little different from the preparation process of **3**. The absorption of the single carbonyl group can be obviously observed at 2060 cm^{-1} in the solid state IR spectrum of complex **8**.

As the preparation of **4**, similar reaction has been extended to complex **9**, which can be isolated as dark-brown solid in 63% yield by the reaction of **8** with $\text{Li}_2\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ in $\text{Et}_2\text{O}/\text{THF}$ solution. The IR spectrum of **9** in the solid state exhibits intense B–H stretching of carborane at about 2581 cm^{-1} . In the ^1H NMR spectrum, two signals for the protons of the Cp rings were observed at 5.70 and 5.31 ppm, while one signal for the silyl groups was at 0.88 ppm.

3. Molecular structures

Diffraction data of **3**, **5**, **6**, **8** and **9** were collected on a Bruker Smart APEX CCD diffractometer (Mo $\text{K}\alpha$ radi-

ation). The structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL-97), all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions (see Table 1).

Crystals of complex **3** were obtained by the diffusion of Et_2O into a dichloromethane solution. The molecular structure of **3** has been established by single crystal X-ray structure analysis (Fig. 1). Two units of three-legged half-sandwich CpCo were linked by one silyl bridge. In each unit, the cobalt atom is η^5 -bond to the cyclopentadienyl ring and δ -bond to two terminal iodine atoms and to one carbonyl group with typical Co–I and Co–C bonding lengths. Due to the repulsion of the bulky iodine atoms, two cyclopentadienyl rings face each other with their non-coordinated sides and the dihedral angle is about 105° . With the rotation property of the Cp rings around the two silyl-cyclopentadienyl bonds, the whole molecular appears *exo-cis* conformation, and both of the metal centers are located far away from each other in a distance of $6.9081(26)\text{ \AA}$ [12].

By the diffusion of the hexane into the CH_2Cl_2 solution, the crystals of complex **5** were successfully obtained. As shown in Fig. 2, the molecular structure of **5** contains a pair of cobalt atoms linked by a single metal–metal bond, one chelated dithiolate carborane ligand and the silyl-bridged cyclopentadienyl group. Bonding to both of the

Table 1
X-ray crystallographic data and processing parameters for **3**, **5**, **6**, **8** and **9**

| Complex | 3 | 5 | 6 | 8 | 9 |
|--|--|---|------------------------------------|--|---|
| Empirical formula | $\text{C}_{14}\text{H}_{14}\text{Co}_2\text{I}_4\text{O}_2\text{Si}$ | $\text{C}_{14}\text{H}_{24}\text{B}_{10}\text{Co}_2\text{S}_2\text{Si}$ | $\text{C}_7\text{H}_{10}\text{Si}$ | $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{Co}_2\text{I}_4\text{OSi}_2$ | $\text{C}_{18.5}\text{H}_{39}\text{B}_{20}\text{ClCo}_2\text{S}_4\text{Si}_2$ |
| Formula weight | 867.80 | 510.50 | 122.24 | 980.86 | 815.43 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ | $P2_1/m$ |
| <i>a</i> (Å) | 7.256(3) | 6.797(5) | 8.900(4) | 12.869(5) | 11.093(4) |
| <i>b</i> (Å) | 12.870(4) | 11.875(8) | 9.090(4) | 13.717(5) | 16.079(6) |
| <i>c</i> (Å) | 23.375(8) | 13.807(10) | 9.362(4) | 15.806(6) | 22.221(8) |
| α (°) | 90 | 90 | 90 | 90 | 90 |
| β (°) | 94.527(5) | 96.792(9) | 108.065(6) | 97.260 | 96.748(6) |
| γ (°) | 90 | 90 | 90 | 90 | 90 |
| Volume (Å ³) | 2176.1(13) | 1106.5(13) | 720.1(6) | 2767.6(18) | 3936(2) |
| <i>Z</i> | 4 | 2 | 4 | 4 | 4 |
| μ (mm ⁻¹) | 7.258 | 1.742 | 0.220 | 5.947 | 1.201 |
| Crystal size (mm) | $0.20 \times 0.10 \times 0.08$ | $0.45 \times 0.15 \times 0.15$ | $0.30 \times 0.15 \times 0.10$ | $0.20 \times 0.10 \times 0.08$ | $0.20 \times 0.10 \times 0.02$ |
| D_{calcd} (mg/m ³) | 2.649 | 1.532 | 1.128 | 2.354 | 1.376 |
| <i>F</i> (000) | 1576 | 516 | 264 | 1808 | 1652 |
| θ range (°) | 1.75–27.20 | 1.49–26.01 | 2.76–27.14 | 1.60–27.16 | 0.92–25.01 |
| <i>h, k, l</i> collected | $\pm 9; -16, 14; -29, 26$ | $\pm 8; -10, 14; -16, 17$ | $-5, 11; \pm 11; -11, 9$ | $-16, 14; \pm 17; -20, 19$ | $\pm 13; -19, 17; -23, 26$ |
| Reflections collected/unique | 10677 / 4734 | 5020/2273 | 3458/1560 | 13625/6048 | 16658/12047 |
| | [$R_{\text{int}} = 0.0703$] | [$R_{\text{int}} = 0.0557$] | [$R_{\text{int}} = 0.0556$] | [$R_{\text{int}} = 0.0700$] | [$R_{\text{int}} = 0.1662$] |
| Data/restraints/parameters | 4734/0/210 | 2273/0/153 | 1560/0/75 | 6048/0/248 | 12047/1/904 |
| Goodness-of-fit on F^2 | 0.917 | 1.017 | 0.978 | 0.842 | 0.792 |
| Final <i>R</i> indices [$I > 2\sigma(I)$] ^a | $R_1 = 0.0448,$ $wR_2 = 0.0883$ | $R_1 = 0.0476,$ $wR_2 = 0.1102$ | $R_1 = 0.0507,$ $wR_2 = 0.1345$ | $R_1 = 0.0429,$ $wR_2 = 0.0935$ | $R_1 = 0.0769,$ $wR_2 = 0.1450$ |
| <i>R</i> indices (all data) | $R_1 = 0.0836,$ $wR_2 = 0.1149$ | $R_1 = 0.0712,$ $wR_2 = 0.1222$ | $R_1 = 0.0621,$ $wR_2 = 0.1409$ | $R_1 = 0.0796,$ $wR_2 = 0.1032$ | $R_1 = 0.2370,$ $wR_2 = 0.1935$ |
| Largest diffraction peak and hole (e Å ⁻³) | 0.995 and -1.425 | 0.624 and -0.647 | 0.397 and -0.237 | 1.005 and -0.819 | 0.481 and -0.743 |

[a] $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$, $wR_2 = [\sum(|F_o|^2 - |F_c|^2) / \sum(F_o^2)]^{1/2}$.

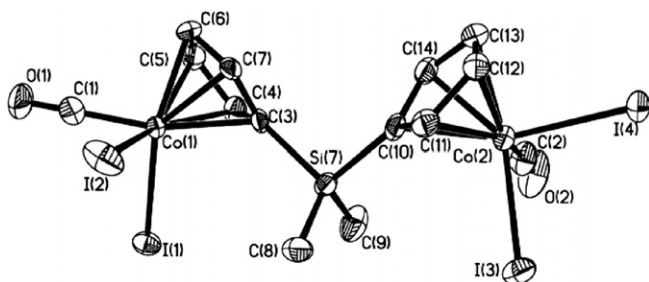


Fig. 1. Molecular structure of **3**. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–C(1) 1.768(12), Co(1)–C(6) 2.040(9), Co(1)–I(2) 2.5533(15), Co(1)–I(1) 2.5657(15), Co(2)–C(2) 1.746(11), Co(2)–C(13) 2.051(10), Co(2)–I(3) 2.5683(14), Co(2)–I(4) 2.5744(15), O(1)–C(1) 1.120(12), O(2)–C(2) 1.142(12), Co(1)···Co(2) 6.9081(26); C(1)–Co(1)–I(1) 90.7(4), C(1)–Co(1)–I(2) 86.0(4), C(2)–Co(2)–I(3) 87.9(4), C(2)–Co(2)–I(4) 87.1(4), I(2)–Co(1)–I(1) 95.51(5), I(3)–Co(2)–I(4) 95.32(5), O(1)–C(1)–Co(1) 177.4(11), O(2)–C(2)–Co(2) 175.9(12), C(3)–Si(7)–C(10) 101.4(4), C(8)–Si(7)–C(9) 112.1(6).

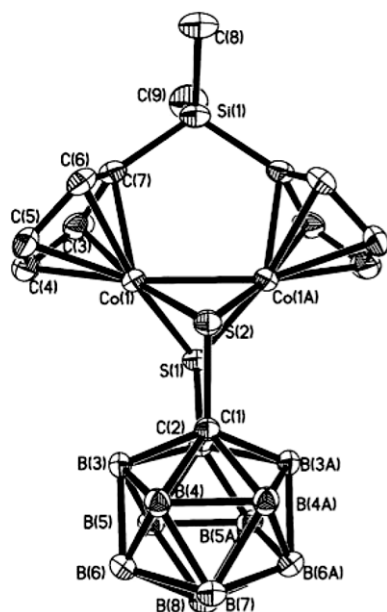


Fig. 2. Molecular structure of **5**. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–S(1) 2.2077(16), Co(1)–S(2) 2.2167(16), Co(1)–Co(1A) 2.3467(19), S(1)–C(2) 1.836(5), S(1)–Co(1A) 2.2077(16), S(2)–C(1) 1.826(5), S(2)–Co(1A) 2.2167(16); S(1)–Co(1)–S(2) 85.20(6), S(1)–Co(1)–Co(1A) 57.90(3), S(2)–Co(1)–Co(1A) 58.04(3), Co(1)–S(1)–Co(1A) 64.21(6), Co(1A)–S(2)–Co(1) 63.92(7), C(2)–S(1)–Co(1) 102.66(15), C(2)–S(1)–Co(1A) 102.66(15), C(1)–S(2)–Co(1A) 102.58(14), C(1)–S(2)–Co(1) 102.58(14).

bridging sulfur atoms, each of the cobalt belongs to a five-membered metallacycle CoS_2C_2 . Different from complex **3**, two metal fragments coordinated in an *endo* fashion with respect to the rings and in a mutually *cis* orientation, which induces the bridging interaction and the M–M bonding of the metal centers [12]. The Co–Co length (2.3467(19) Å), is a little shorter than that of the analogue with the ether-bridged Cp ligand [8], due to the restriction of the silyl group between the Cp rings.

In the crystal structure of ligand **6**, two cyclopentadienyl rings are held in a fairly close position to each other, and

the dihedral angle between them is less than 1° , indicating that the two rings are almost parallel. The central six-membered ring, which is formed by two silicons and four carbons, adopts a typical chair conformation [11,13].

The structure of complex **8** has also been confirmed by X-ray diffraction, a view of the molecule is shown in Fig. 3. The crystal structure, as for complex **3**, shows the typical three-legged coordination around each cobalt atom in a *pseudo*-octahedral framework. Besides the presence of the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{Si}_2\text{Me}_2)_2$ group, one cobalt center bonds to two iodine atoms, while the other one bonds to one iodine, and one carbonyl group. The fourth iodine atom coordinates to both of the metal centers, acting as a bridging ligand. The Co–I bonding lengths between the two cobalt centers are not exactly the same, attribute to the different bulky level between the iodine atom and the carbonyl group. With the bridging coordination of the fourth iodine, the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{Si}_2\text{Me}_2)_2$ group adopts a bent conformation with a flat boat conformation of the central six-membered ring. The fold angle between the two cyclopentadienyl rings is 19° . The Co–Co length (4.3699(19) Å) is a little longer than that of complex **7** [11a], induced by the repulsion of the bulky bridging iodine (see Fig. 4).

The single crystal of complex **9** was grown from the concentrated dichloromethane solution at low temperature. Fig. 5 indicates there are two fragments of $\text{CpCoS}_2\text{C}_2\text{-B}_{10}\text{H}_{10}$ [8] in one molecule, connected by two silyl bridges. Both of the metal centers adopt a three-legged piano-stool conformation. Each of the cobalt atoms is bond to one Cp ring and two bridging-sulfur atoms of the dithiolate carborene, to form a nearly planar five-membered metallacycle CoS_2C_2 . Besides the δ -bonding, there is also a π donation between the lone pair of electrons on the coordinated sulfur atom and the d orbit of the cobalt center, which suggests that some of multiple-bond character may exist in the Co–S bonds [5]. Different from complex **5**, the molecular structure is not symmetrical, with a 15° -fold-angle between the CoS_2C_2 rings in two fragments. Free of any bridging atom, the distance between two metal atoms (5.2010(16) Å) is

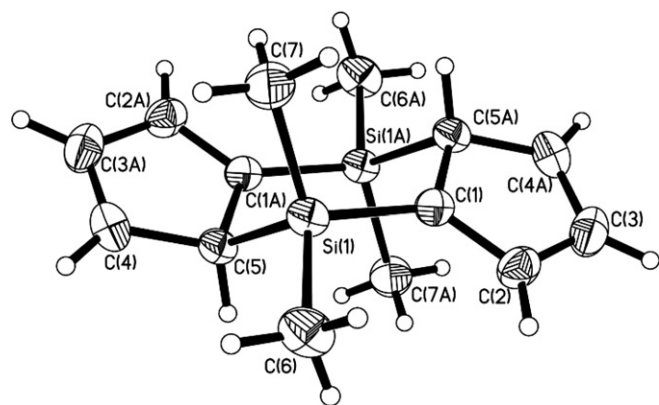


Fig. 3. Molecular structure of **6**. Selected bond lengths (Å) and angles (°): Si(1)–C(1) 1.848(2), Si(1)–C(7) 1.855(2), Si(1)–C(6) 1.858(2), Si(1)–C(5) 1.908(2), C(1)–C(2) 1.351(3); C(1)–Si(1)–C(7) 110.40(11), C(7)–Si(1)–C(6) 111.75(13), C(1)–Si(1)–C(5) 104.77(9).

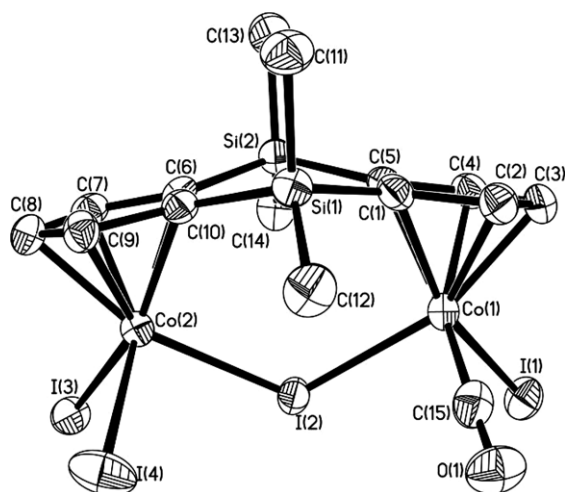


Fig. 4. Molecular structure of **8**. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–C(15) 1.739(10), Co(1)–C(1) 2.059(7), Co(1)–I(1) 2.5643(12), Co(1)–I(2) 2.5706(12), Co(2)–C(8) 2.038(7), Co(2)–I(2) 2.5825(14), Co(2)–I(3) 2.5895(12), Co(2)–I(4) 2.5915(13), O(1)–C(15) 1.150(10), Co(1)⋯Co(2) 4.3699(19); C(15)–Co(1)–I(1) 89.1(2), C(15)–Co(1)–I(2) 89.0(3), I(1)–Co(1)–I(2) 90.42(4), I(2)–Co(2)–I(3) 86.93(3), I(2)–Co(2)–I(4) 92.98(4), I(3)–Co(2)–I(4) 93.94(5), O(1)–C(15)–Co(1) 178.9(8), Co(1)–I(2)–Co(2) 115.98(4).

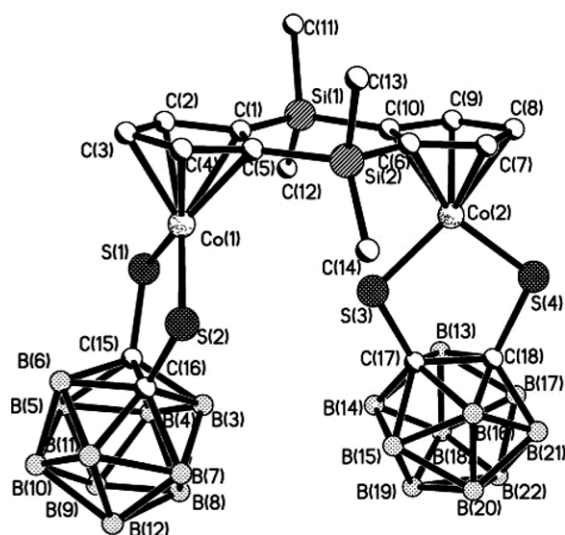


Fig. 5. Molecular structure of **9**. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–C(3) 2.0471(7), Co(2)–C(8) 2.0332(7), Co(1)–S(2) 2.1371(6), Co(1)–S(1) 2.1429(5), Co(2)–S(3) 2.1022(5), Co(2)–S(4) 2.1398(5), S(1)–C(15) 1.7862(6), S(2)–C(16) 1.7960(7), S(3)–C(17) 1.8300(7), S(4)–C(18) 1.8600(7), Co(1)⋯Co(2) 5.2010(16), C(15)–C(16) 1.5507(8), C(15)–B(3) 1.6512(7), C(17)–C(18) 1.5697(8), C(17)–B(13) 1.6247(9), S(2)–Co(1)–S(1) 96.93(3), C(15)–S(1)–Co(1) 103.40(3), C(16)–S(2)–Co(1) 104.56(3), C(16)–C(15)–S(1) 118.86(3), S(3)–Co(2)–S(4) 97.93(3), C(17)–S(3)–Co(2) 104.62(3), C(18)–S(4)–Co(2) 104.64(3), C(17)–C(18)–S(4) 114.39(3).

longer than that of complex **8**. In the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{Si}_2\text{Me}_2)_2$ group, two cyclopentadienyl rings together with two silicon atoms are almost coplanar, suggesting that there is a repulsion between the two fragments, which is also the reason of preventing any M–M bonding in the molecule.

4. Conclusion

In this paper, we have successfully synthesized binuclear half-sandwich cobalt halides with two kinds of silyl-bridged bis(cyclopentadienyl) groups. These complexes can be further converted to binuclear half-sandwich *ortho*-carboranedithiolato cobalt complexes. Crystal structures of **3**, **5**, **6**, **8** and **9** reveal different conformations of the CpCo fragments in each complex. For the $(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2$ complexes, coordination of the fragments CpCo favors a *exo-cis* conformation for steric reasons due to the rotation of Cp rings in the mono-bridged ligand $(\text{C}_5\text{H}_5)_2\text{SiMe}_2$, which induces the long distances between the cobalt centers and large dihedral angles. With the rigid structure of the dibridged ligand $(\text{C}_5\text{H}_4)_2(\text{SiMe}_2)_2$, only *cis* isomers of the corresponding $(\eta^5\text{-C}_5\text{H}_3)_2(\text{Si}_2\text{Me}_2)_2$ complexes are formed. Bridging interaction and fragments repulsion can be observed in the crystal structures of the complexes with the dibridged ligand. The study of binuclear half-sandwich *ortho*-carboranedithiolato cobalt complexes also augurs that the rotatable ligand $(\text{C}_5\text{H}_5)_2\text{SiMe}_2$ and relatively rigid ligand $(\text{C}_5\text{H}_4)_2(\text{SiMe}_2)_2$ are able to form some appropriate early/late heterobimetallic complexes with *cis* conformation, which may activate some small polar molecules, such as carbon monoxide [11a]. The research on the corresponding rhodium and iridium compounds is under investigation.

5. Experimental

5.1. General

All the reactions were carried out with the standard Schlenk techniques under nitrogen atmosphere. Solvents were dried and deoxygenated by M. Braun Solvent Purification System (4464) and collected just before use. $\text{Li}_2\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ were synthesized according to the procedures described in the literature [14]. The silica gel and neutral Al_2O_3 had been activated at 200 °C over night and kept under nitrogen before the process of column chromatography or filtration. All other reagents were purchased from commercial sources, and used without additional purifications. The element analyses were performed on a Rapid HN-O 240 C Analyzer. Infrared spectra were recorded on Nicolet-FT-IR-50X spectrophotometer; only characteristic frequencies of each product were listed. ^1H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{11}B NMR (160 MHz) spectra were obtained using Bruker DMX-500 spectrophotometer in CDCl_3 , respectively. Chemical shifts (downfield from TMS (^1H and ^{13}C) and BF_3OEt_2 (^{11}B)) and coupling constants are reported in ppm and in Hz, respectively.

5.2. Preparation of $(\text{C}_5\text{H}_5)_2\text{SiMe}_2$ (**1**)

$\text{Me}_2\text{Si}_2\text{Cl}_2$ (28 ml, 0.23 mol) was added to a solution of $\text{C}_5\text{H}_5\text{Na}$ (42.2 g, 0.48 mol) in THF (50 ml) at 0 °C, and

the solution was stirring overnight. The solvent was evaporated under reduced pressure and then 200 ml hexane was added to the reaction mixture. Insoluble materials were removed by filtration. Solvent and all the volatiles are removed at oil aspirator pressure, affording the light yellow oil. After the distillation at 74 °C (6 mmHg), **1** (35.1 g, 81%) was collected as yellow oil, which contained three isomers in the NMR spectrum. IR (film): $\nu(\text{methyl})$ 1251 cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , ppm): δ 6.90–6.72 (m, 6H, Cp), 3.28–3.24 (m, 4H, Cp), 0.29–0.27 (m, 6H, Me_2Si).

5.3. Preparation of $[(\eta^5\text{-C}_5\text{H}_4)\text{Co}(\text{CO})\text{I}_2]_2\text{SiMe}_2$ (**3**)

A solution containing $\text{Co}_2(\text{CO})_8$ (1.23 g, 3.60 mmol) and **1** (1.06 g, 5.64 mmol) in CH_2Cl_2 (30 ml) was refluxed for 5 h and then solvent was removed in vacuo. The residue was dissolved in 20 ml ether and filtered through 3-cm layer of neutral Al_2O_3 . The red filtrate was collected. The solvent was evaporated under reduced pressure and afforded **2** (732 mg, 49% according to the $\text{Co}_2(\text{CO})_8$) as red liquid. IR (film): $\nu(\text{CO})$ 2022, 1959 cm^{-1} , $\nu(\text{methyl})$ 1255 cm^{-1} . A solution containing iodine (937 mg, 3.8 mmol) in ether (20 ml) was added dropwise to a solution of **2** (732 mg, 1.76 mmol) in ether (30 ml) at 0 °C. The color of the solution changed from red to dark and the black-purple precipitate was formed. The solution was allowed to warm to room temperature and then stirred for 3 hours. After filtration, the black-purple solid was washed with ether (2 × 15 ml). Recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ afforded black-purple crystals of **3** (1.36 g, 43% according to the $\text{Co}_2(\text{CO})_8$). Anal. Calc. for $\text{C}_{14}\text{H}_{14}\text{Co}_2\text{I}_4\text{O}_2\text{Si}$ (867.80 g/mol): C, 19.38; H, 1.63. Found: C, 19.13; H, 1.43%. IR (KBr): $\nu(\text{CO})$ 2064 cm^{-1} , $\nu(\text{methyl})$ 1250 cm^{-1} . ^1H NMR (500 MHz, CHCl_3 , ppm): δ 5.87 (t, 4H, Cp), 5.69 (t, 4H, Cp), 1.06 (s, 6H, Me_2Si).

5.4. Preparation of $[(\eta^5\text{-C}_5\text{H}_4)\text{Co}(\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10})]_2\text{SiMe}_2$ (**4**) and $[(\eta^5\text{-C}_5\text{H}_4)_2\text{Co}_2(\mu_2\text{-S}_2\text{C}_2\text{B}_{10}\text{H}_{10})\text{SiMe}_2$ (**5**)

A solution of $\text{Li}_2\text{S}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ (0.50 mmol in 15 ml of Et_2O) was added to the solution of **3** (217 mg, 0.25 mmol) in THF (30 ml) at 0 °C. The solution was allowed to warm to room temperature and then stirred overnight. The solvent was removed under reduced pressure. The residue was redissolved in THF and purified by column chromatography on silica. The component in the first brown band was eluted with CH_2Cl_2 -hexane (1:1) and recrystallized from THF/hexane at –18 °C to give brown crystals of **5** (8 mg, 6%). Anal. Calc. for $\text{C}_{14}\text{H}_{24}\text{B}_{10}\text{Co}_2\text{S}_2\text{Si}$ (510.50 g/mol): C, 32.94; H, 4.74. Found: C, 32.60; H, 4.62%. IR (KBr): $\nu(\text{B-H})$ 2560 cm^{-1} , $\nu(\text{methyl})$ 1251 cm^{-1} . ^1H NMR (500 MHz, CHCl_3 , ppm): δ 5.35 (t, 4H, Cp), 4.92 (t, 4H, Cp), 0.87 (s, 6H, Me_2Si). ^{11}B NMR (160 MHz, CDCl_3 , ppm): δ –3.45, –4.63, –5.44, –6.88, –8.25, –9.34, –11.54, –12.76. The second band was collected and recrystallized from CH_2Cl_2 /hexane at room tempera-

ture to give red-brown crystals of **4** (104 mg, 58%). Anal. Calc. for $\text{C}_{16}\text{H}_{34}\text{B}_{20}\text{Co}_2\text{S}_4\text{Si}$ (716.87 g/mol): C, 26.81; H, 4.78. Found: C, 26.35; H, 4.55%. IR (KBr): $\nu(\text{B-H})$ 2575 cm^{-1} , $\nu(\text{Si-Me})$ 1259 cm^{-1} . ^1H NMR (500 MHz, CHCl_3 , ppm): δ 5.45 (t, 4H, Cp), 5.30 (t, 4H, Cp), 0.86 (s, 6H, Me_2Si). ^{13}C NMR (125 MHz, CHCl_3 , ppm): δ 93.23, 87.36, 86.11 (s, Cp), 67.96 (s, carborane), 0.99 (s, Me_2Si). ^{11}B NMR (160 MHz, CDCl_3 , ppm): δ –6.30, –7.28, –8.79, –9.74, –10.69.

5.5. Preparation of $(\text{C}_5\text{H}_4)_2(\text{SiMe}_2)_2$ (**6**)

A solution containing **1** (6.58 g, 35 mmol) was added dropwise to solid sodium (0.81 g, 35 mmol) in THF (35 ml) at 0 °C. The solution was allowed to warm to room temperature and then stirred overnight. The excessive sodium was removed after filtration. This $(\text{C}_5\text{H}_4\text{Na})_2\text{SiMe}_2$ solution was directly used in the following step without any further purification.

Me_2SiCl_2 (4.51 g, 35 mmol) was added to the $(\text{C}_5\text{H}_4\text{Na})_2\text{SiMe}_2$ solution at 0 °C. White precipitate was formed immediately. After stirring for 4 h, the solvent was evaporated under reduced pressure. Hexane (30 ml) was added to the reaction mixture and then stirred overnight. Insoluble materials were removed by filtration. Solvent and all the volatiles are removed in reduced pressure, affording the yellow oil. After the distillation at 170 °C (6 mmHg), **6** (6.40 g, 75%) was collected as colorless solid. Recrystallization with a minimal amount in hexane afforded colorless crystals of **6**. IR (film): $\nu(\text{methyl})$ 1252 cm^{-1} . The ^1H NMR spectrum was in good agreement with the reported literature [10].

5.6. Preparation of $[(\eta^5\text{-C}_5\text{H}_3)\text{CoI}_2](\mu\text{-I})[(\eta^5\text{-C}_5\text{H}_3)\text{Co}(\text{CO})\text{I}](\text{SiMe}_2)_2$ (**8**)

A solution of $\text{Co}_2(\text{CO})_8$ (342 mg, 1 mmol) and **6** (300 mg, 1.25 mmol) in THF (25 ml) was refluxed for 6 h. Solvent was removed in vacuo after the solution was cooled to room temperature. The residue was dissolved in 20 ml hexane and filtered through 3-cm layer of neutral Al_2O_3 . The red filtrate was concentrated to 5 ml under reduced pressure and stored at –18 °C to afford brownish red crystals of **7** (388 mg, 82%) from the crude product. IR (film): $\nu(\text{CO})$ 2022, 1962 cm^{-1} , $\nu(\text{methyl})$ 1248 cm^{-1} . A solution containing iodine (481 mg, 1.89 mmol) in ether (10 ml) was added dropwise to a solution of **7** (388 mg, 0.82 mmol) in ether (15 ml) at 0 °C. The color of the solution changed from red to dark and the black-purple precipitate was formed. The solution was allowed to warm to room temperature and then stirred for 3 h. After the evaporation of the solvent, the black-purple solid was washed with hexane (3 × 10 ml) to isolate the excessive iodine. Recrystallization from CH_2Cl_2 /hexane afforded black-purple crystals of **8** (514 mg, 64%). Anal. Calc. for $\text{C}_{15}\text{H}_{18}\text{Co}_2\text{I}_4\text{O-Si}_2 \cdot \text{CH}_2\text{Cl}_2$ (980.86 g/mol): C, 19.59; H, 2.06. Found: C, 19.63; H, 1.98%. IR (KBr): $\nu(\text{CO})$ 2060 cm^{-1} , $\nu(\text{methyl})$

1257 cm⁻¹. ¹H NMR (500 MHz, CHCl₃, ppm): δ 6.16 (t, 2H, Cp), 5.87 (t, 2H, Cp), 5.68 (t, 2H, Cp), 0.87 (s, 12H, Me₂Si).

5.7. Preparation of [(η⁵-C₅H₅)Co(S₂C₂B₁₀H₁₀)]₂-(SiMe₂)₂ (**9**)

A solution of Li₂S₂C₂B₁₀H₁₀ (0.50 mmol in 15 ml of Et₂O) was added to the solution of **8** (224 mg, 0.25 mmol) in THF (30 ml) at 0 °C. The solution was allowed to warm to room temperature and then stirred overnight. The solvent was removed under reduced pressure. The residue was redissolved in THF and purified by column chromatography on silica. Elution with CH₂Cl₂ gave a red-brown zone of the product. Recrystallization from CH₂Cl₂ in -18 °C afforded dark-red crystals of **9** (122 mg, 60%). Anal. Calc. for C₁₈H₃₈B₂₀Co₂S₄Si₂·0.5 CH₂Cl₂ (815.48 g/mol): C, 27.25; H, 4.82. Found: C, 27.52; H, 4.60%. IR (KBr): ν(B-H) 2581 cm⁻¹, ν(methyl) 1256 cm⁻¹. ¹H NMR (500 MHz, CHCl₃, ppm): δ 5.70 (t, 4H, Cp), 5.31 (t, 2H, Cp), 0.88 (s, 12H, Me₂Si). ¹³C NMR (125 MHz, CHCl₃, ppm): δ 93.62, 92.92, 86.15 (s, Cp), 90.35 (s, carborane), 0.99, 0.65 (s, Me₂Si). ¹¹B NMR (160 MHz, CDCl₃, ppm): δ -6.45, -7.41, -8.85, -9.81, -10.78.

5.8. X-ray crystallography

Diffraction data of complexes **3**, **5**, **6**, **8**, and **9** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F² by using full-matrix least-squares techniques (SHELXL), [15] absorption corrections were applied to the data. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions.

6. Supplementary material

CCDC 652939, 652940, 652941, 652942 and 652943 contain the supplementary crystallographic data for **3**, **5**, **6**, **8** and **9**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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