

Synthesis and characterization of hetero-binuclear Co–Rh complexes $[\text{Cp}^*\text{CoS}_2\text{C}_2(\text{B}_9\text{H}_{10})][\text{Rh}(\text{COD})]$ and $[\text{Cp}^*\text{CoSe}_2\text{C}_2(\text{B}_{10}\text{H}_{10})][\text{Rh}(\text{COD})]$

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Abstract

Two hetero-binuclear complexes $[\text{Cp}^*\text{CoS}_2\text{C}_2(\text{B}_9\text{H}_{10})][\text{Rh}(\text{COD})]$ (**2a**) and $[\text{Cp}^*\text{CoSe}_2\text{C}_2(\text{B}_{10}\text{H}_{10})][\text{Rh}(\text{COD})]$ (**2b**) [$\text{Cp}^* = \eta^5$ -pentamethylcyclopentadienyl, COD = *cyclo-octa*-1,5-diene (C_8H_{12})] were synthesized by the reactions of *half*-sandwich complexes $[\text{Cp}^*\text{CoE}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ [E = S (**1a**), Se (**1b**)] with low valent transition metal complexes $[\text{Rh}(\text{COD})(\text{OEt})_2]$ and $[\text{Rh}(\text{COD})(\text{OMe})_2]$. Although the reaction conditions are the same, the structures of two products for dithiolato carborane and diselenolato carborane are different. The cage of the carborane in **2a** was opened; However, the carborane cage in **2b** was intact. Complexes **2a** and **2b** have been fully characterized by ^1H , ^{11}B NMR and IR spectroscopy, as well as by elemental analyses. The molecular structures of **2a** and **2b** have been determined by single-crystal X-ray diffraction analyses and strong metal–metal interactions between cobalt and rhodium atoms (2.6260 Å (**2a**) and 2.7057 Å (**2b**)) are existent.

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Keywords: Cobalt; Hetero-binuclear; Carborane; Metal–metal bonding; Molecular structure

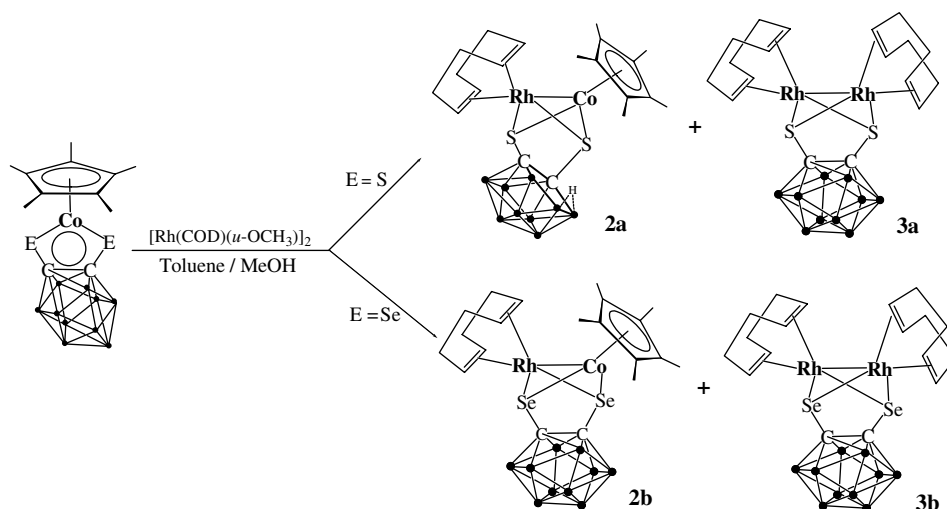
1. Introduction

During the past decades, tremendous efforts have been devoted to dicarba-*closo*-dodecaboranes due to their rich chemistry [1]. An important aspect is the variation of substituents at the carbon atoms in the 1,2-positions [2]. In particular, C-chalcogenolated carborane dianions $\text{C}_2\text{B}_{10}\text{H}_{10}\text{E}_2^{2-}$ (E = S, Se) have received much attention in recent years since they can be incorporated to Cp^*M (M = Co, Rh, Ir) units to form mononuclear 16-electron half-sandwich complexes $[\text{Cp}^*\text{ME}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ (M = Co, Rh, Ir, E = S, Se) [3]. These compounds, containing a “*pseudo*-aromatic” metalladichalcogenolene five-membered ring, have been used as models for further transformations [4], especially for the synthesis of hetero-metallic

clusters with metal–metal bonds stabilized by the ancillary carborane dichalcogenolato ligands [5].

On the other hand, in the history of the development of organometallic chemistry, cyclopentadienide complexes has played an important role since it can be coordinated to metal centers as pentahapto, six- π -electron ligands [6]. As an isolobal analog, the *nido*-carborane dianions $[\text{nido-C}_2\text{B}_9\text{H}_{11}]^{2-}$ not only exhibit the properties of C_5R_5^- ligands [7], but also unique “three-dimensional aromaticity”, which initiated the field of metallacarborane chemistry [8]. Following the synthesis of the first metallacarborane by Hawthorne et al. in 1965 [9], *nido*-carboranes have proved to be excellent bulky and stable building blocks that allow the synthesis of a wide range of heterocarboranes [10], which, in addition to boron and carbon atoms, contain other elements in their skeleton. Such molecules have recently been shown to have a variety of applications in material science [11], catalysis [12], or

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Scheme 1. Syntheses of **2(a,b)** and **3(a,b)**.

medicine [13], which makes carborane chemistry an interesting area of growth. The synthesis of metallacarboranes obtained through *nido*-carboranes have attracted considerable attention in recent years [14]. Particularly, interesting metallacarboranes are those containing intercluster metal–metal bonds, which effectively bridge the two best developed areas of inorganic cluster chemistry, polyhedral boranes and metal clusters [15].

In our previous work, we had obtained unsymmetric homo-binuclear Ir–Ir and hetero-binuclear Ir–Rh complexes based on the ancillary *ortho*-carborane dichalcogenolato ligands [16]. We have now extended our study to the syntheses of hetero-binuclear Co–Rh complexes. It is surprising that the structures of the products for dithiolato carborane and diselenolato carborane are different. Although the carborane cage of complex **2b** remained intact, the corresponding cage in complex **2a** was cleaved to form a *nido*-species. Scheme 1 shows the formation of the two hetero-binuclear clusters. In addition to Co–Rh complexes, two symmetrical homo-binuclear Rh–Rh complexes were also obtained in these two reactions.

2. Results and discussion

2.1. Synthesis of the complexes and spectroscopic characterization

The 16-electron complexes $\text{Cp}^*\text{Co}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ [$\text{E} = \text{S}$ (**1a**), $\text{E} = \text{Se}$ (**1b**)] can be easily synthesized from half-sandwich complex $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ with dilithium 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate and dilithium 1,2-dicarba-*closo*-dodecaborane-1,2-diselenolato [3c]. Reaction of $[\text{Cp}^*\text{CoS}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ with 1 equiv. of $[\text{Rh}(\text{COD})(\text{OEt})_2]$ or $[\text{Rh}(\text{COD})(\text{OMe})_2]$ in toluene/methanol mixture yields two major products, **2a** and **3a** (Scheme 1). Analogous diselenolato complexes **2b** and **3b** can be generated under the same experimental conditions. We have recently reported that complexes **3a** and **3b** can be also obtained by the reac-

tions of the dilithium dichalcogenolato carboranes $\text{Li}_2\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ ($\text{E} = \text{S}, \text{Se}$) with $[\text{Rh}(\text{COD})\text{Cl}]_2$ in moderate yields [17].

Complexes **2a** and **2b** are moderately air-stable in the solid state, but unstable in the solution, and soluble in CH_2Cl_2 or THF. The reaction time for optimum yields of **2a** and **2b** (25–35%) is 10–12 h. However, the yields of **2a** and **2b** increased with longer reaction times. This observation indicates that the coordination ability of metal rhodium to chalcogen is stronger than that of cobalt to chalcogen, which was further confirmed by the reaction of $[\text{Cp}^*\text{CoE}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ [$\text{E} = \text{S}$ (**1a**), $\text{E} = \text{Se}$ (**1b**)] with $[\text{Rh}(\text{COD})\text{Cl}]_2$ in which we only get binuclear complexes **3a** and **3b**.

The IR spectrum of **2a** shows a strong band for the B–H vibration at approximately 2534 cm^{-1} . In addition to a sharp single signal around 1.88 ppm in the ^1H NMR spectrum of **2a**, ascribed to the Cp^* ligand, there are also the signals of methylene groups and olefin protons of COD around 2.13, 2.37, 2.42, 2.63 ppm and 4.46, 4.85, 5.12, 5.30 ppm, respectively. The ^{11}B NMR spectrum of **2a** consists of nine signals around $-6.29, -8.87, -10.48, -17.81, -21.62, -27.28, -31.63, -38.27, -39.23$ ppm, which indicated that the carborane cage was opened. Similarly, we could see the B–H vibration of **2b** at 2533 cm^{-1} . Likewise, the ^1H NMR spectrum of complex **2b** shows two sets of four multiplets from 2.09 ppm to 2.64 ppm and from 4.54 ppm to 5.21 ppm, respectively. The ^{11}B NMR spectrum of **2b** exhibits resonances at $-6.02, -6.86, -8.96, -9.85, -17.59$ ppm which shows that the symmetry of carborane cage is higher than that of **2a**. The elemental analyses of **2a** and **2b** also prove the component of the two complexes.

2.2. Molecular structures of **2a** and **2b**

Complexes **2a** and **2b** can be re-crystallized from CH_2Cl_2 /hexane to give well-formed dark-green single crystals. Complex **2a** crystallized in the triclinic space group $P\bar{1}$

with two molecules in the unit cell. The X-ray structure analysis of **2a** confirms a hetero-bimetallic Co–Rh complex with an opened cage carborane and the structure is shown in Fig. 1. The cluster framework adopted by **2a** is generated by incorporation of a *nido*-C₂B₉ framework into a Co–Rh metal complex. The Co center is six-coordinate with a square-antiprismatic geometry, however, the Rh center adopts five-coordinate geometry. The Cp*Co and (cod)Rh fragments are bridged by two S atoms that are linked to the open C₂B₃ face, and the two S–Co–Rh planes are twisted by 18.9° with respect to one another. The cobaltadithiolenes rings are nonplanar owing to the coordination of the S atoms to Rh. The Co–Rh distance (2.6260 Å) fall within the expected range of metal–metal single bonds [18]. The Co–S bond length of 2.1802 Å is slightly longer than that (2.1448 Å) of a free cobaltadithiolenes ring [3c], further proving that the aromaticity of 16-electron complex has been destroyed. The Rh–C bond distances range from 2.1774 to 2.1994 Å, which are normal values for Rh(I) complexes containing COD ligands *trans* to S donor atoms [19].

A perspective drawing of diselenolate complex **2b** is given in Fig. 2. Different from the structure of **2a**, the carborane cage of **2b** was intact. The molecular structure of **2b** establishes that there is a mirror plane going through the Co–Rh backbone. The metal centers are connected to both selenium atoms and Cp* and COD. Similar to that of complex **2a**, the cobalt and rhodium centres in complex **2b** have the same coordination geometry. The intramolecular Rh(1)–Co(1) distance 2.7057 Å in **2b** is slightly longer than that of **2a**, which also corresponds to a metal–metal single

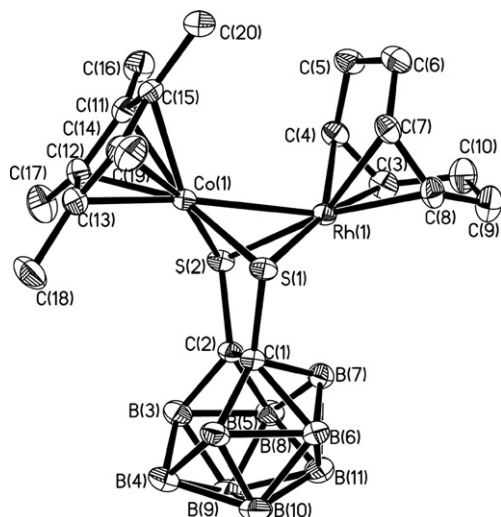


Fig. 1. Molecular structure of **2a** (hydrogen atoms are omitted for clarity): Selected bond lengths(Å) and angles(°): Rh(1)–C(8) 2.177(4), Rh(1)–C(3) 2.187(4), Rh(1)–C(4) 2.198(4), Rh(1)–C(7) 2.199(4), Rh(1)–S(1) 2.3391(11), Rh(1)–S(2) 2.3554(12), Rh(1)–Co(1) 2.6260(8), Co(1)–S(1) 2.1782(13), Co(1)–S(2) 2.1822(13), S(1)–C(1) 1.790(4), S(2)–C(2) 1.811(4), B(7)–C(2) 1.738(6), B(7)–C(1) 1.750(6); S(1)–Rh(1)–Co(1) 51.65(3), S(2)–Rh(1)–Co(1) 51.61(3), S(1)–Co(1)–S(2) 86.76(4), S(1)–Co(1)–Rh(1) 57.37(3), S(2)–Co(1)–Rh(1) 57.78(3), Co(1)–S(1)–Rh(1) 70.98(3), Co(1)–S(2)–Rh(1) 70.60(3).

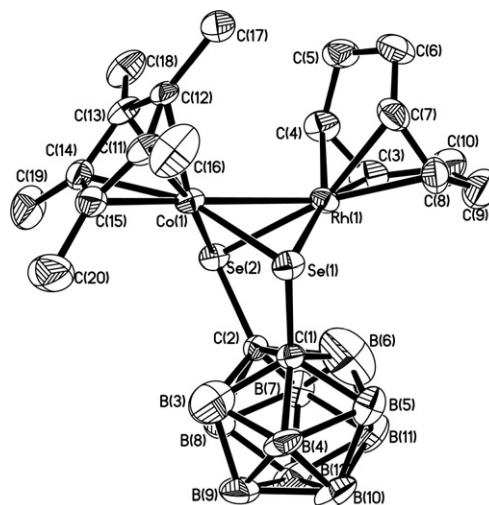


Fig. 2. Molecular structure of **2b** (hydrogen atoms are omitted for clarity): Rh(1)–C(8) 2.152(6), Rh(1)–C(7) 2.167(6), Rh(1)–C(3) 2.171(6), Rh(1)–C(4) 2.172(6), Rh(1)–Se(1) 2.4665(11), Rh(1)–Se(2) 2.4721(9), Rh(1)–Co(1) 2.7057(12), Co(1)–Se(1) 2.2629(12), Co(1)–Se(2) 2.2842(12), Se(1)–C(1) 1.942(5), Se(2)–C(2) 1.940(5), C(1)–C(2) 1.524(7); Se(1)–Rh(1)–Co(1) 51.64(3), Se(2)–Rh(1)–Co(1) 52.12(3), Se(1)–Co(1)–Se(2) 89.53(3), Se(1)–Co(1)–Rh(1) 58.72(3), Se(2)–Co(1)–Rh(1) 58.67(3), Co(1)–Se(1)–Rh(1) 69.64(3), Co(1)–Se(2)–Rh(1) 69.21(3).

bond. The cobaltadiselenolate heterocycle (Co(1)–Se(1)–C(1)–C(2)–Se(2)) in **2b** is bent with a dihedral angle along the Se(1)–Se(2) of 148.8°, due to the addition of the (COD)Rh moiety. The Rh–Se bond lengths in **2b** (2.4693 Å av.) are slightly longer than the reported averaged Rh–Se value (2.457(2) Å) [20] for reduction of electron distribution from the diselenolate ligands, which coordinate both cobalt and rhodium atoms.

In conclusion, we have synthesized two hetero-binuclear Co–Rh complexes based on ancillary carborane dichalcogenolato ligands. Compared to the reactions between 16-electron half-sandwich Ir complex [Cp*IrE₂C₂(B₁₀H₁₀)] (E = S, Se) and [Rh(COD)(OMe)₂] [16], these two reactions indicate that analogous reactions can proceed via different reaction mechanism. Further studies on the formation of metal clusters based on dichalcogenolato ligands and the corresponding mechanistic studies are ongoing.

3. Experimental

All manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were dried and deoxygenated by M. Braun Solvent Purification System (4464) and collected just before use. The starting materials [Cp*CoE₂C₂(B₁₀H₁₀)] [E = S(**1a**), E = Se(**1b**)] [3c], [Rh(COD)(OEt)₂] and [Rh(COD)(OMe)₂] [21] were prepared according to the reported literatures. Elemental analyses were performed on Elementar III Vario EI Analyzer. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer, ¹H NMR (500 MHz) and ¹¹B NMR (160 MHz) spectra were obtained on a Bruker DMX-500 spectrometer.

3.1. Synthesis of $[Cp^*CoS_2C_2(B_9H_{10})][Rh(COD)]$ (**2a**)

$[Rh(COD)(OCH_3)_2]$ (48 mg, 0.1 mmol) or $[Rh(COD)(OEt)_2]$ (51 mg, 0.1 mmol) was added to the green solution of **1a** (80 mg, 0.2 mmol) in toluene (15 ml) and methanol (15 ml). The mixture was stirred at room temperature for 10–12 h. And the color of the solution gradually changed from green to red brown. The solvent was evaporated under reduced pressure. The residue was re-dissolved in 3 ml of dichloromethane and chromatographed on silica gel. Elution with dichloromethane–hexane sequentially gave a red band that contained **3a** (CH_2Cl_2 /hexane = 1:1) (24 mg, 38%) and dark green zone that contained **2a** (CH_2Cl_2 /hexane = 2:1) (40 mg, 33%). Anal. Calc. for $C_{20}H_{37}B_9CoRhS_2$: C, 39.98; S, 9.99; H, 6.16. Found: C, 40.06; S, 10.26; H, 5.49%. 1H NMR (500 MHz, $CDCl_3$, δ /ppm): 1.88 (s, CH_3 , 15 H), 2.13, 2.37, 2.42, 2.63 (br, CH_2 , 8H), 4.46, 4.85, 5.12, 5.30 (br, $CH=$, 4H). ^{11}B NMR (160 MHz, $CDCl_3$, δ /ppm): –6.29, –8.87, –10.48, –17.81, –21.62, –27.28, –31.63, –38.27, –39.23. IR (KBr disk): 2534 cm^{-1} (ν_{B-H}).

3.2. Synthesis of $[Cp^*CoSe_2C_2(B_{10}H_{10})][Rh(COD)]$ (**2b**)

$[Rh(COD)(OMe)_2]$ (48 mg, 0.1 mmol) or $[Rh(COD)(OEt)_2]$ (51 mg, 0.1 mmol) was added to the violet solution of **1b** (95 mg, 0.2 mmol) in toluene (15 mL) and methanol (15 mL). The mixture was stirred for 10–12 h. And the color of the solution turned dark red gradually. The solvent was evaporated under reduced pressure. The residue was re-dissolved in 3 ml of dichloromethane and chromatographed on silica gel. Elution with dichloromethane–hexane sequentially gave a red band that contained **3b** (CH_2Cl_2 /hexane = 1:1) (25 mg, 33%) and dark green zone that contained **2b** (CH_2Cl_2 /hexane = 2:1) (36 mg, 27%). Anal. Calc. for $C_{20}H_{37}B_{10}CoRhSe_2$: C, 34.03; H, 5.24. Found: C, 34.64; H, 4.76%. 1H NMR (500 MHz, $CDCl_3$, δ /ppm): δ 1.76 (s, CH_3 , 15H), 2.10, 2.27, 2.58, 2.64 (br, CH_2 , 8H), 4.54, 4.82, 4.95, 5.21 (br, $CH=$, 4H). ^{11}B NMR (160 MHz, $CDCl_3$, δ /ppm) –6.02, –6.86, –8.96, –9.85, –17.59. IR (KBr disk): 2533 cm^{-1} (ν_{B-H}).

3.3. X-ray crystallography

Suitable crystals of **2a** and **2b** were grown by slow diffusion from dichloromethane/hexane solution. Single crystals of two complexes were mounted by gluing onto the end of a thin glass fiber. X-ray intensity data were collected on the CCD-Bruker SMART APEX system. All the determinations of unit cell and intensity data were performed with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). All the data were collected at room temperature using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were included but not refined.

Table 1

X-ray crystallographic data and processing parameters for **2a** and **2b**

Crystal data	2a	2b
Empirical formula	$C_{20}H_{37}B_9CoRhS_2$	$C_{20}H_{37}B_{10}CoRhSe_2$
Formula weight	600.75	705.36
Temperature (K)	293(2)	293(2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$
a (\AA)	10.909(4)	10.591(4)
b (\AA)	11.679(4)	14.939(6)
c (\AA)	12.718(5)	17.320(7)
α ($^\circ$)	108.396(4)	90
β ($^\circ$)	90.707(4)	94.601(6)
γ ($^\circ$)	117.225(4)	90
v (\AA^3)	1343.4(8)	2731.7(18)
Z	2	4
Absorption coefficient (mm^{-1})	1.396	3.886
D (Mg/m^3)	1.485	1.715
$F(000)$	612	1388
Crystal size (mm)	$0.20 \times 0.15 \times 0.10$	$0.35 \times 0.20 \times 0.10$
θ Range for data collection	1.72–27.1	1.80–27.28
Limiting indices	–10, 13; –14, 14; –16, 11	–13, 13; –19, 14; –20, 22
Reflections collected/unique (R_{int})	6615/5583 (0.0394)	13435/6000 (0.0705)
Completeness to θ ($^\circ$)	27.10 (94.4%)	27.28 (97.7%)
Maximum and minimum transmission	0.8730 and 0.7676	0.6973 and 0.3433
Data/restraints/parameters	5583/15/359	6000/0/322
Goodness-of-fit on F^2	0.996	0.846
Final R indices [$I > 2\sigma(I)$]	$R_1^a = 0.0455$, $wR_2^b = 0.1189$	$R_1 = 0.0446$, $wR_2 = 0.0898$
R indices (all data)	$R_1 = 0.0534$, $wR_2 = 0.1265$	$R_1 = 0.0875$, $wR_2 = 0.1001$
Largest difference peak and hole ($e/\text{\AA}^3$)	1.349 and –2.060	0.764 and –1.067

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$$

All the calculations were carried out with the SHELXTL program [22]. Crystal data, data collection parameters, and the results of the analyses of complexes **2a** and **2b** are listed in Table 1.

4. Supplementary material

CCDC 645450 and 645451 contain the supplementary crystallographic data (excluding structure factors) for **2a** and **2b**. 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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