



Synthesis and characterization of heterometallic Rh/Ru complexes supported by 1,2-dichalcogenolato-*o*-carborane ligands

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ABSTRACT

The 16-electron half-sandwich complexes $\text{Cp}^*\text{Rh}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ ($\text{E} = \text{S}$, **1a**; Se , **1b**) react with $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ under different conditions to give different types of heterometallic complexes. When the reactions were carried out in THF for 24 h, the binuclear Rh/Ru complexes $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_2(\text{COD})\text{Ru}][\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ ($\text{E} = \text{S}$, **2a**; Se , **2b**) bridged by two Cl atoms and the binuclear Rh/Rh complexes $(\text{Cp}^*\text{Rh})_2[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ ($\text{E} = \text{S}$, **3a**; Se , **3b**) with direct Rh–Rh bond can be isolated in moderate yields. $[\text{Ru}(\text{COD})\text{Cl}_2]$ fragments in **2a** and **2b** have inserted into the Rh–E bond. If the $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ was reacted with **1a** in the presence of K_2CO_3 in methanol solution, the product $[\text{Cp}^*\text{Rh}(\text{COD})\text{Ru}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]]$ (**4a**), $\text{K}[(\mu\text{-Cl})(\mu\text{-OCH}_3)\text{Ru}(\text{COD})]_4$ (**5a**) and **3a** were obtained. The B(3)–H activation in complex **4a** was found. However, when the reaction between **1b** and $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ was carried out in excessive NaHCO_3 , the carborane cage opened products $\{\text{Cp}^*\text{Rh}[\text{S}_2\text{C}_2(\text{B}_9\text{H}_9)]\text{Ru}(\text{COD})\}$ (**6b**), $\{\text{Cp}^*\text{Rh}[\text{S}_2\text{C}_2(\text{B}_9\text{H}_9)]\text{Ru}(\text{COD})(\text{OCH}_3)\}$ (**7b**) and **3b** were obtained. All complexes were fully characterized by their IR, ^1H NMR and elemental analyses. The molecular structures of **2a**, **2b**, **3b**, **4a**, **5a**, and **7b** have been determined by X-ray crystallography.

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1. Introduction

The synthesis of structurally defined multinuclear complexes [1–8] has been receiving tremendous attention during the past decades. The greatest stimulus for the development of this research field is the cooperative interaction of two or more coordination centers [9], which offer attractive perspectives in stoichiometric and catalytic transformations [10]. Furthermore, multimetallic compounds have found medical applications [11]. Formation of these compounds by the use of bridging ligands [12–14] has played a decisive role in the systematic investigation of such systems. Among the bridging ligands commonly utilized, *o*-carborane dithiolato ligands have recently began to show the inimitable merits, especially stabilizing the organometallic complexes [2,15,16]. In addition, the B(3,6)–H bonds of the *o*-carborane are reactive sites where they can selectively form *mono*- or *disubstituted o*-carborane derivatives [17,18]. Moreover, the *nido*-carborane anions $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$, which resembles the well-known π -bonding cyclopentadienide ion, can be prepared by the removal of a $\text{BH}^{2+}(3,6)$ unit from the parent carborane under certain conditions [19–24]. Following the synthesis of the first metallacarborane by Hawthorne et al. in 1965, *nido*-carborane have proved to be excellent bulky and stable building blocks that can be used to enhance the solubility of the metal complexes [25–29]. The two best developed areas of inorganic cluster chemistry -- polyhedral

boranes and metal clusters are thus combined, which present us rich cluster chemistry [30].

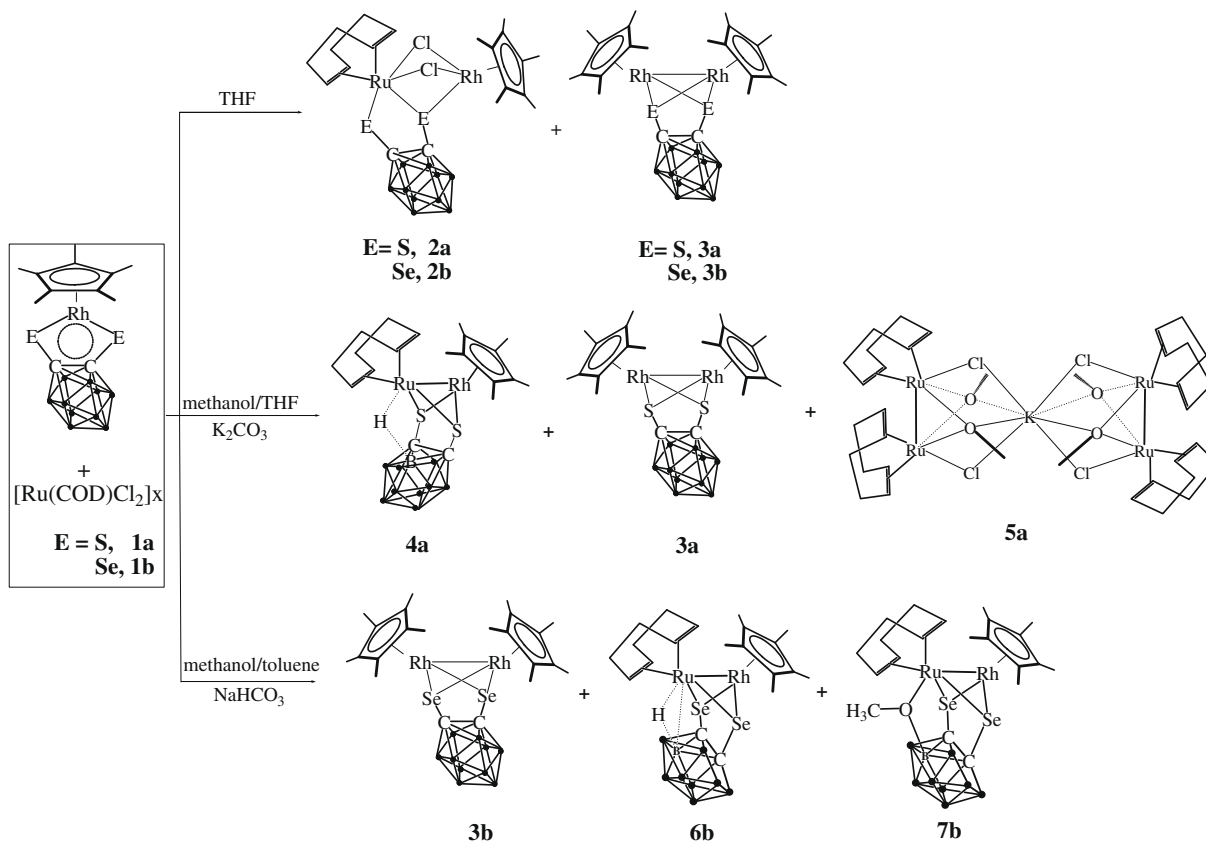
In our previous work, we had obtained a series of cluster complexes with Ir–Ru bonds stabilized by the ancillary carborane dichalcogenolato ligands [31]. In this paper, we focus on the formation of different types of Rh/Ru complexes supported by 1,2-dichalcogenolato-*o*-carborane ligands under different reaction conditions. In our previous results, we stand out the importance of the central metals, because of the difference of central metals, we got different types of carborane cage opened products; however, this paper stress the basic effect to the results. With the gradual increase of base, the products also take on ladderlike change. Herein, we describe the reactions between $\text{Cp}^*\text{Rh}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ ($\text{E} = \text{S}$, **1a**; Se , **1b**) and $[\text{Ru}(\text{COD})\text{Cl}_2]_x$, and different types of products were isolated by changing the reaction conditions (Scheme 1).

2. Results and discussion

2.1. Synthesis of mixed Rh/Ru compounds without direct metal–metal bond

The “pseudo-aromatic” 16-electron complex **1a** or **1b**, which was easily synthesized from the half-sandwich rhodium dichloride complex $[\text{Cp}^*\text{RhCl}(\mu\text{-Cl})_2]$ with dilithium 1,2-dicarba-*closo*-dodecaborane (12)-1,2-dithiolato [32,33], was reacted with $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ in the molar ratio (1:1) at room temperature. When the mixture in THF was stirred for 24 h, the complexes **2a**, **3a** and **2b**, **3b** were

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Scheme 1. Routes to Rh/Ru complexes.

separated by column chromatography, respectively. Their respective yields are: 39%, 32% and 28%, 20%. Complex **3a** as by-product can be also synthesized by reaction of **1a** with $W(CO)_3(py)_3$ [34].

The IR spectrum of **2a** shows a strong band for the B–H vibration at approximately 2565 cm^{-1} , which is near to the corresponding absorption (2556 cm^{-1}) in complex **2b**. The ^1H , ^{13}C NMR and elemental analyses also confirmed the component of the complexes **2a** and **2b**.

Suitable single crystals of compounds **2a** and **2b** were obtained by slow diffusion of hexane into their dichloromethane solution. The molecular structures of **2a** and **2b** are depicted in Fig. 1. The crystal structure of **2a** shows that one $[\text{Ru}(\text{COD})\text{Cl}_2]$ fragments has inserted into one of Rh–S bond to form a hetero-binuclear complex. The distance between Rh and Ru atoms is $3.2736(8)\text{ \AA}$, which is longer than the reported Rh–Ru single bond [35–37]. The Rh atom and Ru atom are bridged by two Cl atoms and one μ_3 -S atom of dithiolate carborane. Another μ_2 -S bridge which bonds with Rh in complex **1a** has been broken off and connected with Ru atom in complex **2a**. Consequently each metal atom has 18 valence electron and thus account for the diamagnetism observed for this complex. The Rh–S bond distance $2.4402(16)\text{ \AA}$ is longer than the corresponding distance in five-membered metallacycle of 16-electron complex **1a** ($2.258(2)\text{ \AA}$), which can be ascribed to the another broken Rh–S bond that destroy the aromaticity of rhodadithiolene cycle. The Ru–S bond lengths range from $2.3574(17)\text{ \AA}$ to $2.4402(16)\text{ \AA}$, which is comparable to the correspondent distance in complex $\text{Cp}_2\text{Ru}_2[\mu\text{-S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]_2$ [38].

The diselenolate complex **2b** is isomorphous to the complex **2a**. The molecular structure of **2b** and important bond distances are shown in Fig. 1b. The Rh–Ru distance is $3.3194(9)\text{ \AA}$, which indicates that there is no direct metal–metal interaction. The μ_3 -Se–Ru bond distance $2.5181(9)\text{ \AA}$ is slightly longer than μ_2 -Se–Ru bond

distance $2.4806(8)\text{ \AA}$, but they are still near to the reported data ($2.4097(10)$ – $2.5687(9)\text{ \AA}$) [39].

The binuclear Rh complex **3b** containing one carborane diselenolate chelate ligand is similar to the corresponding dithiolate complex **3a** in structure [34], which is arranged so that both Se atoms bridge two rhodium atoms (Fig. 2). The molecule contains a mirror plane. The Rh–Rh distance of $2.6570(14)\text{ \AA}$ corresponds to a metal–metal single bond [39]; and the Rh(III) has been reduced to Rh(II), thus **3b** is formally an 18-electron complex.

2.2. Synthesis of mixed Rh/Ru clusters with direct metal–metal bond

To understand different reaction conditions can result in different types of products, weak base was used in the same reaction. After the complex $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ was reacted with K_2CO_3 in CH_3OH for 0.5 h, the complex **1a** in THF was added and then kept to stir for 6 h. In addition to the known complex **3a**, complex **4a** with direct Rh–Ru bond and tetranuclear compound **5a** containing two Ru–Ru bonds have been isolated. The yields of **3a** and **4a** are 53% and 20% based on **1a**, respectively; however, the yield of **5a** is 58% based on $[\text{Ru}(\text{COD})\text{Cl}_2]_x$.

Complex **4a** can be recrystallized from $\text{CH}_2\text{Cl}_2/n$ -hexane to give well-formed red single crystals in the monoclinic space group $P2_1/c$. The X-ray structure analysis of **4a** confirms the binuclear complex containing a Rh–Ru bond and the molecular structure of complex **4a** is depicted in Fig. 3. The crystal structure of **4a** shows that the Cp^*Rh and $(\text{COD})\text{Ru}$ fragments are bridged by two S atoms of dithiolate carborane. The distance between Rh and Ru atoms is $2.7261(9)\text{ \AA}$, which falls within the normal distance of Rh–Ru single bond [35–37]. The interesting phenomenon in crystal of **4a** is that the B(3)–H is activated and bonds with ruthenium, the Ru–H distance $2.2296(7)\text{ \AA}$ shows that they have strong interactions.

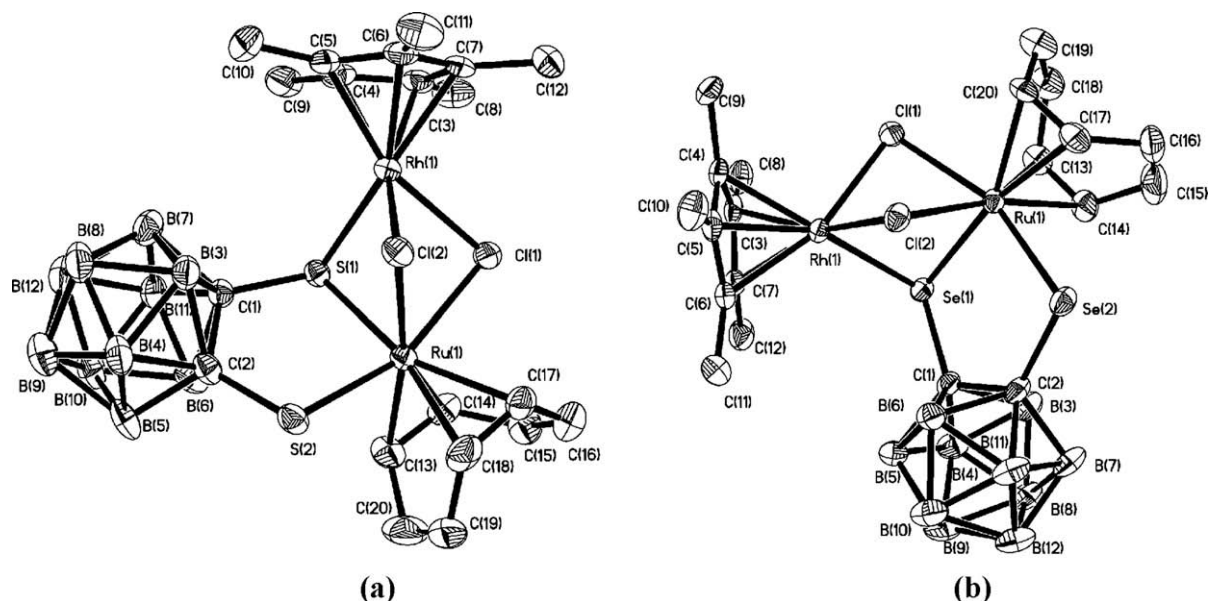


Fig. 1. Molecular structure of **2a** (a) and **2b** (b) with thermal ellipsoids drawn at the 30% level, all hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): (a) Ru(1)–S(2) 2.3574(17), Ru(1)–S(1) 2.4113(17), Rh(1)–S(1) 2.4402(16); S(2)–Ru(1)–S(1) 89.80(6), Cl(1)–Ru(1)–Cl(2) 77.96(5), Cl(2)–Rh(1)–Cl(1) 81.39(6); (b) Rh(1)–Se(1) 2.5408(8), Ru(1)–Se(2) 2.4806(8), Ru(1)–Se(1) 2.5181(9); Se(2)–Ru(1)–Se(1) 90.52(2), Cl(1)–Ru(1)–Cl(2) 78.24(4), Cl(1)–Rh(1)–Cl(2), 81.98(5).

The rhodadithiolate heterocycle in **4a** is bent with a dihedral angle along the S(1)··S(2) of 142.38°, due to the addition of the (COD)Ru moiety.

In this reaction, a multinuclear complex **5a** containing a potassium atom in the center of the molecule has also been isolated. The yellow powder **5a** is paramagnetic and it is soluble in alcohol, but insoluble in ether, dichloromethane and toluene. Suitable single crystals of compounds **5a** were obtained by slow diffusion of diethyl ether into their methanol solution. It can be seen from its molecular structure (Fig. 4) that there are four ruthenium atoms and one potassium atom in each molecular unit. Each (COD)Ru is connected with potassium through one Cl atom and two methoxy

group. The bond distance of Ru(1)–Ru(2) and Ru(3)–Ru(4) range from 2.6729(16) Å to 2.6846(18) Å, which are obviously shorter than the reported Ru–Ru single bond distance [40–42]. The central metal K is eight-coordinate with two groups of Cl atoms and O atoms coordinated to it. Atoms Ru(1), Ru(2), Cl(1), Cl(2) and Ru(3), Ru(4), Cl(3), Cl(4) form two almost perpendicular plane, with dihedral angle 81.22°.

2.3. Synthesis of mixed Rh/Ru clusters with opened carborane cage

The activation of B(3)–H in complex **4a** hint us that the B(3)–H may leave from the carborane cage under certain reaction condi-

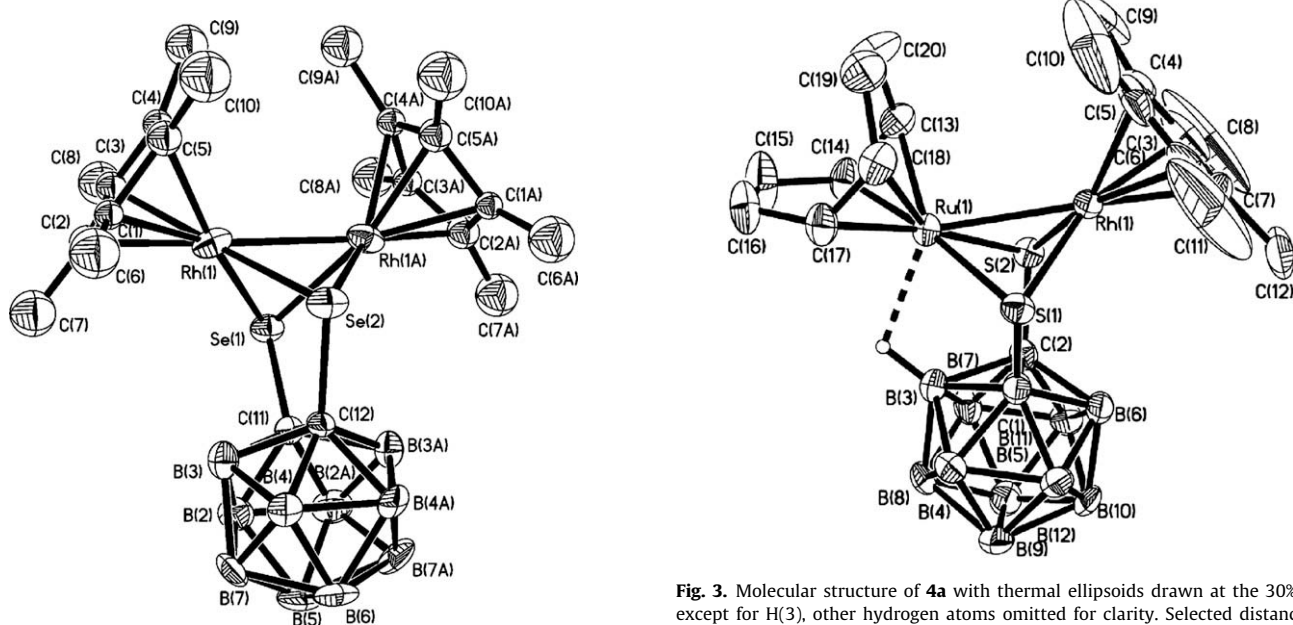


Fig. 2. Molecular structure of **3b** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Rh(1)–Rh(1A) 2.6570(14), Rh(1)–Se(1) 2.4284(15), Rh(1)–Se(2) 2.4303(15); Se(1)–Rh(1)–Se(2) 82.66(5), Rh(1A)–Se(1)–Rh(1) 66.34(6), Rh(1A)–Se(2)–Rh(1) 66.28(6).

Fig. 3. Molecular structure of **4a** with thermal ellipsoids drawn at the 30% level, except for H(3), other hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Rh(1)–S(2) 2.3047(19), Rh(1)–S(1) 2.308(2), Rh(1)–Ru(1) 2.7261(9), Ru(1)–S(1) 2.3860(19), Ru(1)–S(2) 2.4021(19); S(2)–Rh(1)–S(1) 84.79(7), S(2)–Rh(1)–Ru(1) 56.29(5), S(1)–Rh(1)–Ru(1) 55.84(5), S(1)–Ru(1)–S(2) 81.02(7), S(1)–Ru(1)–Rh(1) 53.18(5), S(2)–Ru(1)–Rh(1) 52.95(5), Rh(1)–S(1)–Ru(1) 70.99(6), Rh(1)–S(2)–Ru(1) 70.75(5).

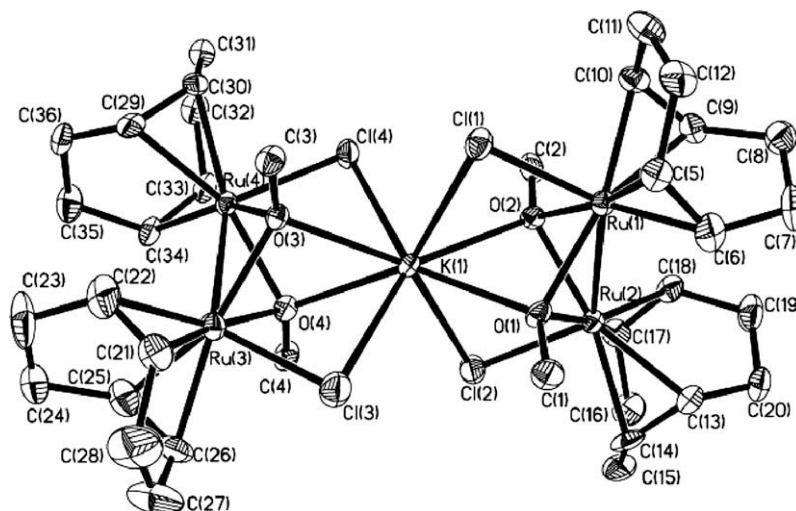


Fig. 4. Molecular structure of **5a** with thermal ellipsoids drawn at the 30% level, all hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Ru(1)–O(2), 2.084(5); Ru(1)–O(1), 2.117(5); Ru(1)–C(10), 2.143(8); Ru(1)–C(9), 2.146(7); Ru(1)–C(5), 2.165(8); Ru(1)–C(6), 2.176(7); Ru(1)–Cl(1), 2.419(3); Ru(1)–Ru(2), 2.6729(16); Ru(1)–K(1), 3.467(2); O(2)–Ru(1)–O(1), 72.10(18); Cl(1)–Ru(1)–Ru(2), 121.08(6); O(2)–Ru(1)–K(1), 45.41(13); O(1)–Ru(1)–K(1), 44.54(12); Cl(1)–Ru(1)–K(1), 53.88(7); Ru(2)–Ru(1)–K(1), 67.20(5).

tions. Hence we tried to react complex **1b** with $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ in excessive NaHCO_3 , and two types of carborane cage opened products **6b**, **7b** and one homobinuclear complex **3b** which is the same as previously reported have been isolated (Scheme 1). The yields of them are 22%, 25%, and 12%, respectively. Although the single crystals suitable for X-ray structure determination for **6b** was not obtained by the recrystallization, the NMR and the elemental analysis confirm **6b** is an analogous dithiolato carborane complex **6a** which has been characterized by X-ray crystallography [31].

The crystal structure of complex **7b** was shown in Fig. 5. The B(6) in complex **1b** is activated to connect with ruthenium through bridging oxygen atom. The NMR spectra and crystal structure determination indicated that the cluster framework adopted in **7b** is generated by incorporation of a *nido* C_2B_9 framework into

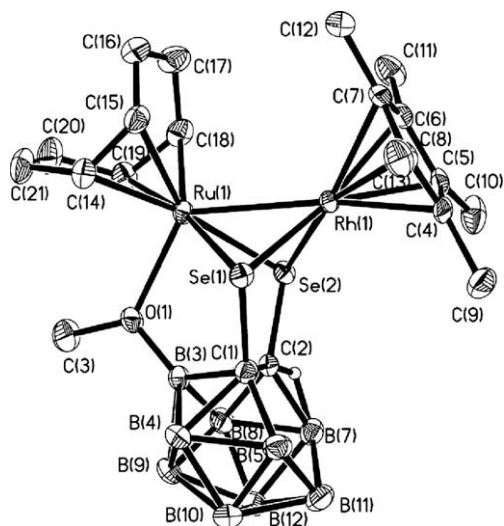


Fig. 5. Molecular structure of **7b** with thermal ellipsoids drawn at the 30% level, except for bridging hydrogen, other hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Rh(1)–Ru(1) 2.7941(11), Rh(1)–Se(1) 2.4344(15), Rh(1)–Se(2) 2.4379(13), Ru(1)–Se(1) 2.5114(12), Ru(1)–Se(2) 2.5354(12), Ru(1)–O(1) 2.269(6), Se(1)–C(1) 1.961(8), Se(2)–C(2) 1.948(8), O(1)–B(3) 1.426(10); Se(1)–Rh(1)–Se(2) 83.57(4), Se(1)–Ru(1)–Se(2) 80.07(4), B(3)–O(1)–Ru(1) 112.9(5), Rh(1)–Se(2)–Ru(1) 68.33(3), Rh(1)–Se(1)–Ru(1) 68.78(3).

a Rh–Ru metal complex. The Cp^*Rh and $(\text{COD})\text{Ru}$ fragments are bridged by two Se atoms that are linked to the open C_2B_3 face. The metal atoms are arranged at one side of the cup-shaped *nido*-carborane just like the handle of a cup. The rhodium center is six-coordinate with antiprismatic geometry, however, the ruthenium adopts seven-coordinate geometry. Consequently, Rhodium and ruthenium atom have 18 valence electrons, respectively, which accounts for the diamagnetism of complex **7b**. The Rh–Ru distance of 2.7941(11) Å is comparable to that of complex **4a**. In addition, compared to coplanar characteristics of rhodadisenolene ring of 16-electron complex $\text{Cp}^*\text{Rh}[\text{Se}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$, the corresponding ring in complex **7b** is bent with dihedral angle of 141.2° along the Se···Se vector, which exhibits that the aromaticity of rhodadisenolene ring in **7b** has been destroyed.

In summary, we have synthesized a series of binuclear Rh/Ru complexes containing dichalcogenolato carborane ligands, which appear to provide useful structural information for further studies on the preparation of other polymetallic species. Although some kinds of carborane supported metallic clusters have been reported, the development of a rational approach for the synthesis of bi- and trimetallic carborane clusters is still an important step forward in the synthesis of this class of compounds. In addition, temperature and solvent effects in the preparation process of hetero-metallic complexes may greatly affect the resultant products, and the further studies of the corresponding clusters are ongoing.

3. Experimental

3.1. General procedures

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by M. Braun Solvent Purification System (4464) and collected just before use. The starting materials $\text{Cp}^*\text{Rh}[\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]$ [32–33] and $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ [43] were prepared by methods reported previously. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer, whereas ^1H (500 MHz), ^{11}B (160 MHz) NMR and ^{13}C (125 MHz) spectra were obtained on a Bruker DMX-500 spectrometer in CDCl_3 solution. Elemental analyses were performed on an Elementar vario EI Analyzer.

3.2. Syntheses of complexes **2a**, **2b** and **3a**, **3b**

To a solution of **1a** (89 mg, 0.20 mmol) or **1b** (106 mg, 0.20 mmol) in THF was added $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ (56 mg, 0.20 mmol). The mixture was stirred for 24 h at room temperature. After evaporating the solvent under reduced pressure, the residue was chromatographed on silica gel. Elution with CH_2Cl_2 –hexane (1:1) gave **2a** or **2b** as a red zone. The second zone **3a** or **3b** (brown) were eluted with CH_2Cl_2 –hexane (2:1), respectively. Complex **2a** (57 mg, 39%). Anal. Calc. for $\text{C}_{20}\text{H}_{37}\text{B}_{10}\text{Cl}_2\text{RhRuS}_2$: C, 33.15; H, 5.15. Found: C, 32.99; H, 5.10%. ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 1.78 (s, 15H, CH_3), 1.89 (m, 2H, CH_2), 2.09 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 2.65 (m, 2H, CH_2), 3.84 (m, 1H, $\text{CH}=\text{}$), 3.93 (m, 1H, $\text{CH}=\text{}$), 4.25 (m, 1H, $\text{CH}=\text{}$), 4.42 (m, 1H, $\text{CH}=\text{}$); ^{13}C NMR (125 MHz, CDCl_3 , δ/ppm): 96.26 (d, $J_{\text{C-Rh}} = 8.5 \text{ Hz}$, Cp^*), 87.04 (s, CS), 92.94, 88.84, 81.25, 79.00 (s, $\text{CH}=\text{}$), 31.47, 30.93, 29.34, 26.66 (s, CH_2), 9.70 (s, CH_3). ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): -6.50, -7.22, -8.93, -9.70, -10.32, -12.06. IR (KBr disk): $\nu = 2996, 2875, 2840 \text{ cm}^{-1}$ (C–H); $\nu = 2565 \text{ cm}^{-1}$ (B–H). Complex **2b** (52 mg, 32%). Anal. Calc. for $\text{C}_{20}\text{H}_{37}\text{B}_{10}\text{Cl}_2\text{RhRuSe}_2$: C, 29.35; H, 4.56. Found: C, 29.19; H, 4.61%. ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 1.77 (s, 15H, CH_3), 2.19–2.56 (m, 8H, CH_2), 3.99 (m, 1H, $\text{CH}=\text{}$), 4.06 (m, 1H, $\text{CH}=\text{}$), 4.24 (m, 1H, $\text{CH}=\text{}$), 4.45 (m, 1H, $\text{CH}=\text{}$); ^{13}C NMR (125 MHz, CDCl_3 , δ/ppm): 98.75 (d, $J_{\text{C-Rh}} = 8.4 \text{ Hz}$, Cp^*), 70.30 (s, CSe), 89.00, 85.32, 80.69, 78.32 (s, $\text{CH}=\text{}$), 31.52, 29.69, 28.01, 26.52 (s, CH_2), 10.23 (s, CH_3). ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): -6.30, -7.60, -8.12, -11.10, -14.35, -15.48. IR (KBr disk): $\nu = 2556 \text{ cm}^{-1}$ (B–H); $\nu = 1651 \text{ cm}^{-1}$ (C=C). Complex **3a** (19 mg, 28%). Anal. Calc. for $\text{C}_{22}\text{H}_{40}\text{B}_{10}\text{Rh}_2\text{S}_2$: C, 38.68; H, 5.91. Found: C, 38.97; H, 5.95%. ^1H NMR (160 MHz, CDCl_3 , δ/ppm): 1.86 (s, 30H, CH_3). IR (KBr disk): $\nu = 2997, 2910 \text{ cm}^{-1}$ (C–H); $\nu = 2581 \text{ cm}^{-1}$ (B–H). Complex **3b** (16 mg, 20%). Anal. Calc. for $\text{C}_{22}\text{H}_{40}\text{B}_{10}\text{Rh}_2\text{Se}_2$: C, 34.03; H, 5.19. Found: C, 34.10; H, 5.17%. ^1H NMR (160 MHz,

CDCl_3 , δ/ppm): 1.79 (s, 30H, CH_3). IR (KBr disk): $\nu = 2989 \text{ cm}^{-1}$ (C–H); $\nu = 2575 \text{ cm}^{-1}$ (B–H).

3.3. Syntheses of complexes **3a**, **4a** and **5a**

To a solution of K_2CO_3 (16 mg, 0.1 mmol) in CH_3OH was added $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ (56 mg, 0.20 mmol), after stirred for 0.5 h, the solution of **1a** (89 mg, 0.20 mmol) in THF was added, the mixture was stirred for another 6 h and filtrated. The residue was dissolved in CH_3OH and diffused by diethyl ether to isolate yellow product **5a**, and the filtrate was evaporated under reduce pressure and chromatographed on silica gel. Elution with CH_2Cl_2 –hexane (1:2) gave **4a** as a rufous zone. The second zone **3a** (brown) was eluted with CH_2Cl_2 –hexane (2:1). Complex **3a** (36 mg, 53%). Complex **4a** (26 mg, 20%). Anal. Calc. for $\text{C}_{20}\text{H}_{37}\text{B}_{10}\text{RhRuS}_2$: C, 36.75; H, 5.70. Found: C, 36.66; H, 5.72%. ^1H NMR (500 MHz, CDCl_3 , δ/ppm): 1.81 (s, 15H, CH_3), 1.94 (m, 2H, CH_2), 2.15 (m, 2H, CH_2), 2.37 (m, 2H, CH_2), 2.67 (m, 2H, CH_2), 3.61 (m, 1H, $\text{CH}=\text{}$), 3.51 (m, 1H, $\text{CH}=\text{}$), 4.74 (m, 1H, $\text{CH}=\text{}$), 4.40 (m, 1H, $\text{CH}=\text{}$); ^{13}C NMR (125 MHz, CDCl_3 , δ/ppm): 96.81 (d, $J_{\text{C-Rh}} = 8.2 \text{ Hz}$, Cp^*), 85.94 (s, CS), 80.25, 78.31, 75.75, 68.91 (s, $\text{CH}=\text{}$), 32.35, 29.70, 28.86, 28.03 (s, CH_2), 10.24 (s, CH_3). ^{11}B NMR (160 MHz, CDCl_3 , δ/ppm): -9.5, -8.08, -9.34, -10.21, -11.09, -14.20. IR (KBr disk): $\nu = 2986, 2871, 2820 \text{ cm}^{-1}$ (C–H); $\nu = 2558 \text{ cm}^{-1}$ (B–H); $\nu = 1652 \text{ cm}^{-1}$ (C=C). Complex **5a** (33 mg, 58%). Anal. Calc. for $\text{KC}_{36}\text{H}_{60}\text{Ru}_4\text{O}_4\text{Cl}_4$: C, 37.86; H, 5.30. Found: C, 37.79; H, 5.41%.

3.4. Syntheses of complexes **3b**, **6b** and **7b**

To a solution of **1b** (107 mg, 0.2 mmol) in toluene (20 ml) and methanol (20 ml) was added $[\text{Ru}(\text{COD})\text{Cl}_2]_x$ (56 mg, 0.2 mmol) and NaHCO_3 (134 mg, 1.6 mmol), the mixture was stirred for 48 h, and the color gradually changed from green to dark-red. After

Table 1

Crystallographic data for complexes **2(a, b)**, **3b**, **4a**, **5a**, **7b**.

	2a	2b	3b	4a	5a	7b
Formula	$\text{C}_{20.50}\text{H}_{37}\text{B}_{10}\text{Cl}_3\text{RhRuS}_2$	$\text{C}_{20.50}\text{H}_{37}\text{B}_{10}\text{Cl}_3\text{RhRuSe}_2$	$\text{C}_{11}\text{H}_{20}\text{B}_5\text{RhSe}$	$\text{C}_{20}\text{H}_{37}\text{B}_{10}\text{RhRuS}_2$	$\text{C}_{36}\text{H}_{60}\text{Cl}_4\text{KO}_4\text{Ru}_4$	$\text{C}_{21}\text{H}_{39}\text{B}_9\text{ORhRuSe}_2$
Formula weight	767.06	859.85	388.19	653.70	1140.00	765.70
Crystal color	Red	Red	Brown	Red	Yellow	green
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>P2₁/m</i>	<i>P2₁/n</i>	<i>P2₁2₁2₁</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	21.242(5)	21.314(6)	8.247(2)	11.108(3)	8.849(7)	10.997(5)
<i>b</i> (Å)	13.606(3)	13.567(4)	17.191(4)	22.840(6)	16.342(13)	12.007(5)
<i>c</i> (Å)	21.408(5)	21.742(7)	10.952(3)	11.160(3)	28.71(2)	13.575(6)
α (°)	90	90	90	90	90	67.207(5)
β (°)	90	90	98.646(5)	98.021(5)	90	89.005(5)
γ (°)	90	90	90	90	90	63.598(5)
<i>V</i> (Å ³)	6187(3)	6287(3)	1535.0(7)	2803.5(13)	4151(6)	1453.8(11)
<i>Z</i>	8	8	4	4	4	2
<i>D</i> _{calc} (Mg/m ³)	1.647	1.817	1.680	1.549	1.824	1.749
Absorption coefficient (mm ⁻¹)	1.429	3.589	3.459	1.286	1.821	3.605
<i>F</i> (000)	3064	3344	760	1312	2276	748
Crystal size (mm)	0.10 × 0.08 × 0.05	0.15 × 0.10 × 0.08	0.10 × 0.05 × 0.05	0.10 × 0.08 × 0.05	0.10 × 0.08 × 0.05	0.20 × 0.15 × 0.15
θ Range (°)	2.13–25.01	1.87–25.01	1.88–25.01	1.78–25.01	1.42–25.01	1.66–27.14
Number of independent reflections	24919	25274	5989	11752	17489	7117
Number of reflections observed [<i>R</i> _{int}]	5444 [0.0819]	5545 [0.0631]	2801 [0.1023]	4936 [0.0618]	7294 [0.0612]	6041 [0.0241]
Number of data/restraints/parameters	5444/0/352	5545/0/367	2801/0/178	4936/0/322	7294/0/442	6041/3/343
Goodness-of-fit (GOF) on <i>F</i> ²	0.816	0.855	0.765	0.833	0.754	1.136
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ = 0.0403, <i>wR</i> ₂ = 0.0811	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0582	<i>R</i> ₁ = 0.0570, <i>wR</i> ₂ = 0.0686	<i>R</i> ₁ = 0.0501, <i>wR</i> ₂ = 0.0850	<i>R</i> ₁ = 0.0388, <i>wR</i> ₂ = 0.0627	<i>R</i> ₁ = 0.0481, <i>wR</i> ₂ = 0.1454
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0841, <i>wR</i> ₂ = 0.0898	<i>R</i> ₁ = 0.0580, <i>wR</i> ₂ = 0.0636	<i>R</i> ₁ = 0.1584, <i>wR</i> ₂ = 0.0858	<i>R</i> ₁ = 0.1016, <i>wR</i> ₂ = 0.0965	<i>R</i> ₁ = 0.0633, <i>wR</i> ₂ = 0.0665	<i>R</i> ₁ = 0.0567, <i>wR</i> ₂ = 0.1490
Largest difference in peak and hole (e Å ⁻³)	0.959 and -0.465	0.834 and -0.387	0.655 and -0.632	0.668 and -0.389	0.951 and -0.703	1.107 and -1.776

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

evaporating the solvent under reduce pressure, the residue was chromatographed on silica gel. Elution with CH₂Cl₂–hexane (1:1) gave **3b**, **6b**, and **7b**, respectively. Crystals of complex **7b** suitable for determination were obtained from CH₂Cl₂–hexane. Complex **3b** (9 mg, 12%). Complex **6b** (32 mg, 22%). Anal. Calc for C₂₀H₃₇B₉RhRuSe₂: C, 32.61; H, 5.06. Found: C, 32.78; H, 5.18%. ¹H NMR (500 MHz, CDCl₃, δ/ppm): 2.12 (s, 15H, CH₃), 2.29 (m, 4H, CH₂), 2.76 (m, 4H, CH₂), 4.14 (m, 2H, CH=), 4.30 (m, 2H, CH=); –12.82 (s, 1H, B–H → Ru). ¹³C NMR (125 MHz, CDCl₃, δ/ppm): 100.55 (d, C–Rh, Cp*), 93.48 (s, CSe), 85.59, 84.11, 83.19, 81.47 (s, CH=), 34.20, 31.92, 29.70, 27.20 (s, CH₂), 11.82 (s, CH₃). ¹¹B NMR (160 MHz, CDCl₃, δ/ppm): –2.41, –5.79, –7.10, –9.83, –17.13, –17.98, –19.56, –29.86, –31.63. IR (KBr disk): ν = 2925, 2854 cm^{–1} (C–H); ν = 2522 cm^{–1} (B–H). Complex **7b** (38 mg, 25%). Anal. Calc. for C₂₁H₃₈B₉ORhRuSe₂: C, 32.94; H, 5.00. Found: C, 32.70; H, 5.03%. ¹H NMR (500 MHz, CDCl₃, δ/ppm): 2.23 (s, 15H, CH₃), 3.63 (s, 3H, OCH₃), 2.76 (m, 2H, CH₂), 2.80 (m, 2H, CH₂), 3.16 (m, 2H, CH₂), 3.23 (m, 2H, CH₂), 3.99 (br, 2H, CH=), 4.14 (s, 1H, CH=), 4.17 (s, 1H, CH=); ¹³C NMR (125 MHz, CDCl₃, δ/ppm): 100.75 (d, J_{C–Rh} = 8.5 Hz, Cp*), 94.38 (s, CS), 90.43, 84.72, 82.34, 78.22 (s, CH=), 34.07, 33.43, 31.58, 29.81 (s, CH₂), 11.74 (s, CH₃), 56.38 (s, OCH₃). ¹¹B NMR (160 MHz, CDCl₃, δ/ppm): 9.38, –1.41, –5.28, –7.80, –11.62, –18.82, –31.59, –34.67, –40.40. IR (KBr disk): ν = 2922, 2852, 2840 cm^{–1} (C–H); ν = 2558 cm^{–1} (B–H).

3.5. X-ray crystallography

Suitable crystals for X-ray analysis of **2a**, **2b**, **3b**, **4a**, **5a** and **7b** were obtained by slow diffusion of hexane into dichloromethane solutions of the corresponding compound, respectively. None showed signals of decomposition during X-ray data collection, which was carried out at room temperature. The structure were solved by direct methods using SHELX-97 and refined by full-matrix least-square calculations, using program system SHELXL-97 [44]. Details of the data collection and refinement are summarized in Table 1.

4. Supplementary material

CCDC 673411, 673412, 673413, 673414, 673415 and 673416 contains the supplementary crystallographic data for **2a**, **2b**, **3b**, **4a**, **5a** and **7b**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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