

# Binuclear complexes of rhodium (I) bridged by 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligands: molecular structures of the complexes $[\text{Rh}_2(\text{COD})_2(\mu_2\text{-E}_2\text{C}_2(\text{B}_{10}\text{H}_{10}))]$ [E = S, Se] and $[\text{Rh}_2(\text{CO})_4(\mu_2\text{-S}_2\text{C}_2(\text{B}_{10}\text{H}_{10}))]$

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Dedicated to Professor Changtao Qian on the occasion of his 70th birthday

## Abstract

Four new dichalcogenolato carborane bridged binuclear rhodium(I) complexes  $[\text{Rh}_2(\text{COD})_2(\mu_2\text{-E}_2\text{C}_2(\text{B}_{10}\text{H}_{10}))]$  [COD = *cyclo-octa*-1,5-diene (C<sub>8</sub>H<sub>12</sub>), E = S (**2a**), Se (**2b**)] and  $[\text{Rh}_2(\text{CO})_2(\mu_2\text{-E}_2\text{C}_2(\text{B}_{10}\text{H}_{10}))]$  [E = S (**3a**), Se (**3b**)] have been prepared by the reactions of the dilithium dichalcogenolato carboranes Li<sub>2</sub>E<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (E = S, Se) with  $[\text{Rh}(\text{COD})\text{Cl}]_2$  or  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ , respectively. The complexes have been fully characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B NMR and IR spectroscopy as well as by element analyses. The molecular structures of **2a**, **2b** and **3a** have been determined by single-crystal X-ray diffraction analyses, which show the strong metal–metal interaction between two rhodium atoms.

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**Keywords:** Rhodium; Binuclear; dichalcogenolato ligands; Carboranes; Molecular structures

## 1. Introduction

In recent years, dinuclear rhodium complexes have been widely investigated because of their catalytic activity. It has been shown that *dinuclear* rhodium complexes with thiolate [1], azolate [2], or aminothiolate [3] bridged ligands are active precursors for the hydroformylation of olefins under mild conditions. Therefore, the design

of such dirhodium complexes containing the bridging ligands has been of considerable interest.

On the other hand, the synthesis and study of organometallic complexes possessing an ancillary *o*-carboranedithiolato ligand have continued to receive attention [4]. In previous paper, we have described the synthesis and characterization of dilithium dichalcogenolato carborane. Although a number of *dinuclear* complexes of Co [5], Fe [6], Ru [6] have been described which contain a bidentate, chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligands,  $[(\text{B}_{10}\text{H}_{10})\text{C}_2\text{E}_2]^{2-}$  (E = S, Se), little is known of dirhodium complexes containing *o*-carboranedichalcogenolato ligands up to date.

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In this paper, we report the syntheses and X-ray structural characterizations of the binuclear complexes of rhodium (I) bridged by  $[(B_{10}H_{10})C_2E_2]^{2-}$  [E = S, Se] ligands.

## 2. Results and discussion

### 2.1. Syntheses

We attempt to synthesis dirhodium complexes using 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligands to hold two metal atoms in close proximity. The dilithium dichalcogenolato carboranes  $Li_2E_2C_2(B_{10}H_{10})$  (E = S (**1a**), Se (**1b**)) were obtained by insertion of elemental chalcogens into the two carbon–lithium bonds of the dilithiated carborane in diethyl ether solution. Although the half-sandwich *dinuclear* complex  $Cp^*_2Ru_2(\mu-Se)[\mu-Se_2C_2(B_{10}H_{10})]$  [6, 7] has been obtained directly by the reaction of  $[Cp^*RuCl(\mu-Cl)]_2$  with the complex **1b**, it was reported that mononuclear 16e half-sandwich complex was the sole product from the chloro-bridged dimer  $[Cp^*RhCl(\mu-Cl)]_2$  ( $Cp^* = Cp^*$  or  $\eta^5-1,3\text{-}^iBu_2C_5H_3$ ) [8]. Fortunately, the reaction of  $[Rh(COD)Cl]_2$  with 1 equiv of  $Li_2E_2C_2B_{10}H_{10}$  (**1a**, **1b**) in ether, at room temperature, affords the dirhodium complexes  $[(COD)_2Rh_2(\mu_2-E_2C_2B_{10}H_{10})]$  [E = S (**2a**), Se (**2b**)] (Scheme 1).

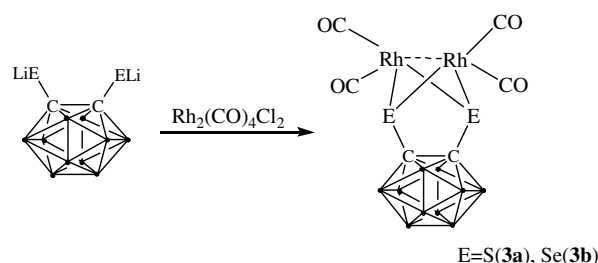
Complexes **2a** and **2b** are moderately air-stable in the solid state, and slightly soluble in *n*-hexane, quite soluble in  $CH_2Cl_2$  or THF.

Similarly, the reactions of dilithium dichalcogenolato carboranes (**1a** and **1b**) with the chloro-bridged carbonyl rhodium complex  $[Rh(CO)_2(\mu-Cl)]_2$  at room temperature gave the products  $[(CO)_4Rh_2(\mu_2-E_2C_2B_{10}H_{10})]$  [E = S (**3a**), Se (**3b**)] (Scheme 2). The crystalline, orange red complexes **3a**, **3b** are also air-stable.

Treatments of complex **2a**, **2b** with carbon monoxide in  $CH_2Cl_2$  solution replacing with the chelating olefin could also afford corresponding carbonyl complexes **3a**, **3b** in high yields (Scheme 3).

### 2.2. Molecular structures of **2a**, **2b** and **3a**

The complexes **2a** and **2b** can be recrystallized from  $CH_2Cl_2/n$ -hexane to give well-formed red single crystals



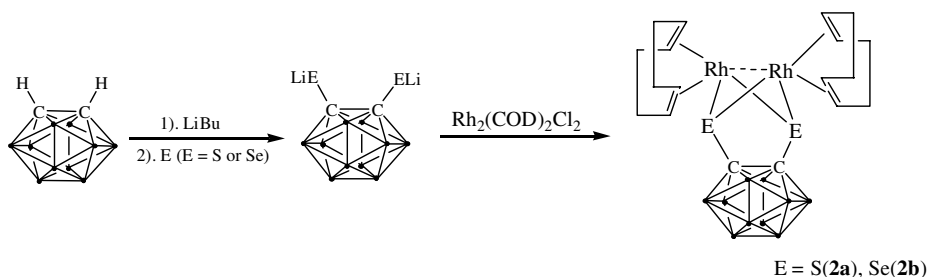
Scheme 2. Synthesis of complexes **3a** and **3b**.

in the triclinic space group  $P\bar{1}$  with four molecules in the unit cell.

The X-ray structure analysis of **2a** confirms a rhodium (I) thiolate dimer complex and the molecular structure is shown in Fig. 1. The crystal structure of **2a** shows that coordination geometry around each rhodium atom is approximately square planar. Two bridging sulfur atoms and a chelating cyclooctadiene are bonded to each metal atom. The  $Rh_2S_2$  ring is highly puckered, the dihedral angle between the planes defined  $Rh(1)-Rh(2)-S(1)$  and  $Rh(1)-Rh(2)-S(2)$  planes being  $71.50(9)^\circ$ . The Rh–S bond lengths ( $Rh(1)-S(1) = 2.407(2)$  Å,  $Rh(1)-S(2) = 2.429(2)$  Å) are in the longer range of bond lengths found for binuclear thiolate-bridged complexes; the longest related bond was reported for  $[Rh(\mu-SC_6F_5)(COD)]_2$  (2.41 Å av.) [9], and the shortest was reported for  $[Rh(\mu-S(CH_2)_3NMe_2)(COD)]_2$  (2.34 Å av.) [10]. The Rh–C bond distances fall in the range (2.119(7)–2.154(7) Å), which are normal values for Rh(I) complexes containing COD ligands *trans* to S donor atoms [11].

The intramolecular  $Rh(1)-Rh(2)$  distance (2.8809(11) Å) is short enough to suggest the existence of some metal–metal interactions, which is slightly shorter than the intermetallic distances found in  $[Rh(\mu-SC_6F_5)(COD)]_2$  (2.955 Å av.) [10] and  $[Rh(\mu-S(CH_2)_3NMe_2)(COD)]_2$  (2.960 Å) [10]. This distance is closer to dinuclear Rh(I) analogues (2.9–3.4 Å) [12].

The diselenolate complex **2b** is isomorphous to the complex **2a**. The molecular structure of **2b** and important bond distances and angles are shown in Fig. 2. The intramolecular  $Rh(1)-Rh(2)$  distance (2.935(3) Å) in **2b** is also comparatively short, only slightly longer



Scheme 1. Synthesis of complexes **2a** and **2b**.

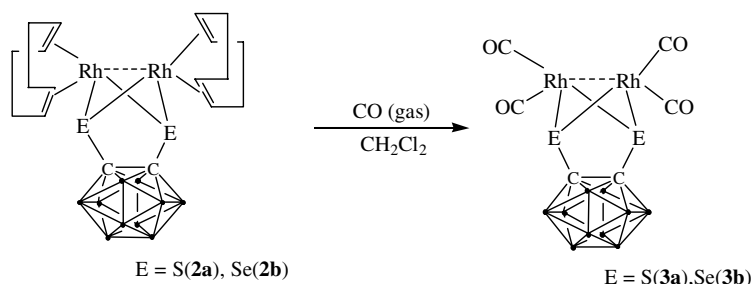
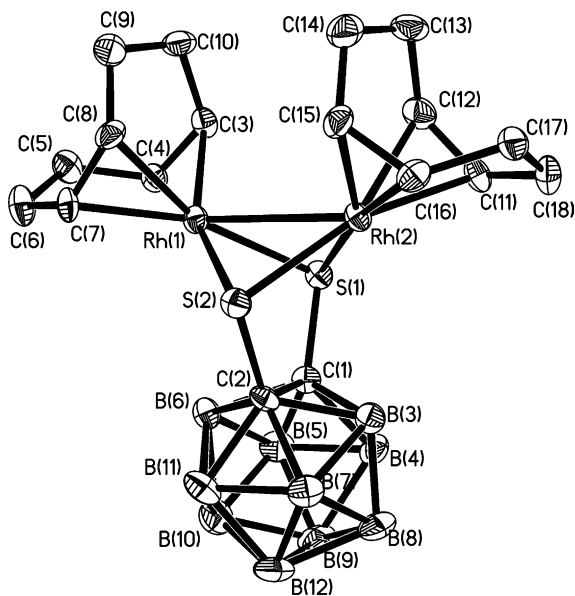
Scheme 3. The reactions of **2a** and **2b** with CO gas.

Fig. 1. Molecular structure of **2a**. Selected distances (Å) and angles (°): Rh(1)–S(1), 2.407(2); Rh(1)–S(2), 2.429(2); Rh(1)–C(3), 2.127(7); Rh(1)–C(7), 2.119(7); Rh(1)–C(8), 2.137(8); Rh(1)–C(4), 2.137(7); Rh(1)–Rh(2), 2.8809(11); C(1)–C(2), 1.660(10); C(3)–Rh(1)–C(4), 37.9(3); C(7)–Rh(1)–C(8), 38.3(3); S(1)–Rh(1)–S(2), 81.10(7); S(1)–Rh(1)–Rh(2), 53.27(5); C(1)–S(1)–Rh(1), 99.5(3); Rh(1)–S(1)–Rh(2), 73.49(6).

than that of **2a** (2.8809(11) Å) and the sum of the Rh atomic radii ( $2 \times 1.345$  Å). The Rh–Se bond lengths in **2b** (2.505 Å av.) are longer than the reported averaged Rh–Se value (2.457(2) Å) [13] for reduction of electron distribution from the diselenolate ligand to each rhodium atom owing to the formation of four Rh–Se bonds.

The dinuclear Rh<sup>I</sup> complex **3a** can be recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane to give well-formed orange single crystals in the orthorhombic space group *Cmcm* with four molecules in the unit cell. The complex **3a** contains one carborane dithiolato chelate ligand, which is arranged so that both S atoms bridge two rhodium atoms (Fig. 3.). The molecule contains two crystallographic mirror plane. The Rh<sub>2</sub>S<sub>2</sub> ring is highly puckered, the dihedral angle between the planes defined Rh(1)–Rh(1A)–S(1) and Rh(1)–Rh(1A)–S(1A) planes being 70.0°. The intramolecular Rh(1)–Rh(1A) distance

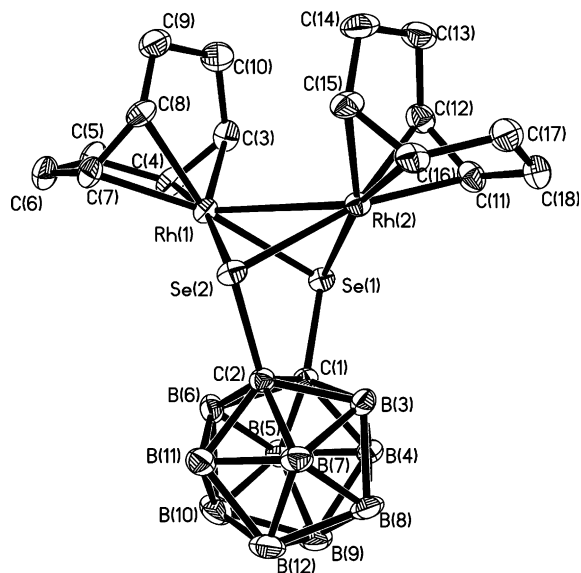


Fig. 2. Molecular structure of **2b**. Selected distances (Å) and angles (°): Rh(1)–Se(2), 2.491(3); Rh(1)–Se(1), 2.503(2); Rh(1)–C(3), 2.133(5); Rh(1)–C(4), 2.137(5); Rh(1)–C(8), 2.137(4); Rh(1)–C(7), 2.142(5); Rh(1)–Rh(2), 2.935(3); C(1)–C(2), 1.635(6); C(3)–Rh(1)–C(4), 38.01(18); C(8)–Rh(1)–C(7), 37.70(17); Se(2)–Rh(1)–Se(1), 82.57(9); Se(2)–Rh(1)–Rh(2), 54.59(4); C(1)–Se(1)–Rh(1), 100.00(15); Rh(1)–Se(1)–Rh(2), 71.74(8).

(2.8900(11) Å) in **3a** is similar in **2a**, and is typical of thiolate-bridged Rh<sup>I</sup> complexes, and might suggest a weak bonding interaction [14].

### 2.3. NMR and IR spectroscopic results

The spectroscopic and analytical data of **2a** and **2b** are in agreement with the formation of rhodium complexes containing with both carborane ligands and COD ligands. The <sup>1</sup>H NMR spectrum of complex **2a** consists of four multiplet signals at 1.92, 2.11, 2.45 and 2.59 ppm, corresponding to the methylene groups of the cyclooctadiene ligand and two multiplet signals at 4.03 and 4.75 ppm due to the olefin protons from cyclooctadiene ligand. The two signals for alkene indicated two different environments due to the dinuclear bent structure as was established in a crystal structure determination. The <sup>13</sup>C {<sup>1</sup>H} NMR spectrum of **2a** is

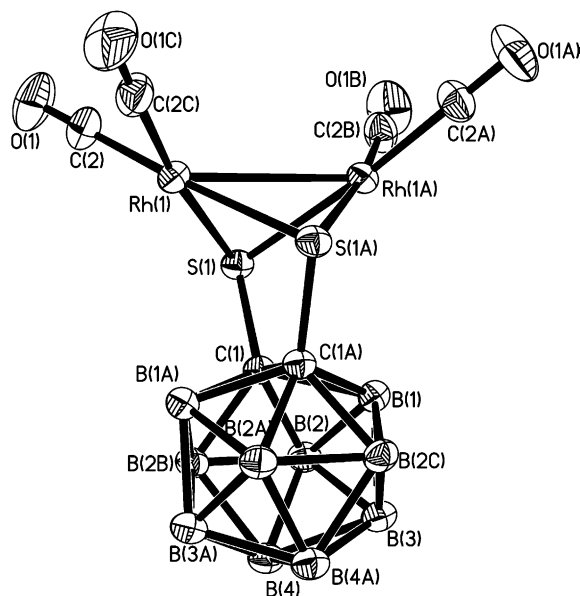


Fig. 3. Molecular structure of **3a**. Selected distances (Å) and angles (°): Rh(1)–Rh(1A), 2.8900(11); Rh(1)–C(2), 1.866(3); Rh(1)–S(1), 2.4037(9); O(1)–C(2), 1.117(4); C(1)–C(1A), 1.647(6); C(2)–Rh(1)–C(2C), 91.8(2); S(1)–Rh(1)–S(1A), 81.76(4); O(1)–C(2)–Rh(1), 178.4(3); S(1)–Rh(1)–Rh(1A), 53.047(18); C(1)–S(1)–Rh(1), 98.28(9); Rh(1)–S(1)–Rh(1A), 73.91(4).

also in agreement with the data discussed above. It consists of two singlets 31.43, and 31.65 ppm due to the methylene groups of the COD ligands and two doublet signals at 80.44 and 80.90 ppm with coupling constants of  $^1J_{\text{Rh-C}} = 12.39$  and 11.44 Hz, respectively, corresponding to the olefinic carbon atoms. Both the coupling constants and the chemical shifts observed are typical for Rh(I) complex [15]. The carbon atoms of the carborane ligand give rise to a singlet at 88.31 ppm, compared to the diselenolate complex **2b** a singlet at 68.60 ppm. The IR spectra of **2a** and **2b** exhibit one  $\nu(\text{C}=\text{C})$  stretching around 1632–1633  $\text{cm}^{-1}$  and intense B–H stretching around 2575–2577  $\text{cm}^{-1}$ .

The complexes **3a**, **3b** are diamagnetic. The  $^{13}\text{C}$  { $^1\text{H}$ } NMR spectrum of **3a** and **3b** shows a singlet at 83.37 ppm due to the thiolate carborane ligand and 66.27 ppm to the selenolate carborane ligand, the carbonyl carbon atoms give two singlet signal at 180.97 and 181.69 ppm. The IR spectra of **3a** and **3b** show strong stretching frequencies for the carbonyl groups at 2094, 2076, 2036  $\text{cm}^{-1}$  for **3a**, 2092, 2071, 2028  $\text{cm}^{-1}$  for **3b** and may therefore be compared with the corresponding frequencies of complex  $[\text{Rh}(\text{CO})_2(\mu\text{-Cl})_2]$  at 2101, 2081, 2019  $\text{cm}^{-1}$  [16].

### 3. Experimental

*General considerations.* All reactions and manipulations were routinely carried out in standard Schlenk

tubes under a dry nitrogen atmosphere. The solvents were kept free of traces of water and oxygen, and distilled in a stream of argon before use. Silica gel, Merck 60 (0.06–0.2 mm) was activated at 400 °C and stored under nitrogen before use in chromatography. The *ortho*-carborane (1,2- $\text{H}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ ) and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  are commercially available. The starting materials,  $[\text{Rh}(\text{COD})\text{Cl}]_2$  [16] and  $\text{Li}_2\text{E}_2\text{C}_2(\text{B}_{10}\text{H}_{10})$  (E = S (**1a**), Se (**1b**)) [7,8] were prepared by literature procedures.

#### 3.1. Syntheses

*Preparations of  $[\text{Rh}_2(\text{COD})_2(m_2\text{-E}_2\text{C}_2\text{B}_{10}\text{H}_{10})]$  [ $E = \text{S}$  (**2a**), Se (**2b**)].*  $[\text{Rh}(\text{COD})\text{Cl}]_2$  (0.25 g, 0.50 mmol) was added to a solution of  $\text{Li}_2\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10}$  (E = S, Se) (0.50 mol) in ether (40 mL) and kept at room temperature to stir for 16 h. After removal of the solvent, the residue was chromatographed on silica gel (2.0 cm  $\times$  40.0 cm). Elution with  $\text{CH}_2\text{Cl}_2$  gave red zone. Evaporation under reduced pressure and crystallization from  $\text{CH}_2\text{Cl}_2$ /hexane afforded **2a**, **2b** as red prismatic crystals. **2a** (0.211 g) yield 67.5%. Elemental Anal. Calc. for  $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{Rh}_2\text{S}_2$ : C, 34.40; H, 5.45. Found: C, 34.63; H, 5.42%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 1.92(m, 4H,  $\text{CH}_2$ ), 2.11(m, 4H,  $\text{CH}_2$ ), 2.45(m, 4H,  $\text{CH}_2$ ), 2.59(m, 4H,  $\text{CH}_2$ ), 4.03(s, 4H,  $\text{CH}=\text{}$ ), 4.75(s, 4H,  $\text{CH}=\text{}$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 88.31(s, CS), 80.90( $\text{CH}=\text{}$ ,  $^1J_{\text{C-Rh}} = 11.44$  Hz), 80.44( $\text{CH}=\text{}$ ,  $^1J_{\text{C-Rh}} = 12.39$  Hz), 31.65(s,  $\text{CH}_2$ ), 31.43(s,  $\text{CH}_2$ ).  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 6.16(2B), -6.26(2B), -8.01(2B), -11.24(4B). IR(KBr disk):  $\nu = 2992, 2917, 2876, 2830$   $\text{cm}^{-1}$ (C–H);  $\nu = 2575$   $\text{cm}^{-1}$ (B–H);  $\nu = 1632$   $\text{cm}^{-1}$ (C=C). **2b** (0.206 g) yield 57.0%. Elemental Anal. Calc. for  $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{Rh}_2\text{Se}_2$ : C, 29.93; H, 4.74. Found: C, 29.84; H, 4.62%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 1.86(m, 4H,  $\text{CH}_2$ ), 2.04(m, 4H,  $\text{CH}_2$ ), 2.36(m, 4H,  $\text{CH}_2$ ), 2.54(m, 4H,  $\text{CH}_2$ ), 4.05(s, 4H,  $\text{CH}=\text{}$ ), 4.93(s, 4H,  $\text{CH}=\text{}$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 68.60(s, C Se), 80.90( $\text{CH}=\text{}$ ,  $^1J_{\text{C-Rh}} = 10.68$  Hz), 79.94( $\text{CH}=\text{}$ ,  $^1J_{\text{C-Rh}} = 12.98$  Hz), 31.64(s,  $\text{CH}_2$ ), 31.59(s,  $\text{CH}_2$ ).  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 4.03(2B), -5.26(2B), -6.67(2B), -10.44(4B). IR(KBr disk):  $\nu = 2938, 2873, 2827$   $\text{cm}^{-1}$ (C–H);  $\nu = 2577$   $\text{cm}^{-1}$ (B–H);  $\nu = 1633$   $\text{cm}^{-1}$ (C=C).

*Preparation of  $[\text{Rh}_2(\text{CO})_2(\mu_2\text{-E}_2\text{C}_2\text{B}_{10}\text{H}_{10})]$  [ $E = \text{S}$  (**3a**), Se (**3b**)].*  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (0.35 g, 0.50 mmol) was added to a solution of  $\text{Li}_2\text{E}_2\text{C}_2\text{B}_{10}\text{H}_{10}$  (E = S, Se) [12] (0.50 mol/L) in ether (100 mL) and kept at room temperature to stir for 16 h. After removal of the solvent, the residue was chromatographed on silica gel (2.0 cm  $\times$  40.0 cm). Elution with  $\text{CH}_2\text{Cl}_2$  gave orange zone. Evaporation and crystallization from  $\text{CH}_2\text{Cl}_2$ /hexane afforded **3a**, **3b** as orange prismatic crystals. **3a** (0.105 g) yield 40.1%. Elemental Anal. Calc. for  $\text{C}_6\text{H}_{10}\text{B}_{10}\text{O}_4\text{Rh}_2\text{S}_2$ : C, 13.75; H, 1.92. Found: C, 13.96; H, 1.75%.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ):

83.37(CS), 180.97(CO), 181.69(CO);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 7.25(2B),  $-4.85(2\text{B})$ ,  $-6.87(2\text{B})$ ,  $-11.17(4\text{B})$ . IR(KBr disk):  $\nu = 2619, 2569\text{ cm}^{-1}(\text{B-H})$ ;  $\nu = 2094, 2076, 2036\text{ cm}^{-1}(\text{CO})$ . **3b** (0.122 g) yield 39.48%. Elemental Anal. Calc. for  $\text{C}_6\text{H}_{10}\text{B}_{10}\text{O}_4\text{Rh}_2\text{Se}_2$ : C, 11.66; H, 1.63. Found: C, 11.84; H, 1.72%.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 66.27(CSe), 180.69(CO), 181.41(CO);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 5.34(2B),  $-4.17(2\text{B})$ ,  $-5.62(2\text{B})$ ,  $-10.71(4\text{B})$ . IR(KBr disk):  $\nu = 2619, 2563\text{ cm}^{-1}(\text{B-H})$ ;  $\nu = 2092, 2071, 2028\text{ cm}^{-1}(\text{CO})$ .

### 3.2. Instrumentation

Elemental analyses were performed on Elementar III Vario EI Analyzer. NMR measurements were carried out using Bruker AC500 spectrometers (chemical shifts are given with respect to  $\text{CHCl}_3/\text{CDCl}_3$   $\delta^1\text{H} = 7.24$ ;  $\delta^{13}\text{C} = 77.0$ ), external  $\text{Et}_2\text{O-BF}_3$  ( $\delta^{11}\text{B} = 0$  for ( $^{11}\text{B}$ ) = 32.08 MHz). Infrared spectra were obtained on a Nicolet FT-IR 360 spectrometer (KBr pellet).

### 3.3. X-ray structure analysis of **2a**, **2b** and **3a**

All three crystal structure determinations were carried out on a CCD diffractometer using Mo  $\text{K}\alpha$  radiation (0.71073 Å) at 293(2) K and solved by direct methods using SHELXS-97. Crystal data for **2a**:  $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{Rh}_2\text{S}_2$ , red prism, Triclinic, space group  $P\bar{1}$ ,  $a = 12.722(3)\text{ Å}$ ,  $b = 12.789(3)\text{ Å}$ ,  $c = 16.978(4)\text{ Å}$ ,  $\alpha = 104.572(3)^\circ$ ,  $\beta = 104.282(3)^\circ$ ,  $\gamma = 97.806(4)^\circ$ ,  $V = 2532.6(11)\text{ Å}^3$ ,  $Z = 4$ ,  $D_c = 1.648\text{ g cm}^{-3}$ ,  $F(000) = 1256$ , CCD, Mo  $\text{K}\alpha$  radiation,  $2\theta$  range  $3.36\text{--}50.02^\circ$ ; 10676 reflections collected, 8776 independent ( $R_{\text{int}} = 0.0468$ ), 597 refined parameters, final  $R$  indices (observed data)  $R_1 = 0.0503$ ,  $wR_2 = 0.0885$ , GOF 0.912, maximum/minimum residual electron density  $1.272/-0.589\text{ e Å}^{-3}$ .

Crystal data for **2b**.  $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{Rh}_2\text{Se}_2$ , red prism, Triclinic, space group  $P\bar{1}$ ,  $a = 12.813(19)\text{ Å}$ ,  $b = 12.903(19)\text{ Å}$ ,  $c = 16.96(3)\text{ Å}$ ,  $\alpha = 104.77(2)^\circ$ ,  $\beta = 103.87(2)^\circ$ ,  $\gamma = 98.04(2)^\circ$ ,  $V = 2571(6)\text{ Å}^3$ ,  $Z = 4$ ,  $D_c = 1.866\text{ g cm}^{-3}$ ,  $F(000) = 1400$ , CCD, Mo  $\text{K}\alpha$  radiation,  $2\theta$  range  $3.34\text{--}50.02^\circ$ ; 10891 reflections collected, 8924 independent ( $R_{\text{int}} = 0.0182$ ), 597 refined parameters, final  $R$  indices (observed data)  $R_1 = 0.0294$ ,  $wR_2 = 0.0679$ , GOF 0.996, maximum/minimum residual electron density  $0.792/-0.512\text{ e Å}^{-3}$ .

Crystal data for **3a**.  $\text{C}_6\text{H}_{10}\text{B}_{10}\text{O}_4\text{Rh}_2\text{S}_2$ , orange prism, Orthorhombic, space group  $\text{Cmcm}$ ,  $a = 14.807(5)\text{ Å}$ ,  $b = 9.510(3)\text{ Å}$ ,  $c = 12.562(4)\text{ Å}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1768.9(10)\text{ Å}^3$ ,  $Z = 4$ ,  $D_c = 1.968\text{ g cm}^{-3}$ ,  $F(000) = 1000$ , CCD, Mo  $\text{K}\alpha$  radiation,  $2\theta$  range  $5.10\text{--}54.16^\circ$ ; 4279 reflections collected, 1058 independent ( $R_{\text{int}} = 0.0214$ ), 77 refined parameters, final  $R$  indices (observed data)  $R_1 = 0.0235$ ,  $wR_2 = 0.0549$ , GOF

1.221, maximum/minimum residual electron density  $0.394/-0.376\text{ e Å}^{-3}$ .

### Supplementary information

Crystallographic for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 251535 for compound **2a**; CCDC No. 251536 for compound **2b**; CCDC No. 251537 for compound **3a**. Copies of these data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44(1223)336-033; email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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### References

- [1] (a) Ph. Kalck, J.M. Frances, P.M. Pfister, T.G. Southern, A. Thorez, *J. Chem. Soc., Chem Commun.* (1983) 510; (b) Ph. Kalck, A. de Meijere, M. Tom Dick (Eds.), *Organometallics in Organic Synthesis*, Springer-Verlag, 1987, pp. 297–320.
- [2] (a) P. Kalck, A. Thorez, M.T. Pinillos, L.A. Oro, *J. Mol. Catal.* 31 (1985) 311; (b) C. Claver, P. Kalck, M. Ridmy, A. Thorez, L.A. Oro, M.T. Pinillos, M.C. Apreda, F.H. Cano, C.F. Foces, *J. Chem. Soc., Dalton Trans.* (1988) 1523; (c) C. Claver, Ph. Kalck, L.A. Oro, M.T. Pinillos, C. Tejel, *J. Mol. Catal.* 43 (1988) 1.
- [3] J.C. Boyon, P. Esteban, J. Real, C. Claver, A. Ruiz, *J. Chem. Soc., Chem. Commun.* (1989) 1056.
- [4] (a) K. Base, M.W. Grinstaff, *Inorg. Chem.* 37 (1998) 1432; (b) O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, *J. Chem. Soc. Dalton Trans.* (1997) 1099; (c) O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, *J. Chem. Soc. Chem. Commun.* (1993) 1696; (d) J.G. Contreras, L.M. Silva-trivino, M.E. Solis, *J. Coord. Chem.* 14 (1986) 309; (e) H.D. Smith Jr., M.A. Robinson, S. Papetti, *Inorg. Chem.* 6 (1967) 1014; (f) H.D. Smith Jr., C.O. Obenland, S. Papetti, *Inorg. Chem.* 5 (1966) 1013; (g) H.D. Smith Jr., *J. Am. Chem. Soc.* 87 (1965) 1817.
- [5] (a) X.F. Hou, X.C. Wang, J.Q. Wang, G.X. Jin, *J. Organomet. Chem.* 689 (2004) 2228; (b) D.H. Kim, J. Ko, K. Park, S. Cho, S.O. Kang, *Organometallics* 18 (1999) 2738; (c) J.H. Won, D.H. Kim, B.Y. Kim, S.J. Kim, C. Lee, S. Cho, J. Ko, S.O. Kang, *Organometallics* 21 (2002) 1443; (d) J.D. Lee, B.Y. Kim, C. Lee, Y.J. Lee, J. Ko, S.O. Kang, *Bull. Korean Chem. Soc.* 25 (2004) 1012.

- [6] (a) S. Lu, G.-X. Jin, S. Eibl, M. Herberhold, Y. Xin, *Organometallics* 21 (2002) 2533;  
(b) G.-X. Jin, *Coord. Chem. Rev.* 248 (2004) 587.
- [7] X.Y. Yu, G.-X. Jin, N.H. Hu, L.H. Weng, *Organometallics* 21 (2002) 5540.
- [8] (a) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* 587 (1999) 252;  
(b) Q. Kong, G.-X. Jin, S.Y. Cai, L.H. Weng, *Chin. Sci. Bull.* 48 (2003) 1733.
- [9] C. Cruz-Garriz, B. Rodriguez, H. Torrens, *Transition Met. Chem.* 9 (1984) 284.
- [10] A. Polo, C. Claver, S. Castillon, A. Ruiz, J.C. Bayon, J. Real, C. Mealli, D. Masi, *Organometallics* 11 (1992) 3525.
- [11] (a) C. Claver, A. Ruiz, A. Masdeu, T. Saballs, F. Lahoz, F. Plau, *J. Organomet. Chem.* 373 (1989) 269;  
(b) M.T. Pinillos, M.P. Jarauta, L.A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, *J. Organomet. Chem.* 339 (1988) 181.
- [12] (a) D. Cruz-Garriz, J. Garcia-Alejandre, H. Torrens, *Transition Met. Chem* 16 (1991) 130;  
(b) R. Choukroun, F. Dahan, D. Gervais, C. Rifai, *Organometallics* 9 (1990) 1982.
- [13] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, *J. Chem. Soc. Dalton Trans.* (1989) S1.
- [14] (a) J.J. Bonnet, P. Kalck, R. Poilblanc, *Inorg. Chem.* 16 (1977) 1514;  
(b) A.M. Masdeu, A. Ruiz, S. Castillon, C. Claver, P.B. Hitchcock, P.A. Chaloner, C. Bo, J.M. Poblet, P. Sarasa, *J. Chem. Soc., Dalton Trans.* (1993) 2689;  
(c) J.R. Dilworth, J.R. Miller, N. Wheatley, M.J. Baker, J.G. Sunley, *J. Chem. Soc., Chem. Commun.* (1995) 1579.
- [15] P.B. Mackenzie, R.J. Coots, R.H. Grubbs, *Organometallics* 8 (1989) 8.
- [16] (a) J. Chatt, L.M. Venanzi, *J. Chem. Soc. A* (1957) 4735;  
(b) G. Giordano, R.H. Crabtree, *Inorg. Synth.* 28 (1990) 88.