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Journal of Organometallic Chemistry 690 (2005) 910–915

Journal of Organometallic Chemistry

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Binuclear complexes of rhodium (I) bridged by 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligands: molecular structures of the complexes $[Rh_2(COD)_2(\mu_2\text{-}E_2C_2(B_{10}H_{10}))]$ [E = S, Se] and $[Rh_2(CO)_4(\mu_2\text{-}S_2C_2(B_{10}H_{10}))]$

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Received 6 October 2004; accepted 19 October 2004
Available online 19 November 2004

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

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Abstract

Four new dichalcogenolate carborane bridged binuclear rhodium(I) complexes $[Rh_2(COD)_2(\mu_2\text{-}E_2C_2(B_{10}H_{10}))]$ [COD = *cyclo-octa*-1,5-diene (C_8H_{12}), E = S (**2a**), Se (**2b**)] and $[Rh_2(CO)_2(\mu_2\text{-}E_2C_2(B_{10}H_{10}))]$ [E = S (**3a**), Se (**3b**)] have been prepared by the reactions of the dilithium dichalcogenolate carboranes $Li_2E_2C_2B_{10}H_{10}$ (E = S, Se) with $[Rh(COD)Cl]_2$ or $[Rh(CO)_2Cl]_2$, respectively. The complexes have been fully characterized by ^1H, ^{13}C, ^{11}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.

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

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1. Introduction

In recent years, dinuclear rhodium complexes have been widely investigated because of their catalytic activity. It has been shown that *di*nuclear 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 dichalcogenolate carborane. Although a number of *di*nuclear 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, $[(B_{10}H_{10})C_2E_2]^{2-}$ (E = S, Se), little is known of dirhodium complexes containing *o*-carboranedichalcogenolato ligands up to date.

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doi:10.1016/j.jorganchem.2004.10.034

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 dichalcogenolate 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 *di*nuclear complex $Cp{*}_2Ru_2(\mu\text{-Se})[\mu\text{-}Se_2C_2(B_{10}H_{10})]$ [6,7] has been obtained directly by the reaction of $[Cp{*}RuCl(\mu\text{-Cl})]_2$ with the complex **1b**, it was reported that mononuclear 16e half-sandwich complex was the sole product from the chloro-bridged dimmer $[Cp'RhCl(\mu\text{-Cl})]_2$ (Cp′ = Cp* or η^5-1,3-${}^t\mathrm{Bu}_2C_5H_3$) [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 $[(COD)_2Rh_2(\mu_2\text{-}E_2C_2B_{10}H_{10})]$ [E = S (**2a**), Se (**2b**)] (Scheme 1).

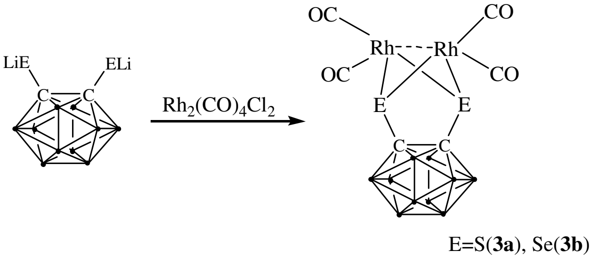
Complexes **2a** and **2b** are moderately air-stable in the solid state, and slightly soluble in *n*-hexane, quite soluble in CH_2Cl_2 or THF.

Similarly, the reactions of dilithium dichalcogenolate carboranes (**1a** and **1b**) with the chloro-bridged carbonyl rhodium complex $[Rh(CO)_2(\mu\text{-Cl})]_2$ at room temperature gave the products $[(CO)_4Rh_2(\mu_2\text{-}E_2C_2B_{10}H_{10})]$ [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 in the triclinic space group $P\bar{1}$ with four molecules in the unit cell.

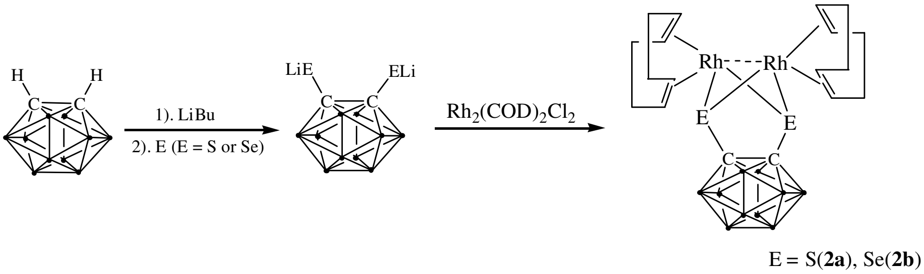


Scheme 2. Synthesis of complexes **3a** and **3b**.

The X-ray structure analysis of **2a** confirms a rhodium (I) thiolate dimmer 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)°. 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 $[Rh(\mu\text{-}SC_6F_5)(COD)]_2$ (2.41 Å av.) [9], and the shortest was reported for $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(\text{-}COD)]_2$ (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 $[Rh(\mu\text{-}SC_6F_5)(COD)]_2$ (2.955 Å av.) [10] and $[Rh(\mu\text{-}S(CH_2)_3NMe_2)(COD)]_2$ (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**.