



# RHENACARBORANE [1,1-(CO)<sub>2</sub>-1,1-I<sub>2</sub>-isonido-1,2,4-ReC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>]<sup>-</sup>. SYNTHESIS, PROPERTIES, AND MOLECULAR STRUCTURE

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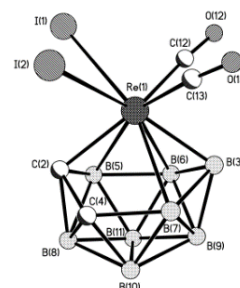
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## Abstract

The reaction of a rhenium carborane complex [1,1,1-(CO)<sub>3</sub>-isonido-1,2,4-ReC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>]<sup>-</sup> tmndH<sup>+</sup> (**1**) with an equimolar amount of I<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 1 h leads to the formation of a complex [1,1-(CO)<sub>2</sub>-1,1-I<sub>2</sub>-isonido-1,2,4-ReC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>]<sup>-</sup> tmndH<sup>+</sup> (**2**). The structure of complex **2** was confirmed by the data of NMR, IR, and UV-Vis spectroscopy, elemental analysis, and X-ray diffraction. In addition, complexes (**1**) and (**2**) were studied by cyclic voltammetry.

**Key words:** renacarboranes, NMR spectroscopy, IR spectroscopy, X-ray diffraction analysis.

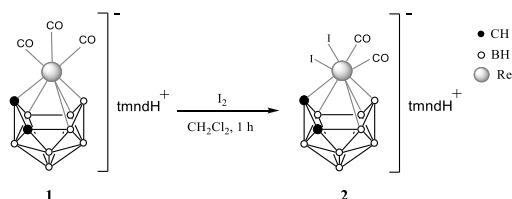


## Introduction

The first tricarbonyl rhenium carborane complex [3,3,3-(CO)<sub>3</sub>-closo-3,1,2-ReC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup>, an analog of [η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Re(CO)<sub>3</sub>], was described by Hawthorne *et al.* in 1968 [1]. Currently, the main areas of promising use of rhenacarboranes are medicinal chemistry [2–5], luminescent materials [6], and catalysis [7]. At the same time, in contrast to 12-vertex renacarboranes, the chemistry of their smaller analogs has been poorly studied [8].

## Results and discussion

The reaction of a yellow rhenium carborane complex [1,1,1-(CO)<sub>3</sub>-isonido-1,2,4-ReC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>]<sup>-</sup> tmndH<sup>+</sup> (**1**) [9] (tmndH<sup>+</sup> is the protonated form of *N,N,N',N'*-tetramethyl-1,8-diaminonaphthalene) with an equimolar amount of I<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 1 h followed by the crystallization (CH<sub>2</sub>Cl<sub>2</sub>–hexane) led to the formation of an orange crystalline compound (complex **2**) (Scheme 1).



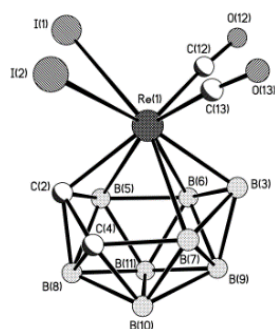
**Scheme 1.** Reaction of [1,1,1-(CO)<sub>3</sub>-isonido-1,2,4-ReC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>]<sup>-</sup> tmndH<sup>+</sup> with I<sub>2</sub>.

The presence of eight doublets in the region from 50.8 to –30.7 ppm in the <sup>11</sup>B NMR spectrum of complex **2** indicated that the reaction of **1** with iodine did not affect the carborane ligand.

At the same time, the presence of only two signals of CO ligands at 197.7 and 194.5 ppm in the <sup>13</sup>C NMR spectrum and two bands at 2036 and 1989 cm<sup>-1</sup> in the IR spectrum indicated the substitution of one of the three carbonyl ligands of the initial complex. Moreover, the <sup>1</sup>H NMR spectrum of **2** exhibited the signals of the tmndH<sup>+</sup> cation. At the same time, the elemental analysis data indicated the presence of two iodine atoms in the molecule, which implied the formation of an anionic *isonido* complex [1,1,1-(CO)<sub>2</sub>-I<sub>2</sub>-isonido-1,2,4-ReC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>]<sup>-</sup> tmndH<sup>+</sup>, rather than neutral complex 1,1-(CO)<sub>3</sub>-1-I-isonido-1,2,4-ReC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>, which could be expected by analogy with the known icosahedral complex 3,3,3-(CO)<sub>3</sub>-3-I-closo-3,1,2-ReC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> formed under similar conditions [10]. A hypsochromic shift (from 415 nm for **1** to 340 nm for **2**) in the UV-Vis spectrum reflected the electron-withdrawing nature of the iodine atoms.

The structure of complex **2** was also confirmed by X-ray diffraction analysis (Fig. 1). According to the XRD data, complex **2** is an anionic 11-vertex *isonido* complex in which the Re<sup>3+</sup> atom is coordinated with two CO groups, two I atoms, and a carborane ligand {C<sub>2</sub>B<sub>8</sub>}. The *isonido* structure of the complex is confirmed by the presence of an open 4-membered face Re–C(2)–C(4)–B(7) in the {Re–C<sub>2</sub>B<sub>8</sub>} moiety due to a significant elongation of the Re–C(4) bond (2.528(7) Å). The latter is characteristic of the previously described 11-vertex *isonido* clusters in which the 6-membered open face (C–C–B–B–B–B) of the {C<sub>2</sub>B<sub>8</sub>} ligand is coordinated to the metal atom in a η<sup>5</sup>-fashion [11–13].

Complexes **1** and **2** were studied by cyclic voltammetry. It was shown that the oxidation of complexes **1** (oxidation state of rhenium +1) and **2** (oxidation state of rhenium +3) occurs in two successive stages; two anodic peaks are present on the voltammograms. The first anodic peak A E<sub>pa</sub> = 0.83V (complex



**Figure 1.** Molecular structure of anionic complex **2** (hydrogen atoms and  $\text{tmndH}^+$  cation are not shown). Selected distances (Å):  $\text{Re}(1)\text{--B}(3)$  2.135(7),  $\text{Re}(1)\text{--C}(2)$  2.140(6),  $\text{Re}(1)\text{--B}(7)$  2.387(7),  $\text{Re}(1)\text{--B}(6)$  2.418(8),  $\text{Re}(1)\text{--B}(5)$  2.500(8),  $\text{Re}(1)\text{--C}(4)$  2.528(7).

**1)** is irreversible, one-electron and corresponds to the  $\text{Re}^{1+/2+}$  transition. The first anodic peak of complex **2**  $A^*$   $E_{\text{pa}} = 0.88\text{ V}$  is reversible, one-electron and corresponds to the  $\text{Re}^{3+/4+}$  transition. The one-electron nature of the electrode processes is evidenced by the fact that the height of peaks **A**,  $A^*$  is comparable with the that of the one-electron peak of ferrocene oxidation obtained under identical conditions. It should be noted that a small difference in the potential values of peaks **A** and  $A^*$  ( $\Delta E = 50\text{ mV}$ ) indicates that the electron deficit at the Re center ( $\text{Re}^{2+}$ ) is compensated by the electron density of carbonyl groups and the boron (carborane) network. The second anodic peaks **B**,  $B^*$  are irreversible, multi-electron with potentials  $E_{\text{pa}} = 1.71\text{ V}$  and  $1.70\text{ V}$ , respectively. The voltammogram of complex **2** contains two irreversible, single-electron reduction peaks at potentials of  $-0.32\text{ V}$  and  $-0.80\text{ V}$ . When scanning the potential back to the anodic region, one anodic peak is observed at a potential of  $-0.13\text{ V}$ . Probably, the first cathodic peak corresponds to the  $\text{Re}^{3+/2+}$  transition with the formation of an unstable dianion.

## Conclusions

The 11-vertex *isonido*-renacarborane  $[1,1\text{--}(\text{CO})_2\text{--}1,1\text{--I}_2\text{--isonido-1,2,4-ReC}_2\text{B}_8\text{H}_{10}]^- \text{tmndH}^+$  was synthesized, in which the ligand environment of the  $\text{Re}^{3+}$  atom consists of a carborane ligand, two CO groups, and two I atoms. The complex was studied by NMR, IR, and UV-Vis spectroscopy, cyclic voltammetry, and elemental analysis. Its structure was confirmed by X-ray diffraction. In the future studies, we are going to investigate the luminescence properties of this complex.

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## Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental details, NMR, IR, and UV-Vis spectra. For ESI, see DOI: 10.32931/ioXXXXx.

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