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Rhenacarborane [1,1-(CO)2-1,1-I2-Isonido-1,2,4-ReC2B8H10]–.  
Synthesis, Properties, and Molecular Structure

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Abstract

The reaction of a rhenium carborane complex [1,1,1-(CO)3-*isonido-*1,2,4-ReC2B8H10]– tmndH+ (**1**) with an equimolar amount of I2 in CH2Cl2 at room temperature for 1 h leads to the formation of complex [1,1-(CO)2-1,1-I2-*isonido-*1,2,4-ReC2B8H10]– tmndH+ (**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:** rhenacarboranes, NMR spectroscopy, IR spectroscopy, X-ray diffraction analysis.

Introduction

The first tricarbonyl rhenium carborane complex [3,3,3-(CO)3-*closo*-3,1,2-ReC2B9H11]–, an analog of [η5-C5H5]Re(CO)3, 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)3-*isonido*-1,2,4-ReC2B8H10]– tmndH+ (**1**) [9] (tmndH+ is the protonated form of *N,N,N',N′*-tetramethyl-1,8-diaminonaphthalene) with an equimolar amount of I2 in CH2Cl2 at room temperature for 1 h followed by the crystallization (CH2Cl2–hexane) led to the formation of an orange crystalline compound (complex **2**) (Scheme 1).

**Scheme 1**. Reaction of [1,1,1-(CO)3-*isonido*-1,2,4-ReC2B8H10]– tmndH+ with I2.

The presence of eight doublets in the region from 50.8 to–30.7 ppm in the 11B 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 13C NMR spectrum and two bands at 2036 and 1989 cm–1 in the IR spectrum indicated the substitution of one of the three carbonyl ligands of the initial complex. Moreover, the 1H NMR spectrum of **2** exhibited the signals of the tmndH+ 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)2-I2-*isonido-*1,2,4-ReC2B8H10]– tmndH+, rather than neutral complex 1,1-(CO)3-1-I-*isonido-*1,2,4-ReC2B8H10, which could be expected by analogy with the known icosahedral complex 3,3,3-(CO)3-3-I-*closo*-3,1,2-ReC2B9H11 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 Re3+ atom is coordinated with two CO groups, two I atoms, and a carborane ligand {C2B8}.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-C2B8} 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 {C2B8} ligand is coordinated to the metal atom in a η5-fashion [11–13].

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

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*pa = 0.83 V (complex **1**) is irreversible, one-electron and corresponds to the Re1+/2+transition. The first anodic peak of complex **2** A\* *E*pa = 0.88 V is reversible, one-electron and corresponds to the Re3+/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\* (∆*E* = 50 mV) indicates that the electron deficit at the Re center (Re2+) 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*pa = 1.71 V and 1.70 V, respectively. The voltammogram of complex **2** contains two irreversible, single-electron reduction peaks at potentials of –0.32 V and –0.80 V. When scanning the potential back to the anodic region, one anodic peak is observed at a potential of –0.13 V. Probably, the first cathodic peak corresponds to the Re3+/2+ transition with the formation of an unstable dianion.

Conclusions

The 11-vertex *isonido*-renacarborane [1,1-(CO)2-1,1-I2-*isonido*-1,2,4-ReC2B8H10]– tmndH+ was synthesized, in which the ligand environment of the Re3+ atom consists of a carborane ligand, two CO groups, and two I atoms. The complex was studied by NMR, IR, and UV-Vis spectroscopy, cylic 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/io2519a.

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