



# 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

Cite this: *INEOS OPEN*,  
2025, 8 (1–3), 60–61  
DOI: 10.32931/io2519a

E. V. Balagurova,<sup>\*a</sup> F. M. Dolgushin,<sup>b</sup> E. G. Kononova,<sup>a</sup>  
A. A. Kissel,<sup>a</sup> and S. M. Peregodova<sup>a,c</sup>

Received 21 October 2024,  
Accepted 15 November 2024

<http://ineosopen.org>

<sup>a</sup> Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,  
ul. Vavilova 28, str. 1, Moscow, 119334 Russia

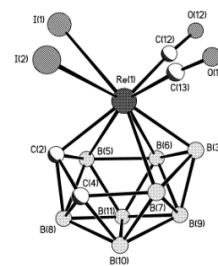
<sup>b</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of  
Sciences, Leninskii pr. 29, Moscow, 119991 Russia

<sup>c</sup> Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences,  
ul. Profsoyuznaya 70, Moscow, 117393 Russia

## 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 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:** rhenacarboranes, NMR spectroscopy, IR spectroscopy, X-ray diffraction analysis.

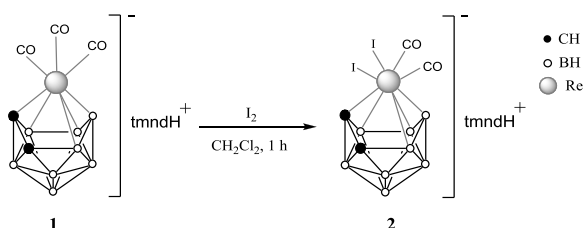


## Introduction

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).



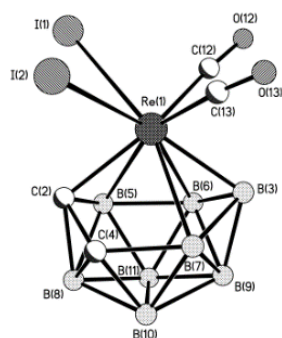
**Scheme 1.** Reaction of [1,1,1-(CO)<sub>3</sub>-isonido-1,2,4-ReC<sub>2</sub>B<sub>8</sub>H<sub>10</sub>]<sup>−</sup> tmndH<sup>+</sup> with I<sub>2</sub>.

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) 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> = 0.83 V (complex



**Figure 1.** Molecular structure of anionic complex **2** (hydrogen atoms and  $\text{tmndH}^+$  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).

**1**) is irreversible, one-electron and corresponds to the  $\text{Re}^{1+/2+}$  transition. The first anodic peak of complex **2**  $A^*$   $E_{\text{pa}} = 0.88$  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  $A^*$  ( $\Delta E = 50$  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  $E_{\text{pa}} = 1.71$  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  $\text{Re}^{3+/2+}$  transition with the formation of an unstable dianion.

## Conclusions

The 11-vertex isonido-renacarbaborane  $[1,1-(\text{CO})_2-1,1\text{-I}_2\text{-isonido-1,2,4-ReC}_2\text{B}_8\text{H}_{10}]^- \text{tmndH}^+$  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.

## Acknowledgements

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (agreement no. 075-00277-24-00) using the equipment of the Center for Collective

Use of INEOS RAS. The X-ray study was performed using the equipment of the JRC PMR of IGIC RAS.

## Corresponding author

\* E-mail: balena.ran@mail.ru. Tel: +7(499)135-9262 (E. V. Balagurova).

## 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.

## References

1. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren Jr., P. A. Wegner, *J. Am. Chem. Soc.*, **1968**, *90*, 879–896. DOI: 10.1021/ja01006a008
2. M. E. El-Zaria, N. Janzen, J. F. Valliant, *Organometallics*, **2012**, *31*, 5940–5949. DOI: 10.1021/om300521j
3. A. S. Louie, L. E. Harrington, J. F. Valliant, *Inorg. Chim. Acta*, **2012**, *389*, 159–167. DOI: 10.1016/j.ica.2012.03.017
4. A. B. Olejniczak, *ARKIVOC*, **2012**, *8*, 90–97. DOI: 10.3998/ark.5550190.0013.808
5. D. G. Pruitt, K. M. Bullock, W. A. Banks, P. A. Jelliss, *Inorg. Chim. Acta*, **2017**, *466*, 139–144. DOI: 10.1016/j.ica.2017.05.060
6. P. A. Jelliss, J. Mason, J. M. Nazzoli, J. H. Orlando, A. Vinson, N. P. Rath, M. J. Shaw, *Inorg. Chem.*, **2006**, *45*, 370–385. DOI: 10.1021/ic051463e
7. K. R. Pichaandi, P. E. Fanwick, M. M. Abu-Omar, *Organometallics*, **2012**, *31*, 1888–1896. DOI: 10.1021/om201222r
8. S. W. Buckner, M. J. Fischer, P. A. Jelliss, R. Luo, S. D. Minter, N. P. Rath, A. Siemiarz, *Inorg. Chem.*, **2006**, *45*, 7339–7347. DOI: 10.1021/ic061071n
9. E. V. Balagurova, F. M. Dolgushin, M. G. Medvedev, E. G. Kononova, I. A. Godovikov, A. F. Smol'yakov, I. T. Chizhevsky, *J. Organomet. Chem.*, **2020**, *911*, 121141. DOI: 10.1016/j.jorganchem.2020.121141
10. M. J. Fischer, P. A. Jelliss, L. M. Phifer, N. P. Rath, *Inorg. Chim. Acta*, **2005**, *358*, 1531–1544. DOI: 10.1016/j.ica.2004.09.037
11. M. Brown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, **1990**, 3039–3049. DOI: 10.1039/DT9900003039
12. E. V. Balagurova, I. V. Pisareva, A. F. Smol'yakov, F. M. Dolgushin, I. A. Godovikov, I. T. Chizhevsky, *Inorg. Chem.*, **2016**, *55*, 11193–11200. DOI: 10.1021/acs.inorgchem.6b01823
13. E. V. Balagurova, I. A. Godovikov, E. G. Kononova, F. M. Dolgushin, M. I. Shevchenko, I. T. Chizhevsky, *Inorg. Chem. Commun.*, **2021**, *128*, 108557. DOI: 10.1016/j.inoche.2021.108557

This article is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License.

