

Electronic supplementary information

RHENACARBORANE [1,1-(CO)₂-1,1-I₂-*isonido*-1,2,4-ReC₂B₈H₁₀]⁻. SYNTHESIS, PROPERTIES, AND MOLECULAR STRUCTURE

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Experimental section

General remarks

Carborane *nido*-5,6-C₂B₈H₁₂ was prepared by the published method [S1]. CH₂Cl₂ was distilled over CaH₂. Synthesis and isolation of complex **2** was carried out in the air. Silica gel from Acros (0.035–0.070 mm 60 Å) was used for column chromatography. The NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. The IR spectra were obtained on a Bruker Tensor 37 FT-IR spectrometer in KBr pellets. The UV-Vis spectra were recorded on a Carl Zeiss Specord M 40 spectrophotometer for solutions of **1** and **2** in CH₂Cl₂.

Syntheses of complex **2**

A solution of I₂ (28 mg, 0.11 mmol) in 5 mL of CH₂Cl₂ was added dropwise to a solution of complex **1** (65 mg, 0.11 mmol) in 10 mL of CH₂Cl₂ at –50 °C. The reaction mixture was brought to room temperature and stirred for 1 h. The solvent was removed under vacuum. The residue obtained was washed with hexane until hexane stopped to be colored. The crystallization was carried out from a CH₂Cl₂–hexane mixture. Complex **2** was obtained as orange crystals. Yield: 60 mg (66%). ¹H NMR (400 MHz, CD₂Cl₂, 20 °C): δ 19.38 (s, 1H, tmndH⁺), 8.06–7.71 (m, 6H, tmndH⁺), 7.12 (sbr, 1H, CH-carb), 3.81 (br. s, 1H, CH-carb), 3.18 (s, 12H, tmndH⁺) ppm. ¹¹B NMR (128 MHz, CD₂Cl₂, 20 °C): δ 50.8 (d, 1B, *J* = 171 Hz), 18.5 (d, 1B, *J* = 156 Hz), 3.5 (d, 1B, *J* = 155 Hz), –8.6 (d, 1B, *J* = 148 Hz), –16.3 (d, 1B, *J* = 178 Hz), –22.1 (d, 1B, *J* = 154 Hz), –25.0 (d, 1B, *J* = 158 Hz), –30.8 (d, 1B, *J* = 147 Hz) ppm. ¹³C NMR (100 MHz, CD₂Cl₂, 20 °C): δ 197.63 (CO), 194.52 (CO), 143.15 (tmndH⁺ (naphth.)), 135.57 (tmndH⁺ (naphth.)), 130.01 (tmndH⁺ (naphth.)), 127.33 (tmndH⁺ (naphth.)), 121.27 (tmndH⁺ (naphth.)), 118.49 (tmndH⁺ (naphth.)), 63.94 (CH-carb.), 46.78 (CH₃ tmndH⁺) ppm. IR (vas. oil, ν/cm^{–1}): 2546 (BH), 2036, 1989 (CO). Anal. Calcd. for C₁₈H₂₉B₈O₂N₂I₂Re: C, 25.98; H, 3.49. Found: C, 25.61; H, 3.20%.

X-ray diffraction analysis of **2**

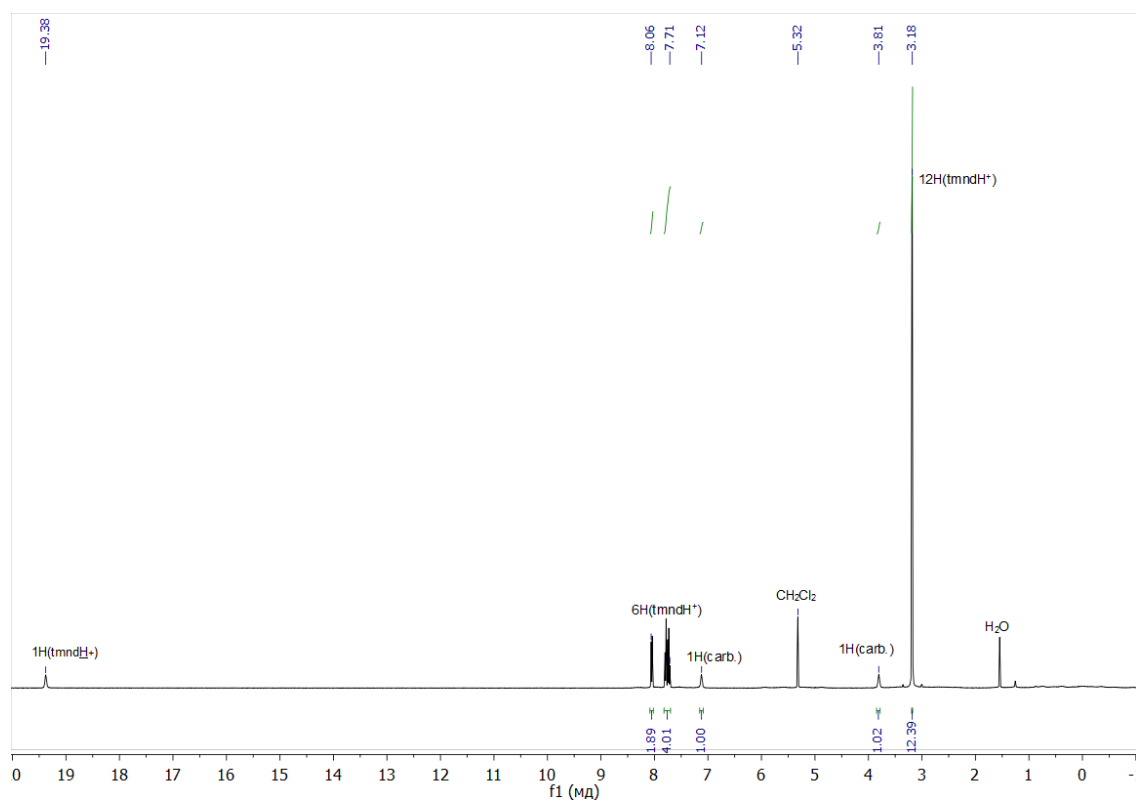
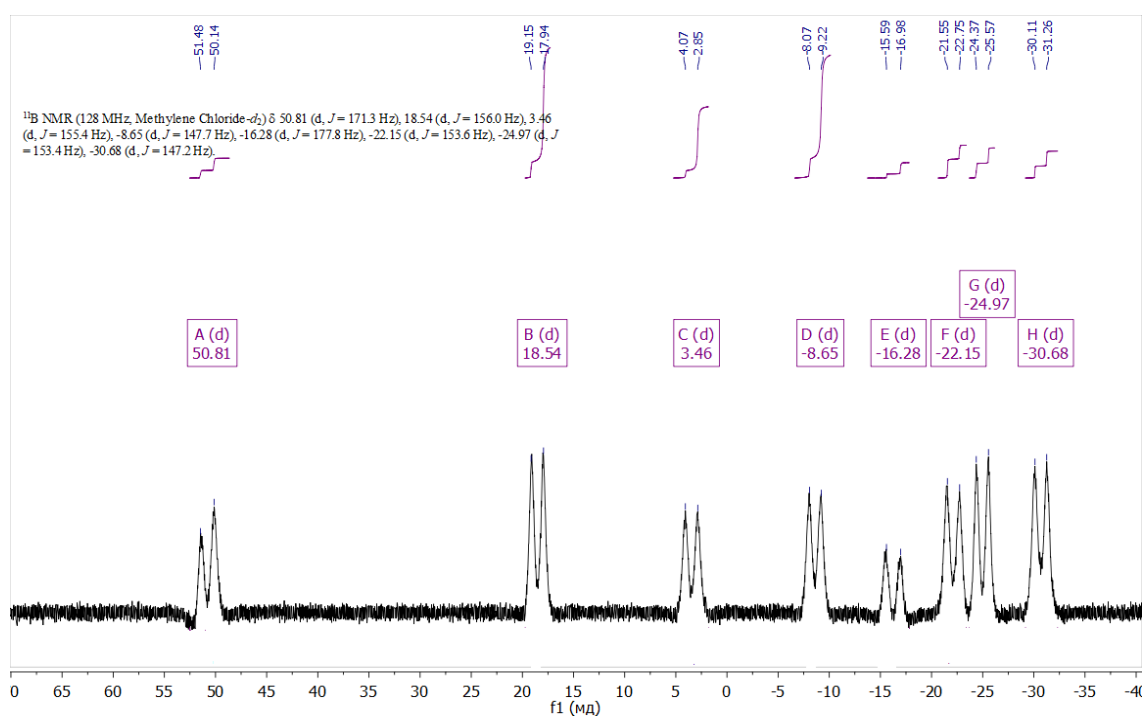
Crystals (C₁₈H₂₉B₈I₂N₂O₂Re, *M* = 831.91) are triclinic, space group *P*-1, at 296K *a* = 7.9715(3), *b* = 12.8346(5), *c* = 14.4779(5) Å, α = 97.2701(13), β = 97.1120(12), γ = 103.4553(13)°, *V* = 1410.86(9) Å³, *Z* = 2, *d*_{calc.} = 1.958 g/cm³, μ = 65.13 cm^{–1}. The data collection was carried out with a Bruker SMART APEX II diffractometer, λ(MoKα) = 0.71073 Å, ω-scan technique, *T* = 296(2) K, 6100 independent reflections (*R*_{int} = 0.0376) with 2θ_{max} = 54.0° collected and used in refinement. The structure was solved by direct methods and refined by the full matrix least-squares technique against *F*² with the anisotropic thermal parameters for all non-hydrogen atoms. Semi-empirical adsorption correction (*T*_{min/max} = 0.217/0.562) was

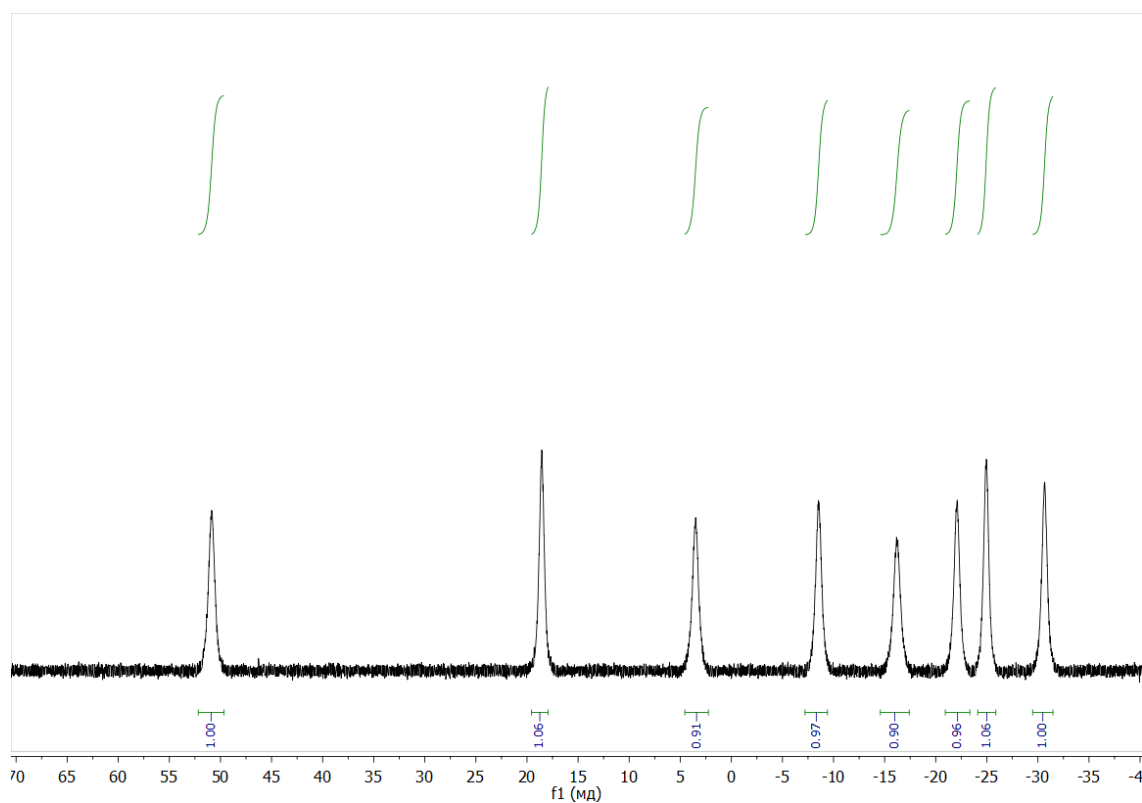
applied using the SADABS program [S2]. At the final stage, the structure was refined as a two-component twin (BASF is 0.059(1)). Hydrogen atoms of the carborane ligand and NH group of the cation were located in the difference Fourier maps and freely refined without constraints. The other hydrogen atoms were placed in calculated positions and refined using a riding model with $U_{iso}(\text{H}) = 1.5U_{eq}(\text{C})$ for hydrogen atoms of methyl groups and $U_{iso}(\text{H}) = 1.2U_{eq}(\text{C})$ for aromatic hydrogen atoms. The refinement converged to $wR_2 = 0.0807$ and $\text{GOF} = 1.163$ for all independent reflections ($R_I = 0.0329$ was calculated against F for 5872 observed reflections with $I > 2\sigma(I)$). All calculations were performed using the SHELXL program package [S3]. CCDC deposition number 2388455 contains the supplementary crystallographic data for this paper.

Electrochemical measurements

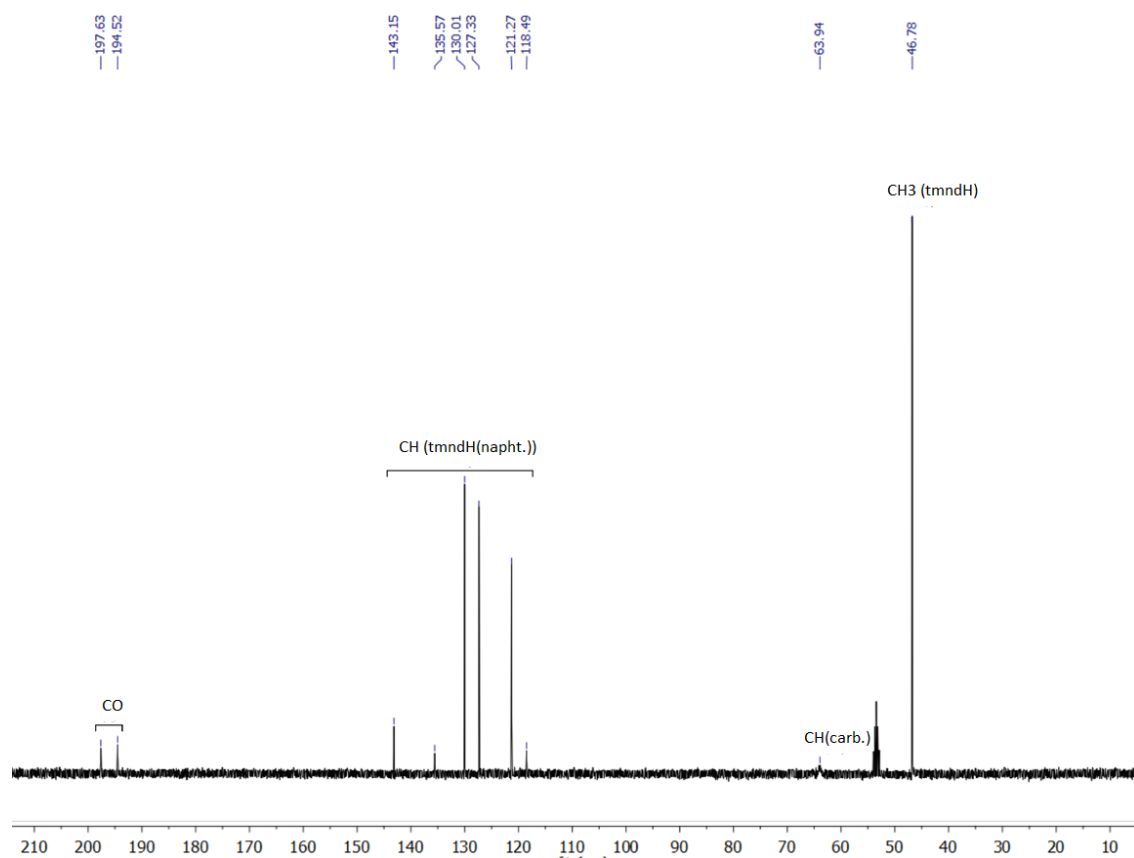
Cyclic voltammetry measurements were performed on an IPC-Pro M potentiostat for *ca.* 10^{-3} M solutions of compounds **1** and **2** in rigorously dried CH_2Cl_2 in a standard three-electrode cell equipped with a glassy carbon working electrode ($S = 2 \text{ mm}^2$), platinum plate as the counter electrode, and SCE (saturated calomel electrode) as the reference electrode. The scan rate was $100 \text{ mV}\cdot\text{s}^{-1}$. A solution containing 0.2 M Bu_4NPF_6 was used as the supporting electrolyte, and a ferrocene–ferrocenium pair ($E^0 = 0.47 \text{ V}$) was applied as the internal standard.

NMR spectra

 ^1H NMR spectrum of compound **2** ^{11}B NMR spectrum of compound **2**

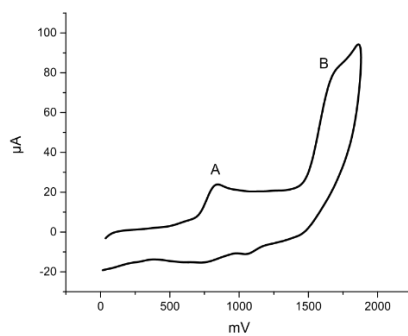


$^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **2**

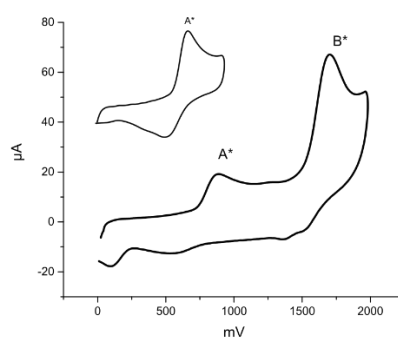


NMR ^{13}C spectrum of compound **2**

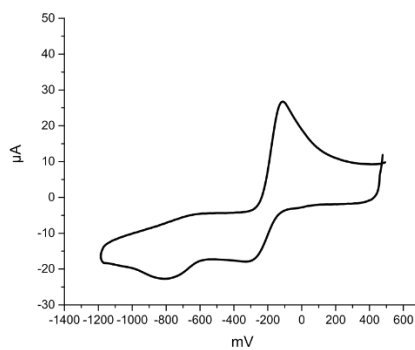
Cyclic voltammetry



Cyclic voltammetry of the oxidation of complex **1** in CH_2Cl_2 $v = 100 \text{ mV/s}$

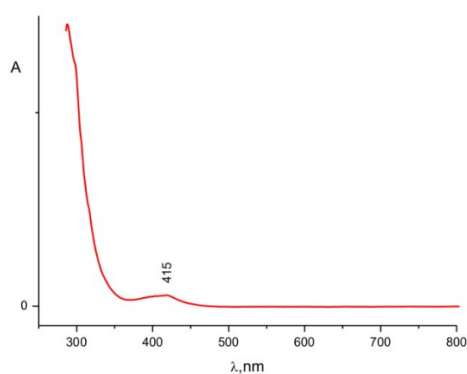


Cyclic voltammetry of the oxidation of complex **2** in CH_2Cl_2 $v = 100 \text{ mV/s}$

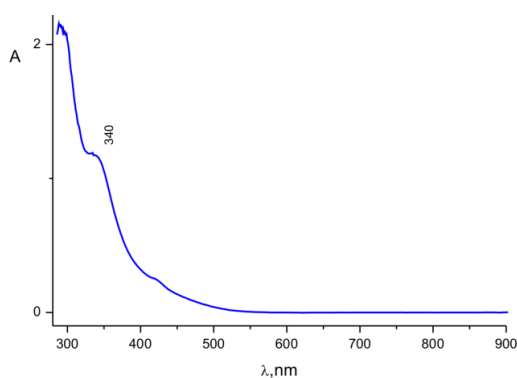


Cyclic voltammetry of the reduction of complex **2** in CH_2Cl_2 $v = 100 \text{ mV/s}$

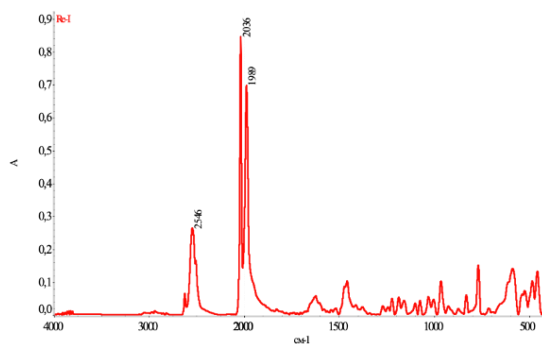
UV-Vis and IR spectra of complex 1 and 2



UV-Vis spectra of complex 1



UV-Vis spectra of complex 2



IR spectrum of complex 2

References

- S1. B. Štíbr, J. Holub, T. Jelínek, B. Grüner, J. Fusek, Z. Plzák, F. Teixidor, C. Viñas, J. D. Kennedy, *Collect. Czech. Chem. Commun.*, **1997**, 62, 1229–1238. DOI: 10.1135/cccc19971229
- S2. SADABS, Version 2016/5, Bruker AXS Inc., Madison, Wisconsin, USA.
- S3. G.M. Sheldrick, *Acta Cryst., Sect. C: Struct. Chem.*, **2015**, 71, 3–8. DOI: 10.1107/S2053229614024218