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# Synthesis and Structural Characterization of the Ruthenium Complex Based on 1,2-Dicarba-*closo*-Dodecaborane-1,2-Dithiolate Ligand and FcCH(OH)C≡CH

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**Abstract**—A new complex $[(p\text{-Cymene})\mathrm{Ru(S_2C_2B_{10}H_9)(CH_2CCH(OH)Fc)}]_2 \cdot 0.5\mathrm{H_2O}$ (Fc = ferrocenyl) based on the 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligand and FcCH(OH)C≡CH has been synthesized successfully and characterized by IR, NMR, MS, elemental analysis and single-crystal X-ray diffraction, in which the alkyne is inserted into one of the Ru—S bonds that may further lead to metal-induced B—H activation, hydrogen atom transfer from the carborane via the metal center to the inserted alkyne, and the generation of a Ru—B bond. The complex crystallizes in triclinic system, space group $P\overline{1}$ with $a = 12.7329(5)$, $b = 13.8422(5)$, $c = 20.0796(7)$ Å, $\alpha = 87.249(3)°$, $\beta = 89.311(3)°$, $\gamma = 62.961(4)°$, $\mathrm{C_{50}H_{73}B_{20}O_{2.5}S_4Fe_2Ru_2}$, $Mr = 1372.37$, $V = 3148.39(19)$ Å$^3$, $\rho_c = 1.448$ g/cm$^3$, $Z = 1$, $F(000) = 1394$, $\mu(\mathrm{Mo}K_\alpha) = 1.094$ mm$^{-1}$, $R = 0.0473$ and $\omega R = 0.0990$ for 9294 observed reflections ($I > 2\sigma(I)$).

*Keywords: ortho*-carborane, chalcogenide element, ruthenium complexes, synthesis, X-ray crystallography

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## INTRODUCTION

The 16-electron complexes containing 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate and ring ligands such as pentamethylcyclopentadienyl (Cp*) or 4-isopropyltoluene (*p*-cymene) are of considerable interest with respect to further transformations [1–3]. The combination of electron deficiency at the coordinatively unsaturated metal center and reactivity of metal—chalcogen bonds renders these complexes interesting candidates for reactions with unsaturated substrates [4–6]. Furthermore, the carborane cage at the site of B3/B6, being close to the metal, have to be considered as potentially reactive centers [7]. On the other hand, polyhedral boron clusters occupy a special position in boron chemistry due to possibility to design molecular platforms based on boron clusters, which can be used in medicine, catalysis, and photochemistry [8–10]. Many studies were devoted to the synthesis and physicochemical properties of boron-containing polymers based on higher boron hydrides and carboranes [11–14].

We have recently reported on the X-ray structural and NMR spectroscopic characterization of **II** $[(p\text{-Cymene})\mathrm{Ru(S_2C_2B_{10}H_9)((OH)H_2CCCHFc)}]$ [15], and have found a remarkable activity not only for the carborane cage but also for the metal chalcogen bonds and terminal alkyne alcohols considered as potentially reactive centers. On the basis of previous studies, in this paper we explore the further reaction of 16-electron complex $(p\text{-cymene})\mathrm{Ru(S_2C_2B_{10}H_{10})}$ (**I**) with FcCH(OH)C≡CH, and a new complex $[(p\text{-Cymene})\mathrm{Ru(S_2C_2B_{10}H_9)(CH_2CCH(OH)Fc)}]_2 \cdot 0.5\mathrm{H_2O}$ (**III**) has been synthesized successfully and characterized (Scheme 1).

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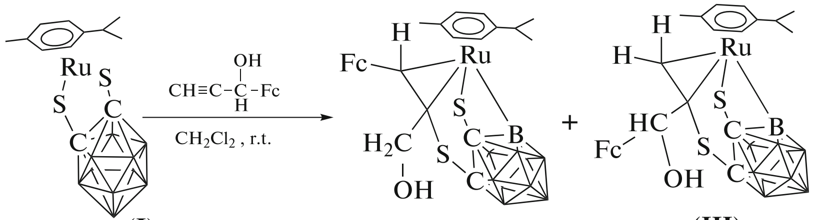

**(I)** **(II)** **(III)**

**Scheme 1.**

## EXPERIMENTAL

**Materials and methods.** The preparative work was carried out under an argon atmosphere using standard Schlenk techniques. Solvents were freshly distilled under nitrogen from either sodium or calcium hydride prior to use. *n*-Butyllithium (2.0 M in cyclohexane, Aldrich), *ortho*-carborane, and other chemicals were used as commercial products without further purification. [(*p*-Cymene)$RuCl_2]_2$ [16], FcCH(OH)C≡CH [17] and (*p*-cymene)$Ru(S_2C_2B_{10}H_{10})$ [18] were prepared according to literature. Crystal structure determination was carried out on a BRUKER SMART APEX II CCD X-ray diffractometer. NMR data were obtained on a Bruker DRX-500 spectrometer. IR spectra were recorded on a Nicolet 360 FT-IR spectrometer with KBr pellets in the 4000–400 $cm^{-1}$ region. C, H, and S analyses were carried out on a CarloErba CHNS-3 FA 1108 automatic elemental analyzer. The content of boron and metals in complexes was determined by the ICP MS method using an iCAP 6300 Duo inductively coupled plasma atomic spectrometer. Finnigan MAT TSQ7000 was used for ESI-MS.

**Synthesis of II and III.** FcCH(OH)C≡CH (96 mg, 0.4 mmol) was added to **I** (176.8 mg, 0.4 mmol) in $CH_2Cl_2$ (15 mL). The mixture was stirred for 24 h at ambient temperature. The color turned gradually from blue to orange. After removal of the solvent, the residue was subjected to chromatography on silica gel. Elution with petroleum ether–$CH_2Cl_2$ (1 : 2 v/v) gave pure compounds **II** (82 mg, 30%) and **III** (76 mg, 28%) as orange solids. Crystals suitable for X-ray crystallography were obtained by slow diffusion of petroleum ether into a dichloromethane solution of the corresponding compound.

**III**: mp (dec.) 174°C.

For $C_{50}H_{73}B_{20}O_{2.5}S_4Fe_2Ru_2$

| | | | | | | |
|---|---|---|---|---|---|---|
| Anal. calcd., % | B, 15.75 | C, 43.76 | H, 5.31 | S, 9.35 | Fe, 8.16 | Ru, 14.99 |
| Found, % | B, 15.51 | C, 43.43 | H, 5.41 | S, 9.46 | Fe, 8.29 | Ru, 14.97 |

ESI-MS (*m/z*): calcd. for $C_{50}H_{72}B_{20}O_2S_4Fe_2Ru_2$, 1363.41; found: 1364.49 ($[M + H]^+$, 100%). $^1H$ NMR ($CDCl_3$; δ, ppm): 1.32, 1.37 (d., $J$ = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.37 (s., 3H, $C_6H_4$–$CH_3$), 2.45 (s., 1H, Ru–$CH_2$), 2.81 (sept., $J$ = 7.0 Hz, 1H, $CH(CH_3)_2$), 3.18 (s., 1H, Ru–$CH_2$), 3.76 (s., 1H, O*H*), 4.14 (s., 1H, Fc), 4.23 (s., 1H, Fc), 4.29 (s., 1H, Fc), 4.42 (s., 5H, Fc), 4.49 (s., 1H, Fc), 5.31 (s., 1H, Ru–C*H*), 5.37 (d., $J$ = 6.0 Hz, 1H, $C_6H_4$), 5.44 (d., $J$ = 6.0 Hz, 1H, $C_6H_4$), 6.20 (d., $J$ = 6.0 Hz, 1H, $C_6H_4$), 6.35 (d., $J$ = 6.0 Hz, 1H, $C_6H_4$). $^{13}C$ NMR ($CDCl_3$; δ, ppm): 19.2 ($C_6H_4$–$CH_3$), 21.5, 24.6 ($CH(CH_3)_2$), 32.1 ($CH(CH_3)_2$), 39.9 (Ru–$CH_2$), 66.3, 66.5, 67.8, 68.7, 69.2, 70.7, 73.6 (Fc), 81.9 (*C*H(OH)), 91.7 (Ru–C), 98.7, 98.9, 99.7, 103.6 (*C*H in *p*-cymene), 96.5, 100.4, 110.4, 118.6 (*o*-carborane and quaternary C in *p*-cymene). $^{11}B\{^1H\}$ NMR ($CDCl_3$; δ, ppm): –1.61, –3.81, –7.55, –8.75, –10.70 (1:3:3:2:1). IR (KBr; ν, $cm^{-1}$): 2572 ν(B–H), 3219 ν(O–H).

**X-ray crystallography.** A single crystal with dimensions of 0.28 × 0.24 × 0.22 mm was put on a BRUKER SMART APEX II CCD diffractometer equipped with a graphite-monochromatized $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å) by using a φ–ω scan mode at 291(2) K. In the range of $2.56° \le \theta \le 26.00°$, a total of 24983 reflections were collected and 12346 were independent with $R_{int}$ = 0.0285, of which 9294 were observed with $I > 2\sigma(I)$. The correction for *Lp* factors was applied. The crystal structure was solved by direct methods using SHELXS-97 [19] and refined by full-matrix least-squares techniques on $F^2$ using SHELXL-97 [20]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were assigned with commonly isotropic displacement factors and included in the final refinement by use of geometrical restrains. The crystallographic data are summarized in Table 1, the selected bond lengths and bond angles are listed in Table 2, and hydrogen bond lengths and bond angles are given in Table 3.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1943443; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

The solid-state structure of complex **III** is fully supported by the solution NMR spectroscopic data, and relevant $^1H$ and $^{13}C$ NMR data are listed in the experimental section. In particular, the $^1H$ NMR spectrum showed the signal attributed to O***H*** at 3.76 ppm and the RuC$\boldsymbol{H}_2$ signals at 2.45 and 3.18 ppm with a small coupling constant of <2 Hz. This is typical of terminal alkene coordinated to metal center. In the $^{13}C$ NMR spectrum, the signal of ***C***H(OH) appeared at 81.9 ppm, while the corresponding ruthenium-coordinated carbon signals are recognized at 39.9 (Ru–$\boldsymbol{C}H_2$) and 91.7 (Ru–***C***) ppm, respectively.

Recently, we have reported the solid-state structure and spectroscopic data of **II** [15]. Structural analysis shows that there are metal-induced B–H activation, the generation of Ru–B bond, and the coordination of the C=C bond in **II** and **III**. However, the hydroxyl group of FcCH(OH)C≡CH ligand has been transferred from the γ-carbon atom to α-carbon atom in **II**. The molecular structure of **III** was solved by single crystal X-ray analysis as given in Fig. 1. Its solid-state structure shows that the C≡C bond of FcCH(OH)C≡CH is inserted into one of the Ru–S bonds, the *ortho*-carborane unit is drawn sufficiently close to the metal center to have initiated B–H activation at B(3)/B(13) sites, hydrogen atom transfer from the carborane via the metal center to the terminal car-

**Table 1.** Crystallographic data and structural refinement details of complex **III**

| Parameter | Value |
|---|---|
| Chemical formula | $C_{50}H_{73}B_{20}O_{2.5}S_4Fe_2Ru_2$ |
| Crystal size, mm | 0.28 × 0.24 × 0.22 |
| Formula weight | 1372.37 |
| Temperature, K | 291(2) |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$, Å | 12.7329(5) |
| $b$, Å | 13.8422(5) |
| $c$, Å | 20.0796(7) |
| $\alpha$, deg | 87.249(3) |
| $\beta$, deg | 89.311(3) |
| $\gamma$, deg | 62.961(4) |
| Reflections collected | 24983 |
| Independent reflns ($R_{int}$) | 12346 (0.0285) |
| Reflections with $I > 2\sigma(I)$ | 9294 |
| Data/restraints/parameters | 12346/0/745 |
| GOOF | 1.062 |
| $R_1/wR_2$ ($I > 2\sigma(I)$) | 0.0473/0.0990 |
| $R_1/wR_2$ (all data) | 0.0686/0.1034 |
| Largest diff. peak/hole, e Å$^{-3}$ | 1.005/–1.164 |

**Table 2.** Selected bond lengths (Å) and bond angles (deg) of complex **III**

| Bond | $d$, Å | Bond | $d$, Å | Bond | $d$, Å |
|---|---|---|---|---|---|
| Ru(1)–S(2) | 2.4187(1) | C(1)–C(2) | 1.701(5) | S(1)–C(1) | 1.756(3) |
| Ru(1)–B(3) | 2.106(4) | C(3)–C(4) | 1.431(5) | S(2)–C(2) | 1.768(4) |
| Ru(1)–C(3) | 2.170(4) | C(4)–C(5) | 1.525(5) | S(1)–C(4) | 1.822(4) |
| Ru(1)–C(4) | 2.152(4) | C(5)–C(6) | 1.515(5) | C(5)–O(1) | 1.419(4) |
| Ru(2)–S(4) | 2.4386(1) | C(26)–C(27) | 1.692(5) | S(3)–C(26) | 1.777(3) |
| Ru(2)–B(13) | 2.137(4) | C(28)–C(29) | 1.428(6) | S(4)–C(27) | 1.770(4) |
| Ru(2)–C(28) | 2.183(4) | C(29)–C(30) | 1.519(5) | S(3)–C(29) | 1.800(4) |
| Ru(2)–C(29) | 2.175(4) | C(30)–C(31) | 1.548(5) | C(30)–O(2) | 1.456(4) |
| Angle | ω, deg | Angle | ω, deg | Angle | ω, deg |
| S(2)Ru(1)B(3) | 71.21(11) | S(2)Ru(1)C(3) | 119.91(10) | S(2)Ru(1)C(4) | 84.38(10) |
| B(3)Ru(1)C(3) | 84.13(15) | B(3)Ru(1)C(4) | 85.55(15) | C(3)Ru(1)C(4) | 38.65(13) |
| S(4)Ru(2)B(13) | 71.07(12) | S(4)Ru(2)C(28) | 119.68(11) | S(4)Ru(2)C(29) | 84.63(10) |
| B(13)Ru(2)C(28) | 84.72(15) | B(13)Ru(2)C(29) | 86.44(14) | C(28)Ru(2)C(29) | 38.26(14) |

bon atom of the alkyne, and the ruthenium atom bonded to a *p*-cymene ring in an $\eta^6$ mode satisfy the 18-electron rule.

The C–C distances (C(3)–C(4) 1.431(5) Å, C(28)–C(29) 1.428(6) Å) are longer than typical C=C double bonds (~1.35 Å) and shorter than typical C–C single bonds (~1.55 Å), consistent with the value of a coordinated olefin [21]. The C–C bond lengths (C(1)–C(2) 1.701(5) Å, C(26)–C(27) 1.692(5) Å) of the carboranes are close to the typical range known for *o*-carborane derivatives of 1.62–1.70 Å [22, 23]. The hydroxyl groups can be established by the bond lengths of C–O (C(5)–O(1) 1.419(4) Å, C(30)–O(2) 1.456(4) Å), which are typical of normal carbon–oxygen single bonds [24,

**Table 3.** Geometric parameters of hydrogen bond for the complex **III***

| D–H···A | Distance, Å | | | Angle DHA, deg |
|---|---|---|---|---|
| | D–H | H···A | D···A | |
| C(22)–H(22)···O(2)$^{\#1}$ | 0.98 | 2.727 | 3.143 | 126.91 |
| C(47)–H(47)···O(1)$^{\#2}$ | 0.98 | 2.455 | 3.099 | 118.50 |

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ *x*, *y*, *z*; $^{\#2}$ –*x*, –*y*, –*z*.

25]. The Ru–S bonds (Ru(1)–S(1) 2.4187(1), Ru(2)–S(4) 2.4386(1) Å) are in the similar range as observed in the sulfur ruthenium complex [(*p*-cymene)$Ru_2(S_2C_2B_{10}H_9)(S_2C_2B_{10}H_{10})]_2$ [26]. Owing to the formation of the Ru–B bonds (Ru(1)–B(3) 2.106(4), Ru(2)–B(13) 2.137(4) Å), the dihedral angles at the S···S vector in the $RuS_2C_3$ rings are 99.2° (Ru(1)–C(4)–S(1)–C(1)–C(2)–S(2)) and 99.5° (Ru(2)–C(2)9–S(3)–C(26)–C(27)–S(4)), respectively. Ru(1), B(3), C(1), S(1) and C(4) are almost coplanar, which is reflected by the deviation (0.1587 Å) from the root mean square planes of the best fit, while C(3) deviates out of the ring, together with C(4), constituting a alkene double bond coordinated to the metal center. In the crystal structure, complex forms dimeric units through hydrogen bonds C–H···O weak interactions (C(22)–H(22)···O(2) 3.143 Å, angle 126.91°), the dimer units link further with each other through non-classical hydrogen bond (C(47)–H(47)···O(1) 3.099 Å, angle 118.50°) to generate a 1D chain, as shown in Fig. 2.

On the basis of these preliminary results and previous related mechanistic studies [27], we speculate that the process may involve the coordination of terminal alkyne to give a π–1-alkyne intermediate **IV**, followed the formation of intermediates **V** and **VI** [28]. Thus the metal atom becomes able to approach to the B(3)/B(13) sites of

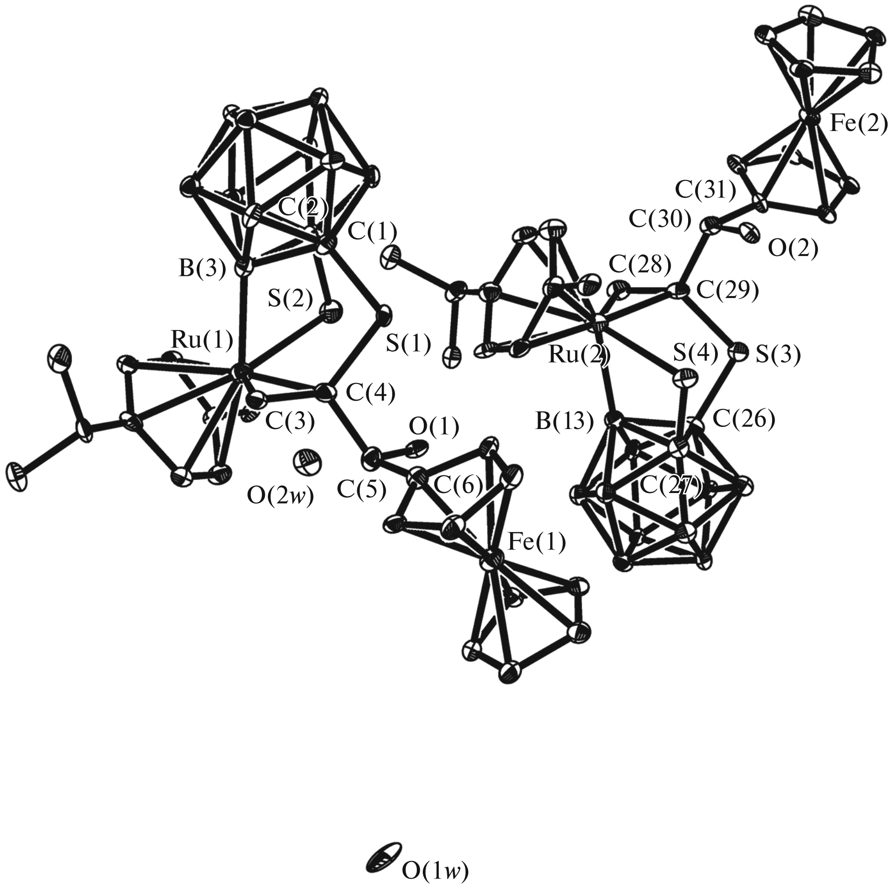

**Fig. 1.** Molecular structure of the complex **III** (hydrogen atoms are omitted for clarity).

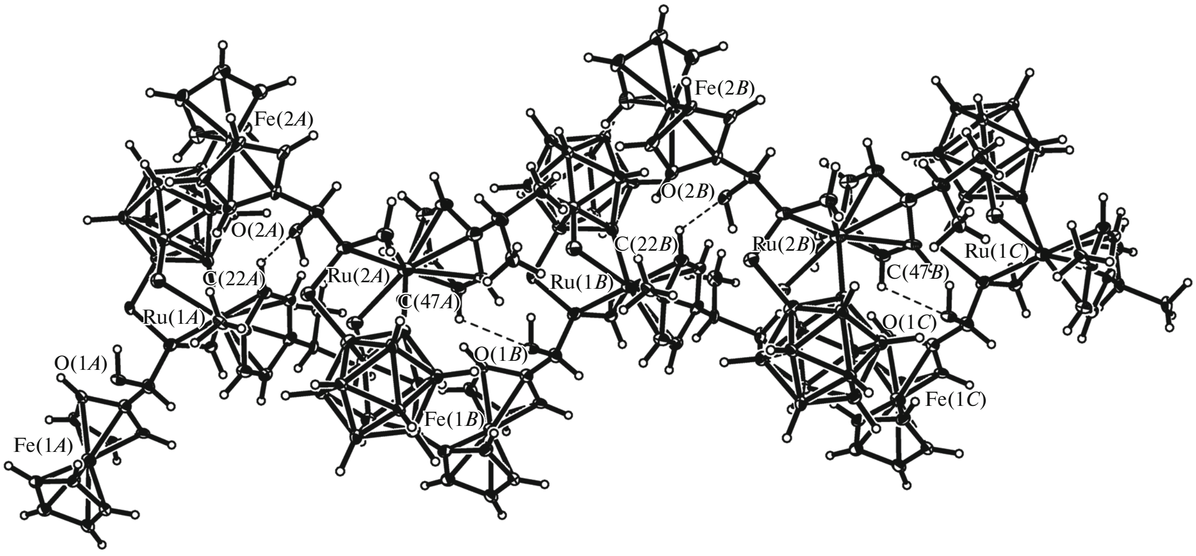

**Fig. 2.** One-dimensional chain of the complex **III**.

the carborane cage, leading to the formation of the Ru—H—B bond (**VII**), Ru—H and B—Ru bonds (**VIII**). The continued transfer of the hydrogen atom from the metal to the terminal carbon atom gives stable **III** (Scheme 2). The proposed formation mechanism for the complex **III** are given below:

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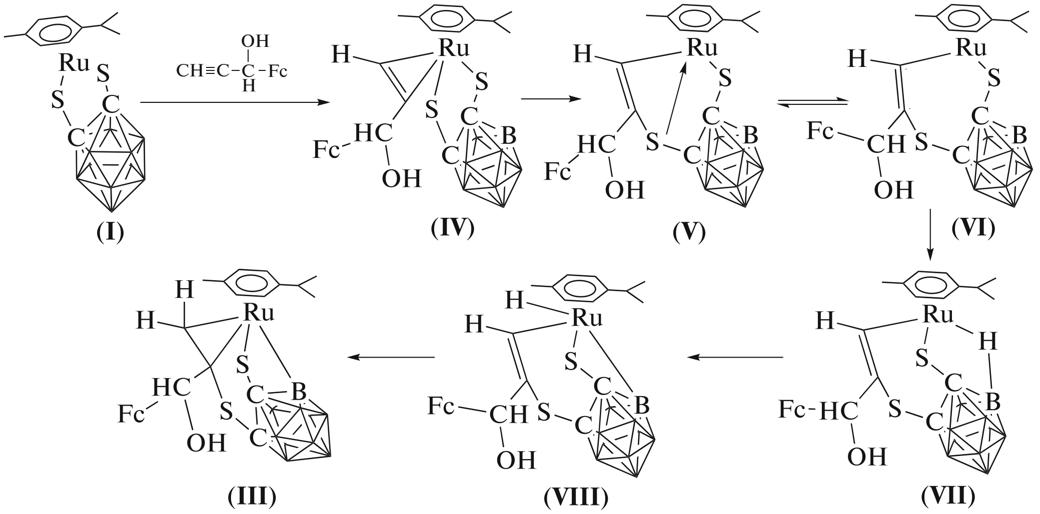

**Scheme 2.**

## ACKNOWLEDGMENTS

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