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Synthesis, Structure, and Mechanism of Half-Sandwich Ruthenium Complexes Based on *ortho*-Carborane-1,2-Dithiolate Ligand and Alkyne Alcohol[1]

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Abstract—A novel complex (p-cymene)Ru($S_2C_2B_{10}H_9$)((OH)H_2CCCHFc) · 0.5CH_2Cl_2 (Fc = ferrocenyl) based on the *ortho*-carborane-1,2-dithiolate ligand and alkyne alcohol has been synthesized successfully and characterized by IR, NMR, MS, elemental analysis and single-crystal X-ray diffraction (CIF file CCDC no. 1007680). The complex crystallizes in monoclinic system, space group $C2/c$ with $a = 27.1243(13)$, $b = 11.8161(6)$, $c = 20.8360(11)$ Å, $\beta = 108.689(3)°$, $C_{51}H_{74}B_{20}O_2S_4Cl_2Fe_2Ru_2$, $Mr = 1448.28$, $V = 6325.9(6)$ Å^3, $\rho_c = 1.521$ g/cm^3, $Z = 4$, $F(000) = 2936$, $\mu(\mathrm{Mo}K_\alpha) = 1.174$ mm^{-1}, $R = 0.0551$ and $wR = 0.1518$ for 5329 observed reflections ($I > 2\sigma(I)$). Structural analysis shows that there are metal-induced B–H activation, the generation of a Ru–B bond, and the coordination of the C=C bond.

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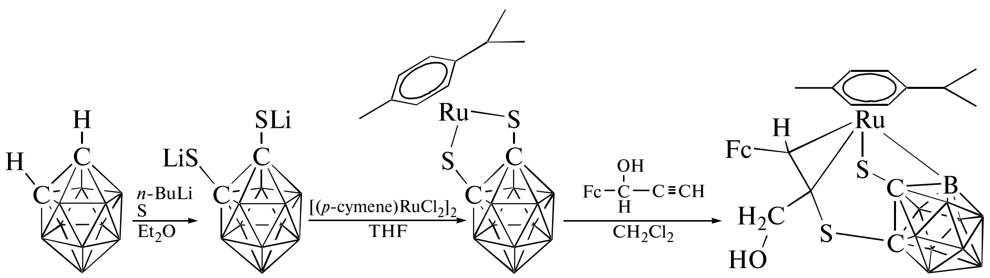
INTRODUCTION

The chemistry of transition metal containing 1,2-dicarba-*closo*-dodecaborane is attracting increasing attention both experimental and theoretical from point of view [1]. In particular, processes involving B–H bond activation are extremely useful for the synthesis of organometallic compounds owing to mild and highly efficient metal-boron bond formation [2–4]. Several approaches have been developed to construct stable 1,2-dicarba-*closo*-dodecaborane derivatives. The common strategies previously employed include polycarborane architectures containing two or more 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate units from 16e half-sandwich Cp*M($E_2C_2B_{10}H_{10}$) (Cp* = η^5-C_5Me_5, M = Co, Rh, Ir, E = S, Se) complexes [5–7], the reactions of 16e complexes containing an o-carborane-1,2-dichalcogenolate ligand with monodentate Lewis bases or alkynes [8–10]. From the preliminary studies it becomes clear that the products depend on the metal center, the chalcogen element and the used alkyne.

We are interested in using alkyne alcohols to prepare half-sandwich *ortho*-carboranedichalocogenolato metal complexes and in studying the impact of functionalized hydroxyl group on the geometric structure of the complexes. Recently, we have described the reaction system of (p-cymene)Ru(μ-E_2)Ru($S_2C_2B_{10}H_{10}$)$_2$ (E = S, Se) and commercially available (*cyclo*-C_6H_{10})(OH)C≡CH [11]. On the basis of previous studies, in this paper we explore the reactivity of the complex (p-cymene)Ru($S_2C_2B_{10}H_{10}$) toward FcCH(OH)C≡CH (see the Scheme):



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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. $[(p\text{-cymene})RuCl_2]_2$ [12] and FcCH(OH)C≡CH [13] 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 N analyses were carried out with a Vario PE-2400 II elemental analyzer. Finnigan MAT TSQ7000 was used for ESI-MS.

Synthesis of the title complex. A 2.0 M solution of *n*-BuLi (0.4 mL, 0.8 mmol) was added to a solution of *ortho*-carborane (58 mg, 0.4 mmol) in dry diethylether (20 mL). After 30 min, sulfur (25.6 mg, 0.8 mmol) was added, followed by addition of $[(p\text{-cymene})RuCl_2]_2$ (123 mg, 0.2 mmol) in dry THF (30 mL) on an ice-water bath. The resulting mixture was stirred for 4 h, and then the temperature gradually rose to ambient temperature. The solvents were evaporated under reduced pressure. FcCH(OH)C≡CH (96 mg, 0.4 mmol) was added to the reaction mixture in CH_2Cl_2 (15 mL). The mixture was stirred for 24 h at ambient temperature. The color turned gradually from blue to dark brown. After removal of the solvent, the residue was subjected to chromatography on silica gel. Elution with CH_2Cl_2–petroleum ether (2 : 1 v/v) gave pure title complex (82 mg, 30%) as orange solids. Suitable single crystal of the complex was obtained by slow diffusion of petroleum ether into its CH_2Cl_2 solution. M.p. (dec.) 176°C.

For $C_{25}H_{36}B_{10}OS_2FeRu$

anal. calcd., %:	C, 44.04;	H, 5.28.
Found, %:	C, 44.39;	H, 5.43.

ESI-MS (*m*/*z*): for $C_{25}H_{36}B_{10}OS_2FeRu$ calcd.: 681.71; found: 682.80 ($[M + H]^+$, 100%). ^1H NMR ($CDCl_3$; δ, ppm): 0.89, 0.97 (d., J = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.20 (s., 3H, C_6H_4–CH_3), 2.71 (sept. J = 7.0 Hz, 1H, $CH(CH_3)_2$), 2.82 (d., J = 10 Hz, 1H, O–CH_2), 3.76 (s., 1H, O*H*), 4.28 (d., J = 10 Hz, 1H, O–CH_2), 4.32 (s., 1H, Fc), 4.33 (s., 1H, Fc), 4.39 (s., 1H, Fc), 4.52 (s., 5H, Fc), 4.81 (s., 1H, Fc), 5.12 (s., 1H, Ru–C*H*), 5.40 (d., J = 6.0 Hz, 1H, C_6H_4), 5.48 (d., J = 6.0 Hz, 1H, C_6H_4), 6.08 (d., J = 6.0 Hz, 1H, C_6H_4), 6.20 (d., J = 6.0 Hz, 1H, C_6H_4). ^{13}C NMR ($CDCl_3$; δ, ppm): 18.4 (C_6H_4–CH_3), 21.5, 26.1 ($CH(CH_3)_2$), 31.9 ($CH(CH_3)_2$), 38.7 (Ru–CH), 60.8 ($CH_2(OH)$), 66.4, 66.5, 68.2, 68.5, 68.8, 70.1, 70.2, 72.7, 73.1, 73.2 (Fc), 88.4 (Ru–C), 94.2, 96.1, 98.6, 103.5 (*C*H in *p*-cymene), 101.8, 106.4, 108.7, 120.2 (*o*-carborane and quaternary C in *p*-cymene). $^{11}B\{^1H\}$ NMR ($CDCl_3$; δ, ppm): –0.97, –2.82, –4.50, –6.85, –9.18 (1 : 3 : 3 : 2 : 1). IR (KBr; ν, cm^{-1}): 2573 ν(B–H).

Table 1. Crystallographic data and structural refinement details of the complex

Parameter	Value
Crystal size, mm	0.26 × 0.24 × 0.20
Formula weight	1448.28
Temperature, K	291(2)
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	27.1243(13)
b, Å	11.8161(6)
c, Å	20.8360(11)
β, deg	108.689(3)
Z	8
ρ_{calcd}, g cm^{-3}	1.521
μ, mm^{-1}	1.174
$F(000)$	2936
θ Range, deg	1.59–28.30
Reflections collected	19160
Independent reflections (R_{int})	7574 (0.0210)
Reflections observed ($I > 2\sigma(I)$)	5329
Parameters	378
GOOF	1.054
R_1/wR_2 ($I > 2\sigma(I)$)	0.0551/0.1518
R_1/wR_2 (all data)	0.0624/0.1533
Largest diff. peak/hole, e Å^{-3}	0.544/–0.816

X-ray crystallography. A single crystal with dimensions of 0.26 × 0.24 × 0.20 mm was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) by using a φ–ω scan mode at 291(2) K. In the range of $1.59° \le \theta \le 28.30°$, a total of 19160 reflections were collected and 7574 were independent with R_{int} = 0.0210, of which 5329 were observed with

Table 2. Selected bond lengths (Å) and bond angles (deg) of the title complex

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Ru(1)–S(1)	2.415(1)	C(1)–C(2)	1.751(6)	S(1)–C(1)	1.788(5)
Ru(1)–B(3)	2.150(6)	C(3)–C(4)	1.514(6)	S(2)–C(2)	1.744(5)
Ru(1)–C(4)	2.153(4)	C(4)–C(5)	1.421(6)	S(2)–C(4)	1.830(4)
Ru(1)–C(5)	2.215(4)	C(5)–C(6)	1.489(6)	C(3)–O(1)	1.358(5)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
S(1)Ru(1)B(3)	70.88(2)	S(1)Ru(1)C(4)	90.90(1)	S(1)Ru(1)C(5)	83.06(1)
B(3)Ru(1)C(4)	81.55(2)	B(3)Ru(1)C(5)	113.56(2)	C(4)Ru(1)C(5)	37.93(2)

$I > 2\sigma(I)$. The correction for *Lp* factors was applied. The crystal structure was solved by direct methods using SHELXS-97 [14] and refined by full-matrix least-squares techniques on F^2 using SHELXL-97 [15]. 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.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 1007680; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The solid-state structure of complex is fully supported by the solution NMR spectroscopic data, and relevant ^{1}H, ^{11}B, and ^{13}C NMR data are listed in the experimental section. In particular, the ^{1}H NMR spectrum showed the RuCH signals at 5.12 ppm and the signals attributed to O–CH_2 at 2.82 and 4.28 ppm. In the ^{13}C NMR spectrum, the signal of CH$_2$(OH) appeared at 60.8 ppm, while the corresponding ruthenium-coordinated carbon signals are recognized at 38.7 (Ru–*C*H) and 88.4 (Ru–*C*) ppm, respectively.

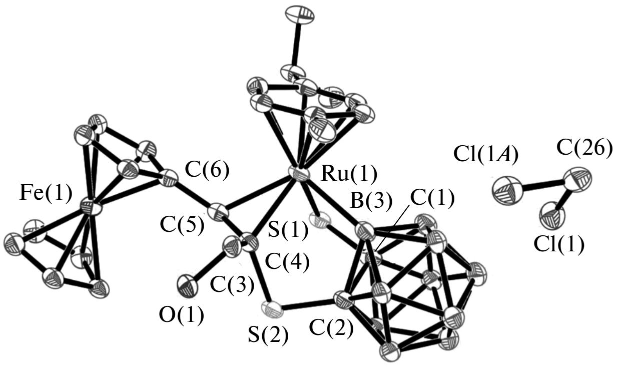

Fig. 1. Molecular structure of the title complex (hydrogen atoms are omitted for clarity).

Molecular structure of the title complex is revealed in Fig. 1. It has been observed from experimental and theoretical data that the *ortho*-carborane unit is drawn sufficiently close to the metal center to have initiated B–H activation at B(3) sites, leading to the corresponding cyclometalated species. The newly generated four-membered ring Ru(1)S(1)C(1)B(3) is nearly planar with a deviation of 0.0011 Å. An analogous example was observed in the complex (p-cymene)Ru($S_2C_2B_{10}H_9$)(H_2CCPh) [16]. In the structure, Ru(1), B(3), C(2), S(2), and C(4) are almost coplanar, which is reflected by the deviation (0.2212 Å) from the RMS planes of the best fit, while C(5) deviates out of the ring, together with C(4), constituting a alkene double bond coordinated to the metal center. The dihedral angle between the five-membered ring and the three-membered ring made up of C(4), C(5), and Ru(1) is 46.4°. And the six-membered metallacycle RuS_2C_3 is highly puckered with a dihedral angle of 100.6° (Ru(1)–C(4)–S(2)–S(1)/S(1)–C(1)–C(2)–S(2)). The C(1)–C(2) bond length (1.751(6) Å) of the carborane is similar to that observed in the ruthenium analogues [17], but longer than in other *o*-carborane derivatives of 1.62–1.70 Å [18]. The Ru–S distance of 2.415(1) Å is close to that of the (p-cymene)Ru[$S_3(C_2B_{10}H_{10})_2$] [19], which is around 2.3642(3) Å. The C(7)–O(1) distance of 1.358(5) Å is typical of a normal carbon-oxygen single bond, which can establish the existence of a hydroxyl group. Notably, the hydroxyl group of FcCH(OH)C≡CH ligand has been transferred from the γ-carbon atom to α–carbon atom to generate alkene coordination as shown by the C(4)–C(5) bond length of 1.421(6) Å, which is 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.

In the crystal structure, complex forms dimeric units through classical O–H···S weak interactions

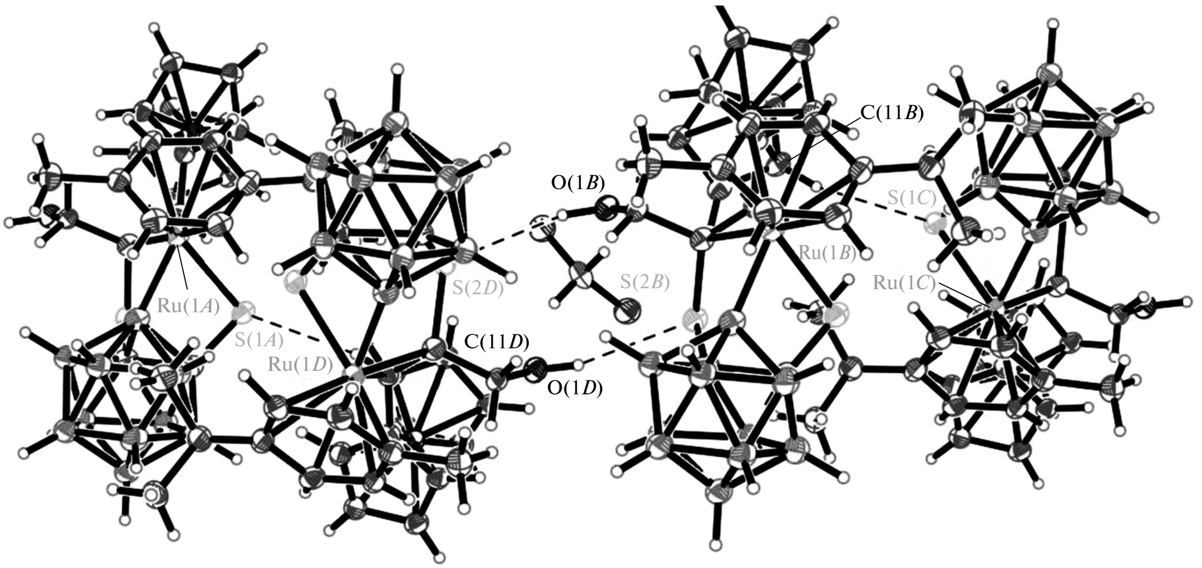

Fig. 2. One-dimensional chain of the title complex.

(O(1)–H(1*B*)···S(2)$^{\#1}$: O–H 0.96, H···S 2.73, O···S 3.665 Å, $^{\#1}$ $-x$, y, $-z + 1/2$; OHS angle 166°), the dimer units link further with each other through nonclassical hydrogen bond C···S (C(11)–H(11*A*)···S(1)$^{\#2}$: C–H 0.98, H···S 2.86, C···S 3.809 Å, $^{\#2}$ $x + 1/2$, $y + 1/2$, z; CHS angle 163°) to generate a 1D chain along the y axis, as shown in Fig. 2. There is no hydrogen bond interaction between the 1D chains, but it is the van der Waals interaction that leads to the stable three-dimensional packing.

The chemoselective formation of complex from the reaction between (*p*-cymene)Ru($S_2C_2B_{10}H_{10}$) and FcCH(OH)C≡CH is typical for the reactions of propargylic alcohols with coordinatively unsaturated transition-metal fragments. Recently, Wakatsuki [20] has reported convincing evidence that the ruthenium-catalyzed rearrangement of propargylic alcohols was expected to produce acrolein. On the basis of these preliminary results and previous related mechanistic studies, we speculate that the process may involve the coordination of terminal alkyne to give a π-1-alkyne intermediate [21], followed the elimination of water to give the allenylidene complex (*p*-cymene)Ru($S_2C_2B_{10}H_{10}$)(C=C=CHFc), and then the nucleophilic attack of H_2O at the C_α atom of the intermediate and the formation of S–C_β bond. Thus, the metal atom becomes able to approach to the B(3) sites of the carborane cage to induce B–H activation [17]. As a result, the agostic M–H–B bonding is generated that goes further to M–H and B–M bonds, and continued transfer of the hydrogen atom from the metal to the terminal carbon atom.

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