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Construction of 18-Electron Arene-Ruthenium Complexes Based on *ortho*-Carborane-1,2-Diselenolate Ligand[1]

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Abstract—Treatment of *ortho*-carborane, *n*-butyl lithium, selenium and [(*p*-cymene)$RuCl_2]_2$ under argon leads to complexes (*p*-cymene)$Ru(Se_2C_2B_{10}H_{10})$ (**I**) and (*p*-cymene)$_2Ru_2(\mu_2$-$Se_2C_2B_{10}H_{10})$ (**II**). The further reaction of 16-electron complex **I** with RC≡CCO_2Me affords addition complexes (*p*-cymene)$Ru(Se_2C_2B_{10}H_{10})$(RC=C–CO_2Me) (**III**) (R = H (**IIIa**); CO_2Me (**IIIb**)). These complexes were characterized by elemental analysis, mass, and NMR spectroscopy. X-ray structural analyses were performed on **II** and **IIIa**.

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INTRODUCTION

Metal complexes with 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligands have received considerable attentions from researchers over the last few years [1]. By complexation of these ligands to metal ions, physical and chemical properties such as solubility, thermal stability, modes of action, and biological activity in vitro could be altered significantly [2]. Recent publications from Jin [3, 4] and Herberhold's group [5, 6], have suggested that the coordinatively unsaturated Co, Rh or Ir compounds bearing $(E_2C_2B_{10}H_{10})^{2-}$ (E = S, Se) units could serve as excellent precursors to study the addition reactions at the metal atom, even to form the heterometallic clusters or discrete supramolecular assemblies.

On the other hand, the half-sandwich (η^6-arene)Ru complexes are of continuing interest because of their high tolerance toward a variety of functional groups and special reactivity [7, 8]. In our recent work, we have designed and synthesized a series of novel polycarborane architectures containing two or more 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate $(E_2C_2B_{10}H_{10})^{2-}$ (E = S, Se) units, and studied the reactivity of the 16*e* (*p*-cymene)$Ru(S_2C_2B_{10}H_{10})$ and (*p*-cymene)$Ru(\mu$-$E_2)Ru(S_2C_2B_{10}H_{10})_2$ (E = S, Se) with alkynes, which allowed us to obtain interesting organometallic ruthenium complexes including stable 18*e* complexes [9] and homometallic clusters [10, 11]. However, to the best of our knowledge, the studies of *ortho*-carborane derivatives containing (*p*-cymene)Ru and one $(Se_2C_2B_{10}H_{10})^{2-}$ unit are relatively less explored. Herein, we report an efficient one-pot synthesis of half-sandwich arene ruthenium complexes containing one $(Se_2C_2B_{10}H_{10})^{2-}$ unit and their further reactivity towards organic molecules were investigated. Synthesis of complexes **I**–**III** is given Scheme.

EXPERIMENTAL

Materials and methods. The preparative work was carried out under an argon atmosphere using standard Schlenk techniques except mentioned. 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)$RuCl_2]_2$ was prepared according to literature [12]. Elemental analysis was performed in an elementar vario EL III elemental analyzer. NMR data were obtained on a Bruker DRX-500 spectrometer. Chemical shifts were given with respect to $CHCl_3/CDCl_3$ (δ ^1H = 7.24) and external Et_2O–BF_3 (δ ^{11}B = 0). The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. Finnigan MAT TSQ7000 was used for ESI-MS.

Synthesis of complex II. To a solution of *ortho*-carborane (58 mg, 0.4 mmol) in dry diethylether (20 mL) a 2.0 M solution of *n*-BuLi (0.4 mL, 0.8 mmol) was added. After 30 min, selenium (94.8 mg, 1.2 mmol) was added, followed by addition of [(*p*-cymene)$RuCl_2]_2$ (246 mg, 0.4 mmol) in dry THF (40 mL) at 0°C. The resulting mixture was stirred for 2 h, and then the temperature gradually rose to ambient temperature. The solvents were evaporated under reduced pressure. The components of the residue were separated by column chromatography on silica gel. Elution with CH_2Cl_2–petroleum ether (1 : 2 v/v) gave pure compound as yellow solid (141 mg, 46% yield). Crystals suitable for X-ray crystallography were obtained by slow diffusion of petroleum ether into a

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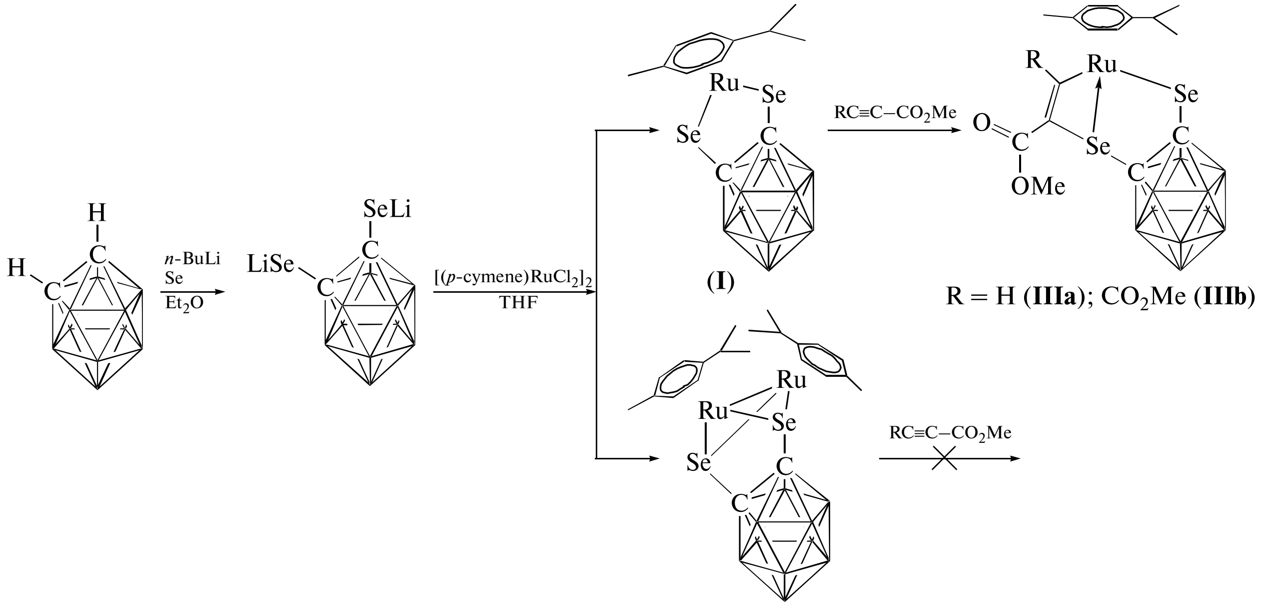

Scheme.

dichloromethane solution of the corresponding compound. M.p. (dec.) 213°C.

For $C_{22}H_{38}B_{10}Se_2Ru_2$

anal. calcd., %:	C, 34.26;	H, 4.93.
Found, %:	C, 34.75;	H, 4.48.

ESI-MS (*m/z*): calcd. for $C_{22}H_{38}B_{10}Se_2Ru_2$, 770.68; found, 771.71 ($[M + H]^+$, 80%). ^1H NMR (δ, ppm): 1.23, 1.26, 1.29, 1.30 (d., $J = 7.0$ Hz, 3H, $CH(CH_3)_2$), 2.30, 2.36 (s., 3H, CH_3), 2.83, 2.92 (sept., 1H, $\mathit{CH}(CH_3)_2$), 5.05, 5.08, 5.23, 5.31, 5.87, 5.91, 6.03, 6.16 (d., $J = 6.0$ Hz, 1H, C_6H_4). $^{11}B\{^1H\}$ NMR (δ, ppm): –2.6, –7.1, –10.8 (2 : 1 : 2). IR (ν, cm^{-1}): 2576 ν(B–H).

Synthesis of complexes IIIa and IIIb. To a solution of *ortho*-carborane (58 mg, 0.4 mmol) in dry diethylether (20 mL) a 2.0 M solution of *n*-BuLi (0.4 mL, 0.8 mmol) was added. After 30 min, selenium (94.8 mg, 1.2 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 2 h, and then the temperature gradually rose to ambient temperature. The solvents were evaporated under reduced pressure. $HC{\equiv}CCO_2Me$ (1 mmol) or $MeO_2CC{\equiv}CCO_2Me$ (1 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 (1 : 2 v/v) gave pure compound **IIIa** (62 mg, 25%) and **IIIb** (76 mg, 28%) as yellow solids. Suitable single crystal of **IIIa** was obtained by slow diffusion of petroleum ether into its CH_2Cl_2 solution.

For $C_{16}H_{28}B_{10}O_2Se_2Ru$ (**IIIa**)

anal. calcd., %:	C, 30.91;	H, 4.52.
Found, %:	C, 30.72;	H, 4.43.

ESI-MS (*m/z*): calcd. for $C_{16}H_{28}B_{10}O_2Se_2Ru$, 619.47; found, 620.50 ($[M + H]^+$, 100%). ^1H NMR (δ, ppm): 1.23, 1.38 (d., $J = 7.0$ Hz, 3H, $CH(CH_3)_2$), 2.22 (s., 3H, CH_3), 2.85 (sept., 1H, $CH(CH_3)_2$), 3.79 (s., 3H, OCH_3), 5.64, 5.76, 5.89, 6.27 (d., $J = 6.0$ Hz, 1H, C_6H_4). ^{13}C NMR (δ, ppm): 19.7 (C_6H_4–CH_3), 22.1, 23.8 ($CH(CH_3)_2$), 31.1 ($CH(CH_3)_2$), 52.6 (CH_3–O), 86.1, 86.8, 88.1, 88.9 (CH in *p*-cymene), 64.6, 66.3, 106.1, 108.3 (*o*-carborane and quaternary C in *p*-cymene), 122.8 (C=CSe), 169.3 (C=O), 187.8 (RuC=C). $^{11}B\{^1H\}$ NMR (δ, ppm): –2.8, –5.2, –6.7, –10.8 (2 : 3 : 2 : 3). IR (ν, cm^{-1}): 2583 ν(B–H).

For $C_{18}H_{30}B_{10}O_4Se_2Ru$ (**IIIb**)

anal. calcd., %:	C, 31.88;	H, 4.43.
Found, %:	C, 31.31;	H, 4.21.

ESI-MS (*m/z*): calcd. for $C_{18}H_{30}B_{10}O_4Se_2Ru$, 677.54; found, 678.58 ($[M + H]^+$, 100%). ^1H NMR (δ, ppm): 1.13, 1.26 (d., $J = 7.0$ Hz, 3H, $CH(CH_3)_2$), 2.21 (s., 3H, C_6H_4–CH_3), 2.87 (sept., 1H, $CH(CH_3)_2$), 3.71 (s., 3H, OCH_3), 3.82 (s., 3H, OCH_3), 5.38, 5.41, 5.43, 5.48 (d., $J = 6.0$ Hz, 1H, C_6H_4). ^{13}C NMR (δ, ppm): 19.3 (C_6H_4–CH_3), 22.2, 23.6 ($CH(CH_3)_2$), 31.6 ($CH(CH_3)_2$), 52.1, 52.6 (CH_3–O), 87.2, 87.9, 89.1,

Table 1. Crystallographic data and structural refinement details of complexes **II** and **IIIa**

Parameter	Value	
	II	**IIIa**
Crystal size, mm	0.13 × 0.11 × 0.10	0.30 × 0.22 × 0.18
Formula weight	770.68	619.47
Temperature, K	291(2)	291(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a, Å	12.0619(6)	14.3288(17)
b, Å	14.7176(7)	10.4610(13)
c, Å	16.8633(8)	16.249(2)
β, deg	90	92.297(2)
V, Å^3	2993.6(3)	2433.6(5)
Z	4	4
ρ_{calcd}, g m^{-3}	1.710	1.691
μ, mm^{-1}	3.453	3.648
F(000)	1504	1208
θ Range, deg	1.84–26.00	1.93–26.00
Reflections collected	16603 (0.0414)	12798 (0.0845)
Independent reflections (R_{int})	5875	4775
Reflections observed ($I > 2\sigma(I)$)	5138	2857
Data/restraints/parameters	5875/0/325	4775/0/280
GOOF	0.965	1.004
R_1, wR_2 ($I > 2\sigma(I)$)	0.0240/0.0410	0.0422/0.0803
R_1, wR_2 (all data)	0.0291/0.0417	0.0850/0.0857
Largest difference peak/hole, e Å^{-3}	0.391/–0.343	0.698/–0.889

89.8 (CH in *p*-cymene), 65.3, 67.1, 106.9, 108.8 (*o*-carborane and quaternary C in *p*-cymene), 123.9 (C=CSe), 158.3, 173.1 (C=O), 188.7 (RuC=C). ^{11}B{^{1}H} NMR (δ, ppm): –1.3, –5.6, –7.7, –11.3 (2 : 3 : 2 : 3). IR (ν, cm^{-1}): 2581 ν(B–H).

X-ray crystallographic studies. Suitable single crystals of **II** and **IIIa** were selected and mounted in air onto thin glass fibers. X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer at 291(2) K using MoK_α radiation (λ = 0.71073 Å) by multi-scan mode. The SAINT program was used for integration of the diffraction profiles. The structures were solved by direct methods using the SHELXS-97 [13] program package and refined against F^2 by full-matrix least-squares with SHELXL-97 [14]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on carbon were set in calculated positions and refined as riding. The crystallographic data are summarized in Table 1 and selected bond lengths and angles are listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 921955 (**II**) and 795093 (**IIIa**); deposit@ ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk).

RESULTS AND DISCUSSION

The spectroscopic data and solid-state structure of **I** have never been reported to date due to its unstable and air-sensitive. To further study the formation and reactivity of **I**, the crude product was directly used in the next step without further purification. Stable insertion product **IIIa** could be isolated in moderate yield when a solution of the crude product in CH_2Cl_2 was treated with $HC\equiv CCO_2Me$ at room temperature [15]. In order to show the influence of the nature of the group R of the alkyne in these type of reactions, we now set out to investigate the reactivity of the complex **I** toward $MeO_2CC\equiv CCO_2Me$. As expected, we have successfully isolated and characterized interesting stable product of alkyne addition **IIIb**. It is worthing note that the reaction of [(*p*-cymene)$RuCl_2]_2$ and 1 equiv $[(Se_2C_2B_{10}H_{10})^{2-}]$ led to formation of the unprecedented dinuclear complex **II**. Owing to the formation of the Ru–Ru bond, electronically satu-

Table 2. Selected bond lengths (Å) and bond angles (deg) for **II** and **IIIa**

Bond	d, Å	Angle	ω, deg
		II	
Ru(1)–Se(1)	2.4423(5)	Se(1)Ru(1)Se(2)	81.229(2)
Ru(2)–Se(2)	2.4401(5)	Se(1)Ru(2)Ru(1)	56.407(1)
Se(2)–C(2)	2.006(4)	Se(1)Ru(2)Se(2)	81.059(2)
Ru(1)–Se(2)	2.4520(5)	Se(2)Ru(1)Ru(2)	56.458(1)
C(1)–C(2)	1.606(5)	Se(1)Ru(1)Ru(2)	57.134(1)
Ru(1)–Ru(2)	2.6880(5)	Se(2)Ru(2)Ru(1)	56.884(1)
Ru(2)–Se(1)	2.4627(5)	Ru(1)Se(1)C(1)	103.30(1)
Se(1)–C(1)	2.015(4)	Ru(2)Se(2)C(2)	102.67(1)
		IIIa	
Ru(1)–Se(1)	2.4825(8)	Se(1)Ru(1)Se(2)	89.26(2)
Ru(1)–Se(2)	2.4943(7)	Se(1)Ru(1)C(3)	68.58(2)
Se(1)–C(1)	1.966(5)	Se(2)Ru(1)C(3)	87.33(2)
Se(2)–C(2)	1.952(5)	Ru(1)C(3)C(4)	110.8(4)
C(1)–C(2)	1.634(7)	C(3)C(4)Se(1)	102.9(4)
Ru(1)–C(3)	2.026(5)	C(5)C(4)Se(1)	125.9(4)
C(3)–C(4)	1.332(7)	Ru(1)Se(1)C(1)	105.67(2)
Se(1)–C(4)	1.917(5)	Ru(1)Se(2)C(2)	103.98(2)

rated (18e) complex **II** showed higher stability than **I** and did not react with RC≡CCO_2Me.

Molecular structure of complex **II** is revealed in Fig. 1a. The complex shows a binuclear structure containing one disubstituted *ortho*-carborane unit $[Se_2C_2B_{10}H_{10}]^{2-}$, and the bridging Se atoms are present instead of the bridging Cl atoms in the starting material $[(p\text{-cymene})RuCl_2]_2$. Each ruthenium is coordinated by one *p*-cymene ligand, single bonded to the other ruthenium atom, and bridged by two μ_2-Se atoms from the diselenolate carborane moiety. Both of the Ru(II) centers take three-legged piano-stool arrangements with a 18-electron configuration. Analogous examples with such a cluster were observed in the Se-bridged dinuclear complex $[(Cp^*Ir)_2(\mu_2\text{-}Se_2C_2B_{10}H_{10})]$ [$Cp^* = \eta^5\text{-}C_5Me_5$] [16]. The Ru–Se bond lengths, varies from 2.4401(5) to 2.4627(5) Å, are comparable to those in $[(p\text{-cymene})Ru(Se_2C_2B_{10}H_9)Ru(Se_2C_2B_{10}H_{10})]_2$ (2.4307(6) to 2.5375(6) Å) [17]. The Ru–Ru distance of 2.6880(5) Å fall in the normal single Ru–Ru bond range, but shorter than that of the $Cp^*_2Ru_2(\mu\text{-Se})(\mu\text{-}Se_2C_2B_{10}H_{10})$ [18], which is around 2.7177(9) Å. The Ru_2Se_2 ring is highly puckered, the dihedral angle between the planes Ru(1)Ru(2)Se(1) and Ru(1)Ru(2)Se(2) is 77.8°. The planar pseudo-aromatic system of the metalladithiolene heterocycle is no longer present in mononuclear 16e half-sandwich compounds $(p\text{-cymene})Ru_2(E_2C_2B_{10}H_{10})$ (E = S, Se), each $RuSe_2C_2$ ring is folded, for example, the dihedral angles at the Se···Se vector in the $RuSe_2C_2$ rings are 45.6° (Ru(1)–Se(1)–C(1)–C(2)–Se(2)) and 133.1° (Ru(2)–Se(1)–C(1)–C(2)–Se(2)), respectively.

Molecular structure of complex **IIIa** is revealed in Fig. 1b. The structure of **IIIa** indicates that an addition of **I** to one of the Ru–Se bonds has taken place to give a four-membered ring containing a C=C bond, a Ru–C σ bond, and a coordinative Se → Ru bond. Complex **IIIa** showed better solubility and higher stability than **I** and could be structurally characterized. The central Ru atom has retained the *p*-cymene rings and taked three-legged piano-stool arrangements with a 18-electron configuration. The coordinative Se(1) → Ru(1) bond (2.4825(8) Å) is slightly shorter (0.0118 Å) than the covalent Se(2)–Ru(1) bond (2.4943(7) Å). The C(3)–C(4) bond length of 1.332(7) Å, indicates a C=C double bond, which are very close to that in the analogous complex [19]. In **IIIa**, the newly generated four-membered ring Ru1C(3)C(4)Se(1) is nearly planar with a deviation of 0.0183 Å. And the five-membered rings $RuSe_2C_2$ are not planar with the dihedral angles 160.7° along Se(1)···Se(2). It is worth noting that the complex forms the dimeric unit through non-classical C–H···O and C–H···Se weak interactions (C(11)–H(11)···O(1) 3.154 Å, 121.5°; C(12)–H(12)···O(1) 3.153 Å, 123.6°; C(3)–H(3)···Se(2) 3.880 Å, 162.6°) (Fig. 2). There is no hydrogen bond interaction between the dimeric units, but it is the van der Waals interaction that leads to the stable three-dimensional packing.

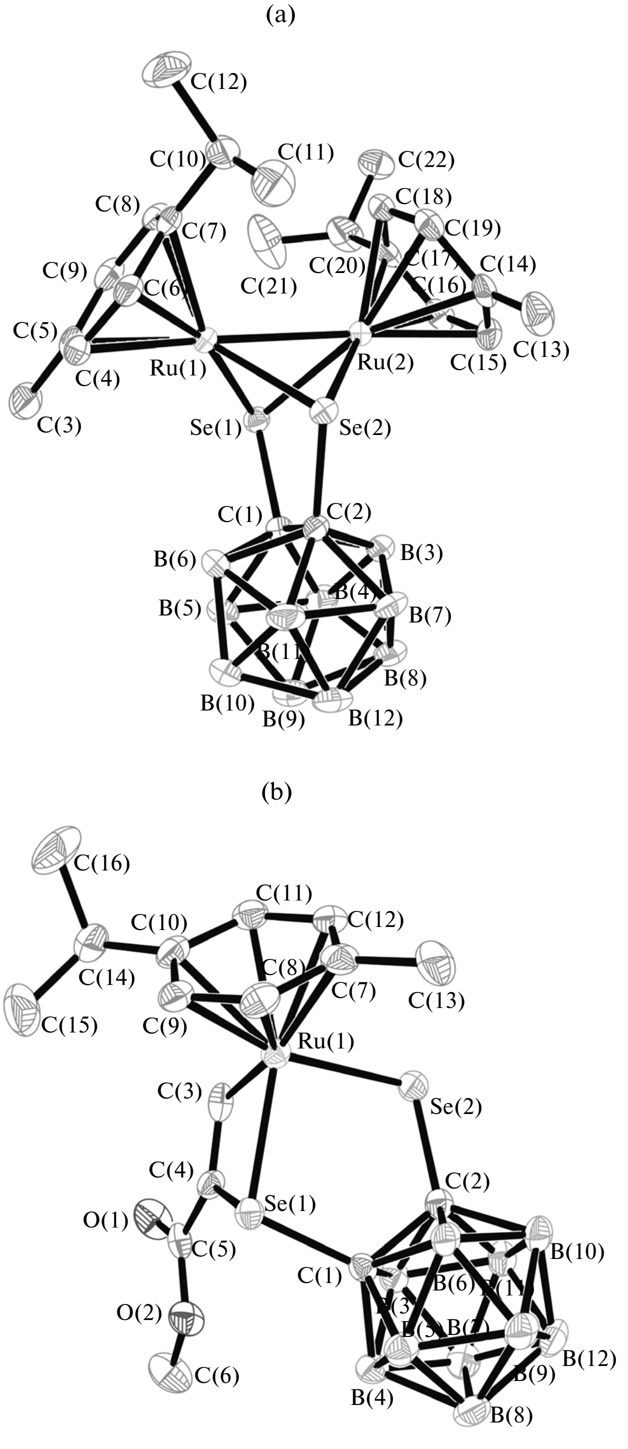

Fig. 1. Molecular structures of **II** and **IIIa**.

The molecular structures of **IIIb** has not been characterized by X-ray diffraction owing to lack of good quality single crystals. However, the solid-state structure of **IIIb** could be suggested as shown in Scheme by spectroscopic data. The chemical shifts of the two olefinic carbon atoms are similar in both **IIIa** and **IIIb**. The ^{13}C NMR spectrum showed additional signals for olefinic carbons at $\delta = 122.8$ ppm (C=CSe), 187.8 ppm (RuC=C) ppm in **IIIa**, and 123.9 ppm (C=CSe), 188.7 ppm (RuC=C) ppm in **IIIb** which were assigned to the new generated four-membered rings (RuSeC$_2$).

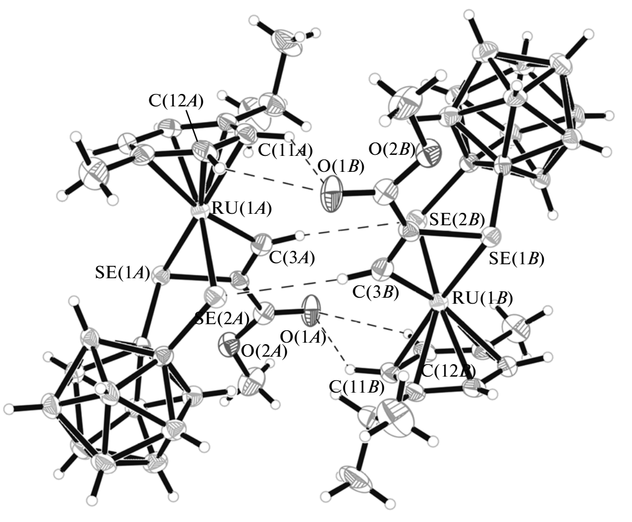

Fig. 2. The dimeric unit of complex **IIIa**.

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