Diruthenium Half-Sandwich Complexes Containing One μ-E_2 (E = S, Se) Unit and Two Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dithiolate Ligands: Reactivity Studies with Methyl Acetylene Carboxylates

De-Hong Wu, Bao-Hua Xu, Yi-Zhi Li, and Hong Yan*

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering,
The Joint Laboratory of Metal Chemistry, Nanjing University-Jin Chuan Group Ltd., Nanjing University,
Nanjing 210093, China

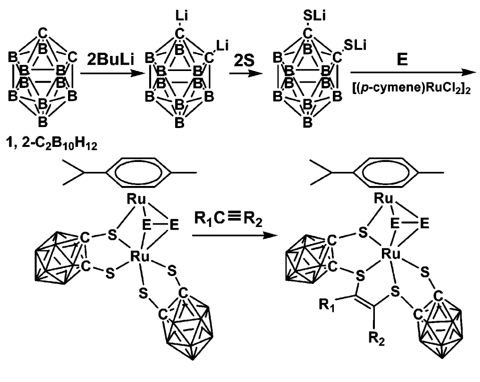
Received August 27, 2007

[(*p*-Cymene)$RuCl_2$]$_2$ reacts with $Li_2[S_2C_2(B_{10}H_{10})]$ in the presence of excess chalcogen elements to generate dinuclear complexes (*p*-cymene)Ru(μ-E_2)Ru($S_2C_2B_{10}H_{10}$)$_2$, **1S** (E = S) and **1Se** (E = Se), in which one E−E bridge between the two ruthenium atoms and two chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligands are present. In **1S** and **1Se**, one ruthenium atom is surrounded by six chalcogen atoms in a geometry of distorted octahedron and electron-deficient (16e). Treatment of **1S** and **1Se** with methyl acetylene carboxylates affords addition complexes, (*p*-cymene)Ru(μ-E_2)Ru($S_2C_2B_{10}H_{10}$)$_2$($R_1C{=}CR_2$) (R_1 = H (CO_2Me), R_2 = CO_2Me (H), **2S**, **2Se** (**3S**, **3Se**); R_1 = R_2 = CO_2Me, **4S**, **4Se**). The terminal alkyne leads to two geometrical isomers that interconvert upon heating. Alkyne addition occurs at sulfur atoms of two different dithiolate ligands that leads to a change of 16e Ru(IV) in **1S** and **1Se** to 18e Ru(II) in **2S**−**4S** and **2Se**−**4Se**, respectively. The complexes were characterized by IR, MS, NMR spectroscopy, and microanalysis. X-ray structural analyses were performed on **1S**−**4S** and **2Se**−**4Se**.

Introduction

During the past decade, research focusing on 1,2-dicarba-*closo*-dodecaborane derivatives has attracted enormous attention due to their unique molecular structures, fundamental properties, and a variety of potential applications in material synthesis, microelectronics, optics, and medicines.[1] In the organometallic field, mononuclear 16e half-sandwich complexes of Co, Rh, Ir, Ru, and Os that contain a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand, $[E_2C_2(B_{10}H_{10})]^{2-}$ (E = S, Se), have been described.[2−5] These sterically congested, mononuclear coordination compounds are stable starting materials and exhibit rich chemistries.[6] For example, these complexes undergo insertion of alkynes to metal−chalcogen bonds leading to B−H bond activation, formation of metal−boron bonding, and functionalization of a carborane cage in positions B(3)/B(6).[5] Moreover, construction of novel poly carborane molecular architectures using two or more $[S_2C_2(B_{10}H_{10})]^{2-}$ units has been reported.[7] One metalation product, [1-(σ-S)-2-(η^5-$C_5H_4CH(Ph)$)-1,2-$C_2B_{10}H_{10}$)]Ti(NMe_2)$_2$, was also synthesized where the appended carboranyl-thiol unit acted as both a linking and a

Scheme 1



1S (E = S)
1Se (E = Se)

2S - 4S (E = S)
2Se - 4Se (E = Se)

E = S	2S	3S	4S
R_1 =	H	CO_2Me	CO_2Me
R_2 =	CO_2Me	H	CO_2Me

E = Se	2Se	3Se	4Se
R_1 =	H	CO_2Me	CO_2Me
R_2 =	CO_2Me	H	CO_2Me

---

* To whom correspondence should be addressed. Fax: (+86)-25-83314502. E-mail: hyan1965@nju.edu.cn.

[1] (a) Plesek, J. *Chem. Rev.* **1992**, *92*, 269. (b) Larsen, A. S.; Holbrey, J. D.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2000**, *122*, 7264. (c) Jin, G.-X. *Coord. Chem. Rev.* **2004**, *248*, 587. (d) Moxham, G. L.; Douglas, T. M.; Brayshaw, S. K.; Kociok-Köhn, G.; Lowe, J. P.; Weller, A. S. *J. Chem. Soc., Dalton Trans.* **2006**, 5492. (e) Grimes, R. N. *Appl. Organomet. Chem.* **1996**, *10*, 209. (f) Crabtree, R. H.; Mingos, D. M. P. *Comprehensive Organometallic Chemistry III*; Elsevier: Oxford, U.K., 2006; Vol. 3, Chapter 3.05, pp 175−264 and references therein.

[2] (a) Herberhold, M.; Jin, G.-X.; Yan, H.; Milius, W.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **1999**, 873; (b) *J. Organomet. Chem.* **1999**, *587*, 252.

[3] Liu, S.; Wang, X.; Jin, G.-X. *J. Organomet. Chem.* **2006**, *691*, 261.

[4] Bae, J.-Y.; Lee, Y.-J.; Kim, S.-J.; Ko, J.; Cho, S.; Kang, S.-O. *Organometallics* **2000**, *19*, 1514.

[5] (a) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Angew. Chem., Int. Ed.* **1999**, *38*, 3689; (b) *J. Organomet. Chem.* **2000**, *598*, 142; (c) *Chem.-Eur. J.* **2002**, *8*, 388; (d) *Chem.-Eur. J.* **2000**, *6*, 3026; (e) *Z. Anorg. Allg. Chem.* **2000**, *626*, 1627; (f) *J. Organomet. Chem.* **2000**, *604*, 170.

[6] Jin, G.-X.; Wang, J.-Q.; Zhang, C.; Weng, L.-H.; Herberhold, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 259.

[7] (a) Wu, D.-H.; Ji, C.; Li, Y.-Z.; Yan, H. *Organometallics* **2007**, *26*, 1560. (b) Wang, J.-Q.; Ren, C.-X.; Jin, G.-X. *Chem. Commun.* **2005**, 4738. (c) Wang, J.-Q.; Ren, C.-X.; Weng, L.-H.; Jin, G.-X. *Chem. Commun.* **2006**, 162. (d) Wedge, T. J.; Hawthorne, M. F. *Coord. Chem. Rev.* **2003**, *240*, 111.

10.1021/om7008556 CCC: $37.00 © 2007 American Chemical Society
Publication on Web 11/07/2007

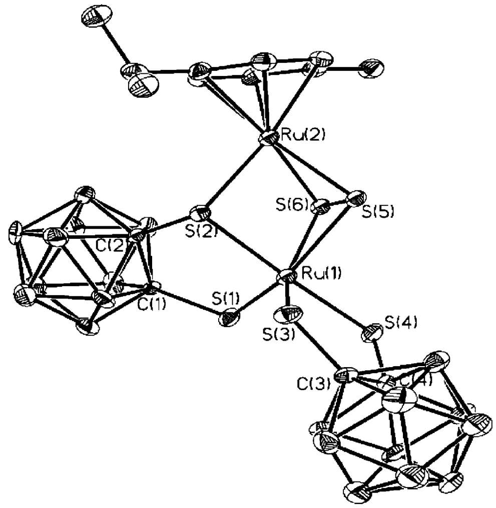


Figure 1. Molecular structure of **1S** (30% probability displacement ellipsoids). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.1997(15), Ru(1)−S(2) = 2.3846(12), Ru(1)−S(3) = 2.1919(14), Ru(1)−S(4) = 2.3769(13), Ru(1)−S(5) = 2.3819(13), Ru(1)−S(6) = 2.4085(12), S(5)−S(6) = 2.0358(17), C(1)−S(1) = 1.804(4), C(2)−S(2) = 1.826(5), C(3)−S(3) = 1.786(5), C(4)−S(4) = 1.787(5), C(1)−C(2) 1.661(6), C(3)−C(4) 1.647(7), Ru(1)···Ru(2) = 3.414; S(1)−Ru(1)−S(3) = 117.30(6), S(1)−Ru(1)−S(4) = 85.22(5), S(5)−Ru(1)−S(6) = 50.29(4).

η^1-bonding group.[8] A novel mixed-valence dinuclear ruthenium complex containing two $[S_2C_2(B_{10}H_{10})]^{2-}$ units and one S−S bridging ligand was communicated by our group.[7a] The Ru(IV) is coordinatively saturated by six sulfur atoms, but electron-deficient (16e). However, it could be converted into an electron-saturated (18e) complex through a reaction with alkyne. As a continuation of this chemistry, we have successfully obtained analogous Se−Se-bridged complex (p-cymene)Ru(μ-Se_2)Ru($S_2C_2B_{10}H_{10}$)$_2$. In the present Article, their structures and reaction chemistries with alkynes are reported in detail.

Results and Discussion

Synthesis of (p-Cymene)Ru(μ-E_2)Ru($S_2C_2B_{10}H_{10}$)$_2$, 1S (E = S) and 1Se (E = Se). The complexes **1S** and **1Se** were obtained by treating $Li_2[S_2C_2(B_{10}H_{10})]$ with $[(p\text{-cymene})RuCl_2]_2$ in the presence of excess sulfur or selenium at ambient temperature (Scheme 1). The solid-state structure of **1S** (Figure 1) shows that a bridging S−S bond is present instead of the two bridging Cl atoms in the starting material $[(p\text{-cymene})RuCl_2]_2$. The p-cymene fragment at Ru(1) is replaced by sulfur atoms of two $[S_2C_2(B_{10}H_{10})]^{2-}$ units that donate five electrons. As a result, Ru(1) is bonded to six sulfur atoms in an arrangement of a distorted octahedron.

Reported in the literature[9] were only two examples with a RuS_6 core, which contain 1,2-dicyanoethylenedithiolate and 2-aminoethanethiolate, respectively. In **1S**, Ru(2) is in a three-legged piano-stool arrangement with the ruthenium atom bonded to the p-cymene ring in an η^6 mode and one S atom stemmed from a $[S_2C_2(B_{10}H_{10})]^{2-}$ ligand. The two S atoms from the bridging μ-S_2^{2-} ligand are shared by two Ru atoms. Ru(1), S(2), S(5), S(6), and Ru(2) form a distorted-bipyramidal geometry with S(5)−S(6) bond length of 2.036 Å. The angles of S(1)−Ru(1)−S(3) and S(1)−Ru(1)−S(4) are 117.3° and 85.2°, respectively. Obviously, the former deviates largely from 90°, thus introducing considerable strain to the structure. Note that Ru(1) is electronically unsaturated (16e) with a charge of +4 and Ru(2) is electronically saturated (18e) with a charge of +2 in **1S**, in contrast to Ru(II)/Ru(II) (18e/18e) in the starting material $[(p\text{-cymene})RuCl_2]_2$. The 16e Ru(IV) center and the large angle of S(1)−Ru(1)−S(3) determine its reactivity and reactive sites. The spectroscopic data (for instance, NMR, MS) of **1S** are consistent with its solid-state structure.

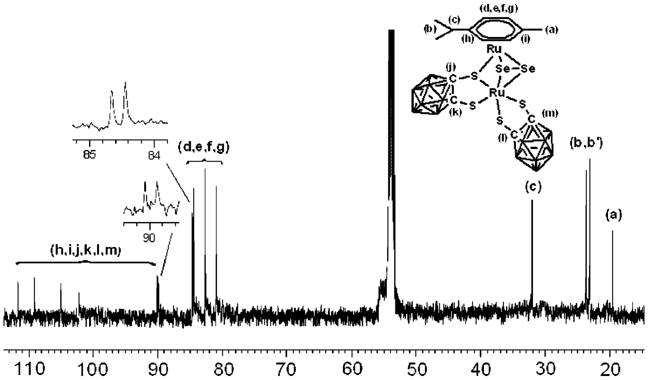


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of **1Se** in CD_2Cl_2 at ambient temperature. All 14 ^{13}C resonances are visible.

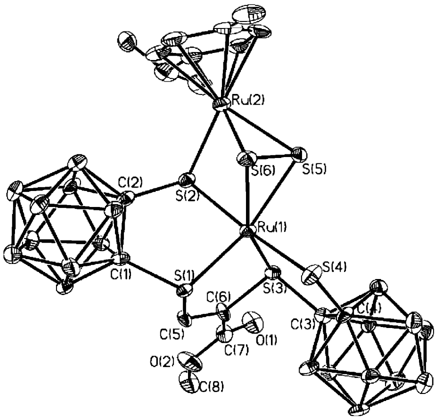


Figure 3. Molecular structure of **2S** (30% probability displacement ellipsoids). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.2519(16), Ru(1)−S(2) = 2.3920(16), Ru(1)−S(3) = 2.2612(15), Ru(1)−S(4) = 2.3651(17), Ru(1)−S(5) = 2.3870(16), Ru(1)−S(6) = 2.4211(15), S(5)−S(6) = 2.043(2), C(5)−S(1) = 1.802(6), C(6)−S(3) = 1.772(6), C(1)−C(2) 1.681(9), C(3)−C(4) 1.655(8), C(5)−C(6) = 1.312(9), Ru(1)···Ru(2) = 3.422; S(1)−Ru(1)−S(3) = 86.87(5), S(1)−Ru(1)−S(4) = 93.56(6), S(5)−Ru(1)−S(6) = 50.29(6).

All attempts to grow single crystals of **1Se** were unsuccessful. Its solubility in $CDCl_3$ is low, but better solubility in CD_2Cl_2 is obtained and all 14 ^{13}C NMR signals are shown in Figure 2. The ESI-MS spectrum displays the most intense peak at m/z 908.03, corresponding to $[M + H]^+$. The IR spectrum in solid state exhibits an intense B−H stretching of carborane cages at 2582(vs) cm^{-1}. Therefore, the spectroscopic data of **1Se** support an analogous structure of **1S**.

Reaction of 1S with Methyl Acetylene Monocarboxylate. The reaction of **1S** with $HC{\equiv}CCO_2Me$ affords **2S** and **3S** in a ratio of approximately 1:1 (Scheme 1). The solid-state structure analyses confirm two regioisomers formed from the nonselective addition of the alkyne. In **2S** and **3S** (Figures 3 and 4), the alkyne addition selectively takes place at S(1) and S(3) sites from two

---

(8) Wang, J.-H.; Zheng, C.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **2003**, *22*, 4839.

(9) (a) Maiti, R.; Shang, M.; Lappin, G. *Dalton Trans.* **2002**, 244. (b) Matsuura, N.; Kamiyama, A. I.; Kawamoto, T.; Konno, T. *Inorg. Chem.* **2006**, *45*, 401.

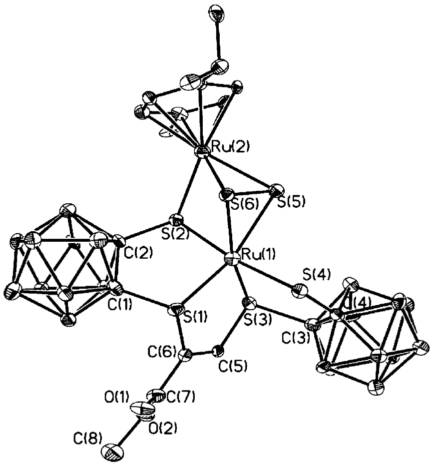


Figure 4. Molecular structure of **3S** (30% probability displacement ellipsoids). The hydrogen atoms and H_2O molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.2582(16), Ru(1)−S(2) = 2.3643(15), Ru(1)−S(3) = 2.2548(15), Ru(1)−S(4) = 2.3879(16), Ru(1)−S(5) = 2.3819(16), Ru(1)−S(6) = 2.4060(15), S(5)−S(6) = 2.041(2), C(6)−S(1) = 1.794(6), C(5)−S(3) = 1.766(6), C(1)−C(2) 1.668(8), C(3)−C(4) 1.584(9), C(5)−C(6) = 1.364(9), Ru(1)···Ru(2) = 3.397; S(1)−Ru(1)−S(3) = 87.88(6), S(1)−Ru(1)−S(4) = 92.85(5), S(5)−Ru(1)−S(6) = 50.28(5).

individual $[S_2C_2(B_{10}H_{10})]^{2-}$ ligands and generates a nearly planar five-membered RuSCCS ring with mean deviation from the plane of 0.1084 Å (**2S**) and 0.0451 Å (**3S**), respectively. The terminal carbon atom of the alkyne is bonded to S(1) in **2S**, whereas it is S(3) in **3S**. As a result, the angle of S(1)−Ru(1)−S(3) changes from 117.3° in **1S** to 86.9° in **2S** and to 87.9° in **3S**, respectively, thus reducing the strain that is present in **1S**. As compared to the angle of S(1)−Ru(1)−S(4) (85.2°) in **1S**, S(1)−Ru(1)−S(4) is slightly changed to 93.6° in **2S** and to 92.9° in **3S**, respectively. In **1S**, the Ru(1)−S(1) (2.200 Å) and Ru(1)−S(3) (2.192 Å) bonds are covalent, but changed to coordinative bonds in the adducts (e.g., 2.252 and 2.261 Å in **2S**, 2.258 and 2.255 Å in **3S**, respectively). Accordingly, the mixed-valence Ru(II)/Ru(IV) (18e/16e) in **1S** are changed to the two Ru(II)/Ru(II) (18e/18e) centers in **2S** and **3S**.

In **2S** and **3S**, the olefinic proton appears at 8.21 and 8.29 ppm, respectively. The carbon signals shown at 142.64 (*C*=CH), 149.14 ppm (C=*C*H) in **2S**, and 144.32 (*C*=CH), 150.73 ppm (C=*C*H) in **3S**, are typical of a C=C bond type, in agreement with the C(5)−C(6) bond distance (1.312 Å in **2S** and 1.364 Å in **3S**). The MALDI-TOF MS spectrum shows intense [M + H^+] peaks for both **2S** and **3S**. Thus, the spectroscopic data of **2S**, **3S** are consistent with their solid-state structures.

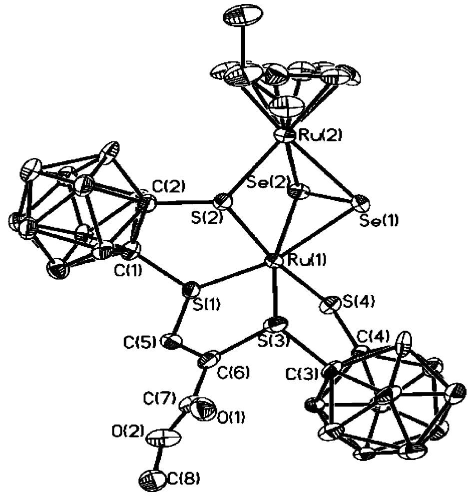


Figure 5. Molecular structure of **2Se** (30% probability displacement ellipsoids). The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.2446(18), Ru(1)−S(2) = 2.3903(18), Ru(1)−S(3) = 2.2715(19), Ru(1)−S(4) = 2.3744(19), Ru(1)−Se(1) = 2.5292(9), Ru(1)−Se(2) = 2.4977(10), Se(1)−Se(2) = 2.3383(12), C(5)−S(1) = 1.785(7), C(6)−S(3) = 1.786(8), C(1)−C(2) 1.668(10), C(3)−C(4) 1.679(10), C(5)−C(6) = 1.346(10), Ru(1)···Ru(2) = 3.500; S(1)−Ru(1)−S(3) = 88.47(7), S(1)−Ru(1)−S(4) = 92.89(7), Se(1)−Ru(1)−Se(2) = 55.43(3).

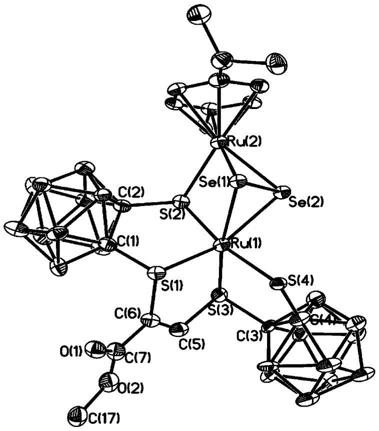


Figure 6. Molecular structure of **3Se** (30% probability displacement ellipsoids). The hydrogen atoms and H_2O molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.2942(13), Ru(1)−S(2) = 2.3490(12), Ru(1)−S(3) = 2.2636(13), Ru(1)−S(4) = 2.3907(12), Ru(1)−Se(1) = 2.5072(6), Ru(1)−Se(2) = 2.5507(8), Se(1)−Se(2) = 2.3386(7), C(5)−S(3) = 1.773(6), C(6)−S(1) = 1.817(5), C(1)−C(2) 1.674(7), C(3)−C(4) 1.696(7), C(5)−C(6) = 1.308(8), Ru(1)···Ru(2) = 3.498; S(1)−Ru(1)−S(3) = 87.87(5), S(1)−Ru(1)−S(4) = 95.66(5), Se(1)−Ru(1)−Se(2) = 55.070(16).

Reaction of 1Se with Methyl Acetylene Monocarboxylate. The treatment of complex **1Se** with $HC\equiv CCO_2Me$ generates **2Se** and **3Se** in about 1:1 ratio (Scheme 1); both solid-state structure analyses and spectroscopic data reveal the presence of two isomers due to alkyne addition. In **2Se** (Figure 5) and **3Se** (Figure 6), the alkyne addition selectively occurs at S(1) and S(3) sites to produce a nearly planar five-membered RuSCCS ring with mean deviation from the plane of 0.0309 Å (**2Se**) and 0.0574 Å (**3Se**), respectively. Similar to **2S** and **3S**, the terminal carbon atom of the alkyne is bonded to S(1) in **2Se**, whereas it is S(3) in **3Se**. The angles of S(1)−Ru(1)−S(3) are 88.5° in **2Se** and 87.9° in **3Se**, respectively, as compared to 86.9° in **2S** and 87.9° in **3S**. The bond length of C(5)−C(6) (1.346 Å in **2Se** and 1.308 Å in **3Se**) is a typical C=C double bond. The covalent bonds Ru(1)−S(1) and Ru(1)−S(3) in **1Se** are converted to coordinative bonds S(1) → Ru(1) and S(3) → Ru(1), accompanied by two saturated Ru(II)/Ru(II) (18e/18e) centers in **2Se** and **3Se** corresponding to the mixed-valence Ru(II)/Ru(IV) (18e/16e) in **1Se**.

The spectroscopic data of **2Se** and **3Se** support their solid-state structures. The olefinic protons are assigned to 8.24 and 8.30 ppm in **2Se** and **3Se**, respectively. The olefinic carbon resonances appear at 142.24 (*C*=CH), 149.22 ppm (C=*C*H) in **2Se** and 140.40 (*C*=CH), 150.91 ppm (C=*C*H) in **3Se**, respectively, similar to those observed in **2S** and **3S**. The MALDI-TOF MS spectrum shows an intense [M + H^+] peak for both **2Se** and **3Se**.

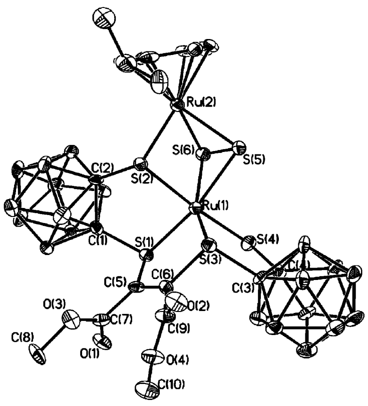


Figure 7. Molecular structure of **4S** (30% probability displacement ellipsoids). The hydrogen atoms and H_2O molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.2640(11), Ru(1)−S(2) = 2.3744(12), Ru(1)−S(3) = 2.2500(12), Ru(1)−S(4) = 2.3759(13), Ru(1)−S(5) = 2.3844(12), Ru(1)−S(6) = 2.4294(12), S(5)−S(6) = 2.0414(16), C(5)−S(1) = 1.804(4), C(6)−S(3) = 1.818(4), C(1)−C(2) 1.684(6), C(3)−C(4) 1.653(6), C(5)−C(6) = 1.326(6), Ru(1)···Ru(2) = 3.420; S(1)−Ru(1)−S(3) = 87.43(4), S(1)−Ru(1)−S(4) = 92.31(4), S(5)−Ru(1)−S(6) = 50.17(4).

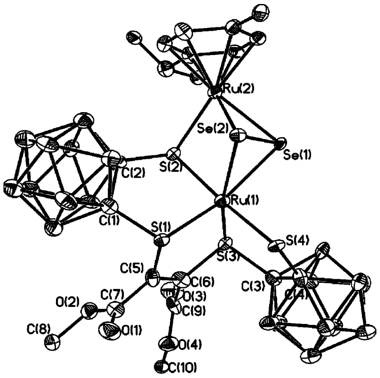


Figure 8. Molecular structure of **4Se** (30% probability displacement ellipsoids). The hydrogen atoms and H_2O molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−S(1) = 2.2484(16), Ru(1)−S(2) = 2.3692(16), Ru(1)−S(3) = 2.2429(16), Ru(1)−S(4) = 2.3811(15), Ru(1)−Se(1) = 2.5187(8), Ru(1)−Se(2) = 2.5354(8), Se(1)−Se(2) = 2.3042(9), C(5)−S(1) = 1.796(7), C(6)−S(3) = 1.798(7), C(1)−C(2) 1.670(9), C(3)−C(4) 1.676(9), C(5)−C(6) = 1.323(10), Ru(1)···Ru(2) = 3.490; S(1)−Ru(1)−S(3) = 88.87(6), S(1)−Ru(1)−S(4) = 89.15(6), Se(1)−Ru(1)−Se(2) = 54.24(2).

Reactions of 1S and 1Se with Dimethyl Acetylene Dicarboxylate. The treatment of **1S** and **1Se** with internal alkyne $MeO_2CC{\equiv}CCO_2Me$ affords **4S** and **4Se**, respectively (Scheme 1). The solid-state structures (Figures 7 and 8) indicate that the alkyne addition selectively takes place at S(1) and S(3) sites with the formation of a nearly planar five-membered RuSCCS ring, as observed in **2S**, **3S**, **2Se**, and **3Se**. The distances of the coordinative bonds S(1) → Ru(1) (2.264 Å) and S(3) → Ru(1) (2.250 Å) in **4S** are slightly longer (0.064 and 0.058 Å) than those covalent bonds Ru(1)−S(1) and Ru(1)−S(3) in **1S**. The angle of S(1)−Ru(1)−S(3) (87.4°) in **4S** is significantly reduced as compared to 117.3° in **1S**. Similarly, the alkyne addition leads to a 18e Ru(II) center from the 16e Ru(IV) in **1S**. The spectroscopic data of **4S** and **4Se** are consistent with their solid-state structures. The ^{13}C resonance peaks observed at 144.89, 148.64 ppm in **4S** and 144.99, 147.10 ppm in **4Se** are typical of an olefin. The MALDI-TOF MS spectrum shows an intense $[M + H^+]$ peak for both **4S** and **4Se**.

In **1S**−**4S** and **2Se**−**4Se**, the average distance of the C−C bond (1.66 Å) of the carborane cages lies in previously observed ranges of 1.62−1.70 Å for 1,2-disubstituted *o*-carborane derivatives.[10] The average S(5)−S(6) distance of 2.040 Å in **1S**−**4S** falls within the typical range of S−S single bond of 1.963−2.159 Å,[11] and the average Se(1)−Se(2) distance of 2.327 Å in **2Se**−**4Se** falls within the typical range of Se−Se single bond of 2.28−2.39 Å.[12] The average distance of the two ruthenium atoms is 3.413 Å in **1S**−**4S** and 3.496 Å in **2Se**−**4Se**, respectively, indicating no Ru−Ru bonding because a typical Ru−Ru single bond is in the range of 2.71−3.02 Å.[13]

Interconversion of Isomers. Upon heating **2S** in boiling toluene for 30 h, a mixture of **2S** and **3S** in a ratio of approximately 1:1 was observed (Scheme 2). The same occurred for **3S**. However, **3S** was slightly slower to convert to **2S**. Heating **2Se** in boiling toluene for approximate 60 h afforded a mixture of **2Se** and **3Se** in about 1:1 ratio. The same was observed for **3Se**. **3Se** was slightly slower to convert to **2Se**. Note that the reaction of **1S** or **1Se** with methyl acetylene monocarboxylate at ambient temperature leads to a mixture of **2S** and **3S** or **2Se** and **3Se** in an approximate ratio of 1:1. These observations suggest that the size of the CO_2Me group does not significantly affect the regioselectivity of the alkyne addition and the energy barrier of the two isomers allows their interconversion.

The proposed mechanism for the interconversion is shown in Scheme 2. Upon heating **2**, the S−S bridge rotates around the axis of Ru(1)···Ru(2) that leads to the Ru(1)−S* bond lengthened, and further the S# atom could approach Ru(1). When the distances of Ru(1)−S* and Ru(1)···S# are close, the transition state (**T-23**) is generated. As the Ru(1)−S* bond is cleaved, the Ru(1)−S# bond is formed to give rise to **3**. In the case of **3**, if heated, the S−S bridge swings around the axis of Ru(1)···Ru(2) in an opposite direction that leads to a longer Ru(1)−S# bond. As a result, the S* atom is getting close to Ru(1). When the distances of Ru(1)−S# and Ru(1)···S* are close, the transition state (**T-32**) is generated. Eventually, the Ru(1)−S# bond is cleaved and the Ru(1)−S* bond is generated to afford **2**. The interconversion of two isomers only involves cleavage and generation of M−S bonds, which are well known in the reaction chemistries of metal−chalcogen clusters.[5]

---

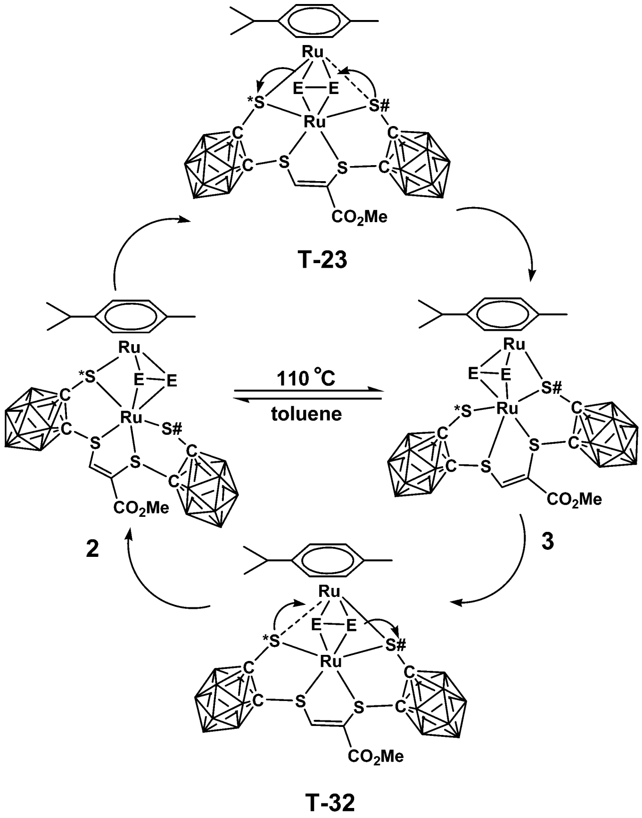
(10) (a) Davidson, M. G.; Hibbert, T. G.; Howard, J. A. K.; Mackinnon, A.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1996**, 2285. (b) Teixidor, F.; Viñas, C.; Rius, J.; Miravitlles, C.; Casabó, J. *Inorg. Chem.* **1990**, *29*, 149. (c) Llop, J.; Viñas, C.; Oliva, J. M.; Teixidor, F.; Flores, M. A.; Kivekäs, R.; Sillanpää, R. *J. Organomet. Chem.* **2002**, *657*, 232. (d) Teixidor, F.; Romerosa, A.; Rius, J.; Miravitlles, C.; Casabó, J.; Viñas, C.; Sanchez, E. *J. Chem. Soc., Dalton Trans.* **1990**, 525.

(11) (a) Brunner, H.; Janietz, N.; Meier, W.; Sergeson, G.; Wachter, J.; Zahn, T.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1060. (b) Roberts, S. A.; Young, C. G.; Cleland, W. E., Jr.; Yamanouchi, K.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1988**, *27*, 2647. (c) Kawano, M.; Hoshino, S.; Matsumoto, K. *Inorg. Chem.* **1992**, *31*, 5158. (d) Goodman, J. T.; Rauchfuss, T. B. *Inorg. Chem.* **1998**, *37*, 5040. (e) Yoshioka, K.; Kikuchi, H.; Mizutani, J.; Matsumoto, K. *Inorg. Chem.* **2001**, *40*, 2234. (f) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114. (g) Matsumoto, K.; Matsumoto, T.; Kawano, M.; Ohnuki, H.; Shichi, Y.; Nishide, T.; Sato, T. *J. Am. Chem. Soc.* **1996**, *118*, 3597. (h) Weberg, R.; Haltiwanger, R. C.; Dubois, M. R. *Organometallics* **1985**, *4*, 1315. (i) Mizobe, Y.; Hosomizu, M.; Kubota, Y.; Hidai, M. *J. Organomet. Chem.* **1996**, *507*, 179. (j) Mizobe, Y.; Hosomizu, M.; Kuwata, S.; Kawabata, J.; Hidai, M. *J. Organomet. Chem.* **1996**, *513*, 231.

(12) (a) Hummel, H. U.; Fischer, T.; Gruss, D.; Franke, A.; Dietzsch, W. *J. Chem. Soc., Dalton Trans.* **1992**, 2781. (b) Kumar, S.; Tripathi, S. K.; Singh, H. B.; Wolmershaeuser, G. *J. Organomet. Chem.* **2004**, *689*, 3046. (c) Zade, S. S.; Panda, S.; Singh, H. B.; Sunoj, R. B.; Butcher, R. J. *J. Org. Chem.* **2005**, *70*, 3693.

(13) (a) Gao, Y.; Jennings, M. C.; Puddephatt, R. J.; Jenkins, H. A. *Organometallics* **2001**, *20*, 3500. (b) Engel, D. W.; Moodley, K. G.; Subramony, L.; Haines, R. J. *J. Organomet. Chem.* **1988**, *349*, 393.

Scheme 2. Proposed Mechanism for the Interconversion of 2 and 3



Unfortunately, the transition states **T-23**/**T-32** were not detected by NMR spectroscopy.

Conclusion

Two dinuclear Ru(II)/Ru(IV) half-sandwich complexes containing one bridging E−E (E = S, Se) ligand and two $[S_2C_2(B_{10}H_{10})]^{2-}$ moieties have been synthesized through the reaction of $[(p\text{-cymene})RuCl_2]_2$ with $Li_2[S_2C_2(B_{10}H_{10})]$ in the presence of excess sulfur or selenium at ambient temperature. The 16e Ru(IV) center in a distorted-octahedron geometry determines their reactivity toward alkynes, and the large S(1)−Ru(1)−S(3) angle determines their reactive sites. The alkyne addition at two of sulfur atoms opposite to the bridging E−E ligand gives rise to more stable products **2S**−**4S** and **2Se**−**4Se** due to reduced strain and the formation of a 18e Ru(II) center. Changing from a S−S bridge to a Se−Se bridge leads to a slightly slower alkyne addition. The terminal alkyne $HC{\equiv}CCO_2Me$ does not significantly affect the regioselectivity of the alkyne addition so that two isomers can be generated that interconvert upon heating. In comparison, the symmetrical internal alkyne $MeO_2CC{\equiv}CCO_2Me$ generates only one species.

Experimental Section

General Procedures. *n*-Butyllithium (2.0 M in cyclohexane, Aldrich), *o*-carborane (Katchem, Czech), methyl acetylene monocarboxylate (Alfa Aesar), and dimethyl acetylene dicarboxylate (Aldrich) were used as commercial products without further purification. The starting material $[(p\text{-cymene})RuCl_2]_2$ was prepared according to the literature.[14] All reactions were carried out under argon using standard Schlenk techniques, unless otherwise stated. All solvents were distilled under nitrogen from sodium−benzophenone (petroleum ether, diethyl ether, THF, and toluene) or calcium hydride (dichloromethane) prior to use. Elemental analysis was performed in a Perkin-Elmer 240C elemental analyzer. NMR measurements were obtained on a Bruker AM-500 spectrometer. Chemical shifts were given with respect to $CHCl_3/CDCl_3$ (δ ^1H = 7.27, δ ^{13}C = 77.0) or $CDHCl_2$ (δ ^{13}C = 53.8), 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. Matrix-assisted laser desorption/ionization (MALDI) in a linear time-of-flight (TOF) mass spectrometer (MS) was recorded in a Bruker autoflex TOF/TOF equipped with an acquisition operation mode of reflector and signal averaging of 30 laser shots.[15] Finnigan MAT TSQ7000 was used for ESI-MS.

Synthesis of 1S. *o*-Carborane (58 mg, 0.4 mmol) was dissolved in diethyl ether (15 mL) and lithiated by the addition of a 2.0 M cyclohexane solution of *n*-butyllithium (0.6 mL, 1.2 mmol). The addition of sulfur (43 mg, 1.34 mmol) led to a slightly yellow suspension, and then a solution of $[(p\text{-cymene})RuCl_2]_2$ (123 mg, 0.2 mmol) in THF (40 mL) was added. The color of the resultant mixture gradually changed from orange to green. After 10 h, the solvents were removed under reduced pressure and the residue was chromatographed on silica. Elution with petroleum ether/CH_2Cl_2 (1:2) gave a green complex of **1S**. Suitable green crystals for X-ray analysis were obtained from petroleum ether/CH_2Cl_2 in 2 weeks. **1S**: yield 105 mg (65%); mp 205 °C dec. Anal. Calcd for $C_{14}H_{34}B_{20}Ru_2S_6$: C, 20.68; H, 4.21. Found: C, 20.80; H, 4.13. ESI-MS (*m*/*z*): calcd for $C_{14}H_{34}B_{20}Ru_2S_6$, 813.11; found, 814.10 ($[M + H]^+$, 100%). ^1H NMR ($CDCl_3$): δ 1.28 (d, *J* = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.39 (d, *J* = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.32 (s, 3H, CH_3), 2.73 (sept, *J* = 7.0 Hz, 1H, $CH(CH_3)_2$), 5.23 (d, *J* = 6.0 Hz, 1H, C_6H_4), 5.32 (d, *J* = 6.0 Hz, 1H, C_6H_4), 6.12 (d, *J* = 6.0 Hz, 2H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 18.87 ($C_6H_4{-}CH_3$), 22.78, 23.39 ($CH(CH_3)_2$), 31.58 ($CH(CH_3)_2$), 81.95, 83.52, 84.38, 85.55 (CH in *p*-cymene), 86.43, 88.08, 102.23, 104.81, 108.95, 111.82 (*o*-carborane and quaternary C in *p*-cymene). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −8.1, −7.2, −6.4, −5.5, −4.5 (1:1:1:3:4). IR (KBr, cm^{-1}): ν 2587 (ν_{B-H}).

Synthesis of 2S and 3S. Methyl acetylene monocarboxylate (0.08 mL, 1 mmol) was added to **1S** (81 mg, 0.1 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 16 h at ambient temperature. After removal of the solvent, the residue was chromatographed to afford **2S** (petroleum ether/CH_2Cl_2 (1:2)) and **3S** (petroleum ether/CH_2Cl_2 (1:5)). **2S**: yield 36 mg (40%); mp 230 °C dec. Anal. Calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_6$: C, 24.09; H, 4.27. Found: C, 24.28; H, 4.35. MALDI-TOF MS (*m*/*z*): calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_6$, 897.130; found, 898.224 ($[M + H]^+$, 75%). ^1H NMR ($CDCl_3$): δ 1.21 (d, *J* = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.35 (d, *J* = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.19 (s, 3H, CH_3), 2.68 (sept, *J* = 7.0 Hz, 1H, $CH(CH_3)_2$), 3.99 (s, 3H, OCH_3), 5.04 (d, *J* = 6.0 Hz, 1H, C_6H_4), 5.08 (d, *J* = 6.0 Hz, 1H, C_6H_4), 6.12 (d, *J* = 6.0 Hz, 1H, C_6H_4), 6.14 (d, *J* = 6.0 Hz, 1H, C_6H_4), 8.21 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$): δ 18.87 ($C_6H_4{-}CH_3$), 22.97, 23.39 ($CH(CH_3)_2$), 31.78 ($CH(CH_3)_2$), 54.71 (OCH_3), 80.58, 81.81, 82.51, 85.73 (CH in *p*-cymene), 90.31, 93.56, 94.28, 99.68, 100.16, 107.78 (*o*-carborane and quaternary C in *p*-cymene), 142.64 (*C*=CH), 149.14 (H*C*=C), 162.42 (C=O). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −6.9, −4.3, −2.0 (4:2:4). IR (KBr, cm^{-1}): ν 2581 (ν_{B-H}), 1635 ($\nu_{SC=CS}$). **3S**: yield 33 mg (39%); mp 232 °C dec. Anal. Calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_6 \cdot 1.25H_2O$: C, 23.50; H, 4.44. Found: C, 23.88; H, 4.32. MALDI-TOF MS (*m*/*z*): calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_6$, 897.130; found, 898.224 ($[M + H]^+$, 75%). ^1H NMR ($CDCl_3$): δ 1.24 (d, *J* = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.37 (d, *J* = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.24 (s, 3H, CH_3), 2.71 (sept, *J* = 7.0 Hz, 1H, $CH(CH_3)_2$), 3.95 (s, 3H,

---

[14] Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.

[15] (a) Whittal, R. M.; Russon, L. M.; Weinberger, S. R.; Li, L. *Anal. Chem.* **1997**, *69*, 2147. (b) Whittal, R. M.; Li, L. *Anal. Chem.* **1995**, *67*, 1950.

Table 1. Summary of Crystallographic Data for 1S−4S

	1S	2S	3S	4S
formula	$C_{14}H_{34}B_{20}Ru_2S_6$	$C_{18}H_{38}B_{20}O_2Ru_2S_6$	$4(C_{18}H_{38}B_{20}O_2Ru_2S_6)\cdot 5H_2O$	$2(C_{20}H_{40}B_{20}O_4Ru_2S_6)\cdot H_2O$
crystal size (mm)	0.35 × 0.25 × 0.20	0.32 × 0.26 × 0.24	0.28 × 0.18 × 0.16	0.26 × 0.24 × 0.12
formula weight	813.11	897.18	3679.06	1928.58
temp (K)	298(2)	298(2)	291(2)	273(2)
radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	13.053(3)	12.0780(16)	13.434(3)	10.5166(16)
b (Å)	10.024(2)	13.0508(18)	14.267(3)	20.192(3)
c (Å)	25.586(5)	13.4696(19)	23.072(5)	19.339(3)
α (deg)	90.00	106.665(2)	90.101(4)	90.00
β (deg)	98.120(12)	97.858(2)	97.344(3)	98.882(3)
γ (deg)	90.00	108.704(2)	116.697(3)	90.00
V (Å^3)	3314.3(12)	1864.4(4)	3909.5(15)	4057.4(11)
Z	4	2	1	2
ρ_{calc} (g cm^{-3})	1.630	1.598	1.563	1.579
absorp coeff (mm^{-1})	1.302	1.169	1.120	1.085
F(000)	1608	892	1834	1924
θ range (deg)	1.40−21.61	2.48−21.84	2.29−16.91	2.41−17.89
reflns collected	17 663 (R_{int} = 0.049)	10 187 (R_{int} = 0.030)	26 693 (R_{int} = 0.055)	21 988 (R_{int} = 0.049)
indep reflns	6513	7160	15 376	7964
reflns obs [$I > 2\sigma(I)$]	4778	5155	10 488	5828
data/restraints/params	6513/0/379	7160/0/433	15 376/0/900	7964/0/479
GOF	1.042	1.039	1.074	1.011
R_1/wR_2 [$I > 2\sigma(I)$]	0.0477/0.0924	0.0634/0.1409	0.0683/0.1430	0.0477/0.0972
R_1/wR_2 (all data)	0.0686/0.0955	0.0932/0.1470	0.0971/0.1491	0.0698/0.1016
larg peak/hole (e Å^{-3})	0.629/−0.791	0.756/−1.537	0.959/−1.089	0.363/−0.584

OCH_3), 5.07 (d, J = 6.0 Hz, 1H, C_6H_4), 5.13 (d, J = 6.0 Hz, 1H, C_6H_4), 6.12 (d, J = 6.0 Hz, 1H, C_6H_4), 6.14 (d, J = 6.0 Hz, 1H, C_6H_4), 8.29 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$): δ 18.61 ($C_6H_4-CH_3$), 22.68, 23.07 ($CH(CH_3)_2$), 31.45 ($CH(CH_3)_2$), 54.10 (OCH_3), 80.23, 81.15, 82.14, 84.98 (CH in *p*-cymene), 89.84, 90.18, 97.45, 99.09, 103.52, 107.26 (*o*-carborane and quaternary C in *p*-cymene), 144.32 (*C*=CH), 150.73 (H*C*=C), 161.69 (C=O). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −6.8, −4.5, −2.3 (4:2:4). IR (KBr, cm^{-1}): ν 2579 (ν_{B-H}), 1622 ($\nu_{SC=CS}$).

Synthesis of 4S. Dimethyl acetylene dicarboxylate (0.1 mL, 1 mmol) was added to **1S** (81 mg, 0.1 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 18 h at ambient temperature. After removal of the solvent, the residue was chromatographed to give **4S** (petroleum ether/CH_2Cl_2 (1:2)). **4S**: yield 74 mg (78%); mp 236 °C dec. Anal. Calcd for $C_{20}H_{40}B_{20}O_4Ru_2S_6\cdot 0.5H_2O$: C, 24.91; H, 4.29. Found: C, 24.32; H, 4.07. MALDI-TOF MS (*m/z*): calcd for $C_{20}H_{40}B_{20}O_4Ru_2S_6$, 955.136; found, 956.478 ([M + H]$^+$, 45%). ^1H NMR ($CDCl_3$): δ 1.23 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.36 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.22 (s, 3H, CH_3), 2.70 (sept, J = 7.0 Hz, 1H, $CH(CH_3)_2$), 3.92 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 5.06 (d, J = 6.0 Hz, 1H, C_6H_4), 5.11 (d, J = 6.0 Hz, 1H, C_6H_4), 6.14 (d, J = 6.0 Hz, 1H, C_6H_4), 6.15 (d, J = 6.0 Hz, 1H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 18.49 ($C_6H_4-CH_3$), 22.59, 23.00 ($CH(CH_3)_2$), 31.42 ($CH(CH_3)_2$), 54.16, 54.31 (OCH_3), 80.36, 81.46, 82.29, 85.55 (CH in *p*-cymene), 91.06, 91.64, 92.11, 99.87, 101.67, 107.52 (*o*-carborane and quaternary C in *p*-cymene), 144.89, 148.64 (C=C), 163.39, 163.97 (C=O). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −6.6, −4.1, −2.0 (4:2:4). IR (KBr, cm^{-1}): ν 2579 (ν_{B-H}), 1635 ($\nu_{SC=CS}$).

Synthesis of 1Se. *o*-Carborane (58 mg, 0.4 mmol) was dissolved in diethyl ether (15 mL) and lithiated by the addition of a 2.0 M cyclohexane solution of *n*-butyllithium (0.6 mL, 1.2 mmol). The addition of sulfur (25.6 mg, 0.8 mmol) led to a colorless solution. After 30 min, selenium (47 mg, 0.6 mmol) was added to the above solution to lead to a gray suspension, and then a solution of [(*p*-cymene)$RuCl_2$]$_2$ (123 mg, 0.2 mmol) in THF (40 mL) was added. The color of the resultant mixture gradually changed from orange to green. After 10 h, the solvents were removed under reduced pressure and the residue was chromatographed on silica. Elution with petroleum ether/CH_2Cl_2 (1:1) afforded a green compound of **1Se**: yield 72 mg (40%); mp 238 °C dec. Anal. Calcd for $C_{14}H_{34}B_{20}Ru_2S_4Se_2$: C, 18.54; H, 3.78. Found: C, 18.97; H, 3.51. ESI-MS (*m/z*): calcd for $C_{14}H_{34}B_{20}Ru_2S_4Se_2$, 906.96; found, 908.03 ([M + H]$^+$, 100%). ^1H NMR ($CDCl_3$): δ 1.28 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.39 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.34 (s, 3H, CH_3), 2.74 (sept, J = 7.0 Hz, 1H, $CH(CH_3)_2$), 5.16 (d, J = 6.0 Hz, 1H, C_6H_4), 5.33 (d, J = 6.0 Hz, 1H, C_6H_4), 6.07 (d, J = 6.0 Hz, 2H, C_6H_4). ^{13}C NMR (CD_2Cl_2): δ 19.51 ($C_6H_4-CH_3$), 23.07, 23.65 ($CH(CH_3)_2$), 32.03 ($CH(CH_3)_2$), 80.94, 82.61, 84.45, 84.66 (CH in *p*-cymene), 89.88, 90.07, 102.18, 105.02, 109.04, 111.65 (*o*-carborane and quaternary C in *p*-cymene). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −7.5, −6.2, −3.8, −2.4, −1.8 (2:3:1:1:3). IR (KBr, cm^{-1}): 2582 (ν_{B-H}).

Synthesis of 2Se and 3Se. Methyl acetylene monocarboxylate (0.08 mL, 1 mmol) was added to **1Se** (91 mg, 0.1 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 36 h at ambient temperature. After removal of the solvent, the residue was chromatographed to give **2Se** (petroleum ether/CH_2Cl_2 (2:3)) and **3Se** (petroleum ether/CH_2Cl_2 (1:3)). **2Se**: yield, 44 mg (45%), mp 246 °C dec. Anal. Calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_4Se_2$: C, 21.81; H, 3.86. Found: C, 21.66; H, 4.07. MALDI-TOF MS (*m/z*): calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_4Se_2$, 991.021; found, 992.205 ([M + H]$^+$, 70%). ^1H NMR ($CDCl_3$): δ 1.19 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.33 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.20 (s, 3H, CH_3), 2.72 (sept, J = 7.0 Hz, 1H, $CH(CH_3)_2$), 4.00 (s, 3H, OCH_3), 5.02 (d, J = 6.0 Hz, 1H, C_6H_4), 5.05 (d, J = 6.0 Hz, 1H, C_6H_4), 6.08 (d, J = 6.0 Hz, 1H, C_6H_4), 6.10 (d, J = 6.0 Hz, 1H, C_6H_4), 8.24 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$): δ 18.64 ($C_6H_4-CH_3$), 22.50, 23.25 ($CH(CH_3)_2$), 31.41 ($CH(CH_3)_2$), 54.27 (OCH_3), 78.32, 80.19, 80.77, 84.61 (CH in *p*-cymene), 93.45, 93.84, 93.89, 98.75, 99.47, 107.46 (*o*-carborane and quaternary C in *p*-cymene), 142.24 (*C*=CH), 149.22 (H*C*=C), 162.04 (C=O). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −6.9, −5.6, −3.2 (7:1:2). IR (KBr, cm^{-1}): ν 2580 (ν_{B-H}), 1654 ($\nu_{SC=CS}$). **3Se**: yield, 46 mg (46%), mp 243 °C dec. Anal. Calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_4Se_2\cdot 3H_2O$: C, 20.69; H, 4.24. Found: C, 20.34; H, 4.04. MALDI-TOF MS (*m/z*): calcd for $C_{18}H_{38}B_{20}O_2Ru_2S_4Se_2$, 991.021; found, 992.126 ([M + H]$^+$, 90%). ^1H NMR ($CDCl_3$): δ 1.23 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 1.36 (d, J = 7.0 Hz, 3H, $CH(CH_3)_2$), 2.26 (s, 3H, CH_3), 2.74 (sept, J = 7.0 Hz, 1H, $CH(CH_3)_2$), 3.96 (s, 3H, OCH_3), 5.07 (d, J = 6.0 Hz, 1H, C_6H_4), 5.10 (d, J = 6.0 Hz, 1H, C_6H_4), 6.09 (d, J = 6.0 Hz, 1H, C_6H_4), 6.10 (d, J = 6.0 Hz, 1H, C_6H_4), 8.30 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$): δ 18.89 ($C_6H_4-CH_3$), 22.67, 23.30 ($CH(CH_3)_2$), 31.51

Table 2. Summary of Crystallographic Data for 2Se−4Se

	2Se	**3Se**	**4Se**
formula	$C_{18}H_{38}B_{20}O_2Ru_2S_4Se_2$	$C_{18}H_{38}B_{20}O_2Ru_2S_4Se_2\cdot 3H_2O$	$C_{20}H_{40}B_{20}O_4Ru_2S_4Se_2\cdot H_2O$
crystal size (mm)	0.28 × 0.24 × 0.20	0.32 × 0.26 × 0.24	0.30 × 0.26 × 0.18
formula weight	991.02	1045.03	1067.08
temp (K)	291(2)	291(2)	291(2)
radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	11.8523(16)	11.274(2)	12.8264(17)
b (Å)	12.0728(16)	22.082(5)	13.6352(17)
c (Å)	13.9244(19)	20.768(5)	13.7639(17)
α (deg)	86.559(2)	90.00	92.990(2)
β (deg)	85.718(2)	103.722(3)	103.591(2)
γ (deg)	68.181(2)	90.00	108.031(2)
V (Å^3)	1843.4(4)	5022.7(19)	2204.5(5)
Z	2	4	2
ρ_{calc} (g cm^{-3})	1.785	1.382	1.608
absorp coeff (mm^{-1})	3.044	2.242	2.556
F(000)	964	2048	1044
θ range (deg)	2.30−21.90	2.22−21.34	2.35−22.82
reflns collected	9971 (R_{int} = 0.032)	27 058 (R_{int} = 0.033)	12 214 (R_{int} = 0.032)
indep reflns	7087	9818	8501
reflns obs [$I > 2\sigma(I)$]	4849	8043	6294
data/restraints/params	7087/0/425	9818/0/509	8501/0/501
GOF	1.071	1.059	1.050
R_1/wR_2 [$I > 2\sigma(I)$]	0.0604/0.1283	0.0482/0.1142	0.0595/0.1286
R_1/wR_2 (all data)	0.0887/0.1344	0.0653/0.1199	0.0769/0.1324
larg peak/hole (e Å^{-3})	1.572/−1.592	0.432/−0.979	0.736/−1.114

(*C*H(CH$_3$)$_2$), 54.06 (OCH$_3$), 78.51, 80.34, 80.68, 84.12 (CH in *p*-cymene), 89.71, 90.44, 96.73, 99.20, 103.43, 107.26 (*o*-carborane and quaternary C in *p*-cymene), 140.40 (*C*═CH), 150.91 (H*C*═C), 161.70 (C═O). ^{11}B{^{1}H} NMR (CDCl$_3$): δ −6.2, −4.5, −2.1 (7:1:2). IR (KBr, cm^{-1}): ν 2582 (ν_{B-H}), 1651 ($\nu_{SC=CS}$).

Synthesis of 4Se. Dimethyl acetylenedicarboxylate (0.1 mL, 1 mmol) was added to **1Se** (91 mg, 0.1 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred for 72 h at ambient temperature. After removal of the solvent, the residue was chromatographed to give **4Se** (petroleum ether/CH$_2$Cl$_2$ (1:2)). **4Se**: yield, 84 mg (80%), mp 208 °C dec. Anal. Calcd for $C_{20}H_{40}B_{20}O_4Ru_2S_4Se_2\cdot H_2O$: C, 22.51; H, 3.97. Found: C, 22.93; H, 4.19. MALDI-TOF MS (*m*/*z*): calcd for $C_{20}H_{40}B_{20}O_4Ru_2S_4Se_2$, 1049.018; found, 1050.450 ([M + H]$^+$, 50%). ^{1}H NMR (CDCl$_3$): δ 1.21 (d, J = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 1.35 (d, J = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 2.23 (s, 3H, CH$_3$), 2.73 (sept, J = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 3.92 (s, 3H, OCH$_3$), 3.94 (s, 3H, OCH$_3$), 5.04 (d, J = 6.0 Hz, 1H, C$_6$H$_4$), 5.09 (d, J = 6.0 Hz, 1H, C$_6$H$_4$), 6.10 (d, J = 6.0 Hz, 1H, C$_6$H$_4$), 6.11 (d, J = 6.0 Hz, 1H, C$_6$H$_4$). ^{13}C NMR (CDCl$_3$): δ 18.69 (C$_6$H$_4$−*C*H$_3$), 22.54, 23.28 (CH(*C*H$_3$)$_2$), 31.46 (*C*H(CH$_3$)$_2$), 54.13, 54.27 (OCH$_3$), 78.56, 80.40, 80.85, 84.83 (CH in *p*-cymene), 91.49, 91.85, 95.25, 99.54, 101.29, 107.58 (*o*-carborane and quaternary C in *p*-cymene), 144.99, 147.10 (C═C), 163.48, 164.10 (C═O). ^{11}B{^{1}H} NMR (CDCl$_3$): δ −6.8, −4.1, −1.9 (7:1:2). IR (KBr, cm^{-1}): ν 2578 (ν_{B-H}), 1644 ($\nu_{SC=CS}$).

X-ray Structure Determination. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with the SADABS program.[16] The structures were solved by direct methods using the SHELXL-97 program.[17] All non-hydrogen atoms were found from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. Crystal data and details of data collection and structure refinements of **1S−4S** and **2Se−4Se** are given in Tables 1 and 2.

Acknowledgment. Financial support by the National Science Foundation of China (No. 20471017) is gratefully acknowledged.

Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of compounds **1S−4S** and **2Se−4Se**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7008556

---

[16] Sheldrick, G. M. *SADABS, A Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1998.

[17] Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.