化 学 学 报
ACTA CHIMICA SINICA

研究论文
Article

DOI: 10.6023/A13030346

含桥连 Se—Se 基团和两个$(S_2C_2B_{10}H_{10})^{2-}$离子的不饱和双核钌化合物与 l-乙炔基环己醇的反应性

胡久荣*,[a,b]　彭化南[b]　胡昕[b]　叶红德[b]　燕红*,[a]

([a]南京大学 化学化工学院配位化学国家重点实验室　南京 210093)

([b]上饶师范学院化学化工学院　上饶 334001)

摘要　在二氯甲烷中, 化合物(*p*-cymene)$Ru_2(\mu\text{-}Se_2)(S_2C_2B_{10}H_{10})_2$ (**1**)与 l-乙炔基环己醇反应得到加成产物(*p*-cymene)-$Ru_2(\mu\text{-}Se_2)(S_2C_2B_{10}H_{10})_2$ ($R^1C{=}CR^2$) [R^1=H, R^2=(*cyclo*-C_6H_{10})(OH) (**2**); R^1=(*cyclo*-C_6H_{10})(OH), R^2=H (**3**)]. 化合物 **2** 和 **3** 在氯仿中加热回流可脱水分别生成 **4** 和 **5**, 二者在甲苯中进一步加热回流可实现相互转化. 所有化合物中, 炔烃碳碳三键选择性地加成在两个不同的$(S_2C_2B_{10}H_{10})^{2-}$配体的硫原子[S(2)和 S(3)]上, 从而使混合价双钌中心 Ru^{II}/Ru^{IV} (18*e*/16*e*)转变为单一价态的 Ru^{II}/Ru^{II} (18*e*/18*e*), 得到进一步稳定的配合物. 所有化合物通过元素分析、质谱、核磁共振进行了表征, 并解析了化合物 **2** 的 X 衍射单晶结构.

关键词　邻位-碳硼烷; l-乙炔基环己醇; 硫族元素; 钌配合物; 合成

Reactivity of Dinuclear Ruthenium Complex Containing One μ-Se_2 Unit and Two 1,2-Dicarba-*closo*-dodecaborane-1,2-dithiolate Ligands toward (*cyclo*-C_6H_{10})(OH)C≡CH

Hu, Jiurong*,[a,b]　Peng, Huanan[b]　Hu, Xin[b]　Ye, Hongde[b]　Yan, Hong*,[a]

([a] *State Key Laboratory of Coordination Chemistry*, *School of Chemistry and Chemical Engineering*, *Nanjing University*, *Jiangsu 210093*)

([b] *School of Chemistry and Chemical Engineering*, *Shangrao Normal University*, *Jiangxi 334001*)

Abstract　Treatment of (*p*-cymene)$Ru_2(\mu\text{-}Se_2)(S_2C_2B_{10}H_{10})_2$ (**1**) with (*cyclo*-C_6H_{10})(OH)C≡CH in dichloromethane led to addition complexes, (*p*-cymene)$Ru_2(\mu\text{-}Se_2)(S_2C_2B_{10}H_{10})_2$($R^1C = CR^2$) [$R^1$ = H, R^2 = (*cyclo*-C_6H_{10})(OH) (**2**); R^1 = (*cyclo*-C_6H_{10})(OH), R^2=H (**3**)]. In boiling chloroform both **2** and **3** spontaneously lose water to generate two geometrical isomers (*p*-cymene)$Ru_2(\mu\text{-}Se_2)(S_2C_2B_{10}H_{10})_2$ ($R^1C{=}CR^2$) [R^1=H, R^2=*cyclo*-C_6H_9 (**4**); R^1=*cyclo*-C_6H_9, R^2=H (**5**)], respectively. Complexes **4** and **5** could be interconverted in refluxing toluene. In all products alkyne addition occurs at the sulfur atoms of the two individual chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligands that leads to a change of the 16*e* Ru(IV) center in **1** to the 18*e* Ru(II) center in **2**～**5**. The molecular structure of complex **2** has been determined by X-ray crystallography. All these complexes were characterized by elemental analysis, mass and NMR spectroscopy.

Keywords　*ortho*-carborane; (*cyclo*-C_6H_{10})(OH)C≡CH; chalcogenide element; ruthenium complexes; synthesis

1　Introduction

Dicarba-*closo*-dodecaborane derivatives have attracted considerable attention due to their unique properties and useful applications.[1~3] During the past decade, a large number of organometallic complexes containing 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate chelating ligands have been reported.[4~6] Recently, some interesting reactions of $Li_2[E_2C_2B_{10}H_{10}]$ (E = S, Se) and $[(p\text{-cymene})RuCl_2]_2$ were described which led to the formation of stable ruthenium compounds.[7,8] In the course of synthesis of multinuclear organometallic compounds, unsaturated dinuclear ruthenium complexes (*p*-cymene)Ru(μ-E_2)Ru $(S_2C_2B_{10}H_{10})_2$ (E=S, Se) were successfully isolated, and the reactivity of the sulfur analog toward alkynes has been discussed.[9] These reactions were initiated by coordination of alkyne to the sulfur atoms of two different dithiolate ligands, and thus improving stability to some extent. On the basis of previous studies, in this paper we report the reactivity of the selenium complex (*p*-cymene)-$Ru(\mu\text{-}Se_2)Ru(S_2C_2B_{10}H_{10})_2$ (**1**) toward commercially available (*cyclo*-C_6H_{10})(OH)C≡CH.

* E-mail: hyan1965@nju.edu.cn; jiuronghu@163.com

Received March 29, 2013; published May 2, 2013.

Project supported by the National Natural Science Foundation of China (Nos. 21261020, 21271102), the Scientific and Technological Landing Project of Higher Education of Jiangxi Province (No. KJLD12094), and the Science and Technology Research Project of Key Laboratory of Higher Institutions of Jiangxi Province (No. GJJ12704).

项目受国家自然科学基金(Nos. 21261020, 21271102)、江西省高等学校科技落地计划(No. KJLD12094)和江西省普通高校重点实验室科研项目(No. GJJ12704)资助.

2 Results and discussion

Treatment of $Li_2[S_2C_2(B_{10}H_{10})]$ with [(*p*-cymene)-$RuCl_2]_2$ in the presence of selenium powder for 4 h led to the dinuclear complex **1**, which could be isolated in 65% yield.[10] The X-ray crystal structure of **1** has been reported which showed that Ru(1) bearing a *p*-cymene unit is electronically saturated (18e) with a charge of +2 but Ru(2) is electronically unsaturated (16e) with a charge of +4, in contrast to Ru(II)/Ru(II) in the starting material [(*p*-cymene)$RuCl_2]_2$. Both the 16e Ru(IV) center and the distorted angle of S(2)—Ru(2)—S(3) [117.28(6)°] in **1** predict further reactivity.

In the investigation on the reaction of **1** with 1-ethynyl-1-cyclohexanol [*cyclo*-C_6H_{10}](OH)C≡CH], we found that **1** could undergo alkyne addition to generate two geometrical isomers **2** and **3** in a ratio of approximately 1∶1. In solid state under an inert atmosphere, these complexes are stable enough. For example, no visible decomposition was observed for one month at room temperature and for several months at 0 ℃. However, in solution **2** readily converted to **4** and **3** converted to **5** by loss of one water molecule in refluxed chloroform. In boiling toluene, complexes **4** and **5** could be interconverted to eventually lead to a mixture of an approximate ratio of 1∶1 (Scheme 1). All the compounds have been characterized by elemental analysis, mass, and NMR spectroscopy. The spectroscopic data are consistent with our proposed structural formulation.

The structure of complex **2** has been confirmed by X-ray diffraction, as depicted in Figure 1. In **2**, the alkyne addition selectively takes place at S(2) and S(3) sites from two individual $(S_2C_2B_{10}H_{10})^{2-}$ ligands, and the terminal carbon atom of the alkyne is bonded to S(3). The new generated five-membered ring [Ru(2)/S(3)/C(5)/C(6)/S(2)] is close to planar as reflected by the small deviation (0.1102°) from the rms planes of the best fit. The C(5)—C(6) distance in the central ring is 1.403(9) Å, which is nearly identical to the reported one in (*p*-cymene)Ru(μ-S_2)Ru($S_2C_2B_{10}H_{10})_2$ (HC＝CPh) [1.394(1) Å].[10] The C(7)—O(1) distance of 1.494(8) Å is typical of a normal carbon-oxygen single bond, which can establish the existence of a hydroxyl group. The bond lengths of Ru(2)—S(2) [2.3327(2) Å] and Ru(2)—S(3) [2.3618(2) Å] are a little longer than those [2.2030(2) Å and 2.2146(2) Å][10] in complex **1**, indicating Ru(IV) (16e) in **1** has been changed to Ru(II) (18e) in **2**.

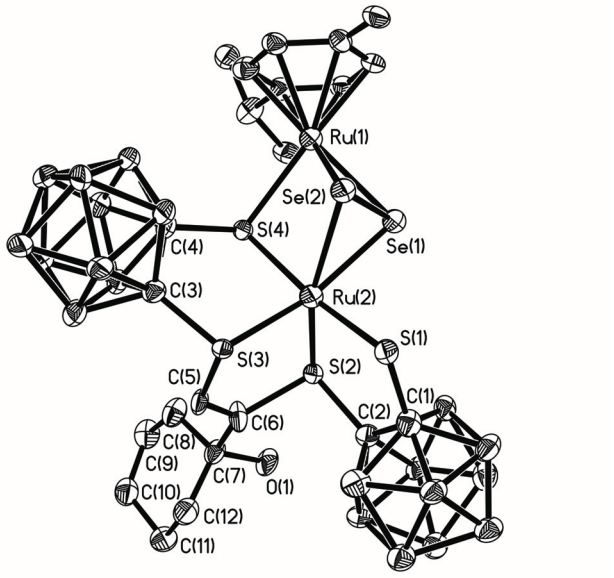
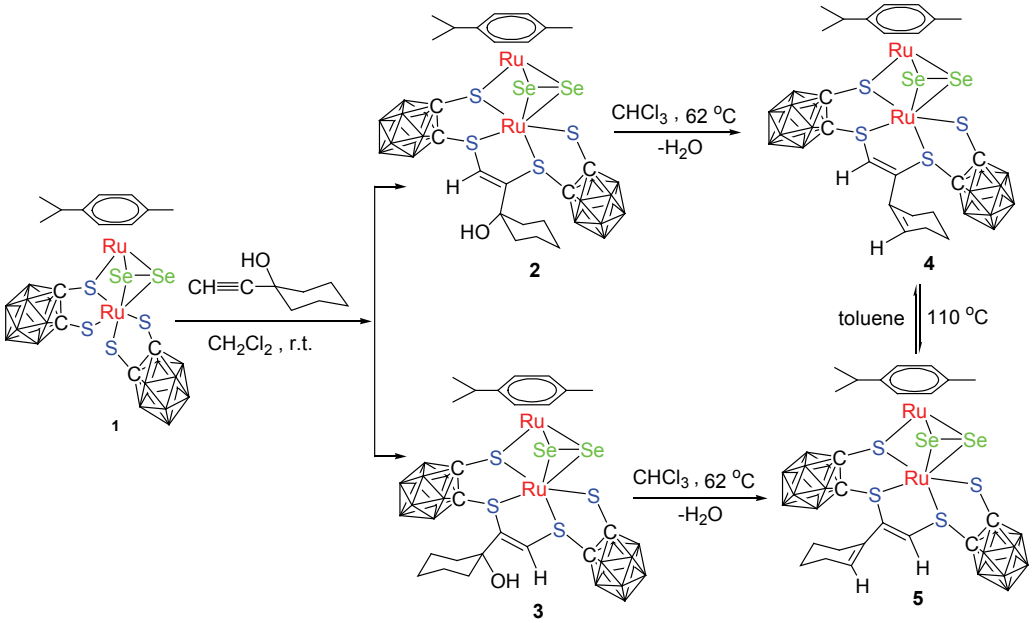


Figure 1 Molecular structure of **2** (30% probability displacement ellipsoids), hydrogen atoms and H_2O molecules are omitted for clarity

In comparison of NMR spectra complex **3** shows similar data as in **2**. The olefinic proton appears at δ 7.08 in **2** and δ 7.07 in **3**, respectively. The OH groups appear at δ 3.76 in **3** and δ 3.77 in **2**, respectively. In the ^{13}C NMR spectra, the carbon signals at 136.67 (**C**＝CH), δ 159.15 (H**C**＝C) in **2** are in agreement with C(5)—C(6) double bond in



Scheme 1 The reactivity of **1** with (*cyclo*-C_6H_{10})(OH)C≡CH

the solid-state structure. In **3** the signals at 136.57 (**C**=CH), 159.09 (H**C**=C) also reflect a typical of C=CH bond. In particular, the ^{13}C NMR signal at δ 75.81 in **2** is attributed to **C**OH and complex **3** also shows a similar one at δ 75.76, indicating the existence of a carbon-oxygen single bond. The MALDI-TOF MS spectra show intense $[M+H]^+$ peaks for both **2** and **3**. Thus it is reasonably assumed that **3** is the geometrical isomer of **2** where the terminal carbon of the alkyne is bonded to S(2) rather than S(3). This assumption can also be supported by the reported reaction of (*p*-cymene)Ru(μ-S_2)Ru($S_2C_2B_{10}H_{10}$)$_2$ and the alkyne.[7c]

The molecular structures of **4** and **5** have not been characterized by X-ray diffraction owing to lack of good quality single crystals. However, in reference to the reaction of (*p*-cymene)Ru(μ-S_2)Ru($S_2C_2B_{10}H_{10}$)$_2$ with 1-ethynyl-1-cyclohexanol, the formation **4** and **5** could be suggested as shown in Scheme 1 by spectroscopic data. Indeed, in the ^{1}H NMR spectra signals assigned to olefinic proton were observed at δ 6.71 (C=C**H**, *cyclo*-C_6H_9), δ 6.89 (**H**C=C—S) in **4**, and δ 6.73 (C=C**H**, *cyclo*-C_6H_9), δ 6.91 (**H**C=C–S) in **5**. And the OH signals in both **4** and **5** disappeared. The ^{13}C NMR spectrum showed additional signals for olefinic carbons at δ 127.98 (**C**=CH, *cyclo*-C_6H_9), δ 131.34 (H**C**=C, *cyclo*-C_6H_9) in **4**, and δ 128.08 (**C**=CH, *cyclo*-C_6H_9), δ 131.62 (H**C**=C, *cyclo*-C_6H_9) in **5** which were assigned to the new generated cyclohexenyl units as confirmed by 2D C－H correlation experiments (*i.e.* NMQC, HMBC). The MALDI-TOF MS show the same molecular ion peaks $[M+H]^+$ for both **4** and **5**. Hence, **4** and **5** are derived from **2** and **3**, respectively, showing the paralell results relative to the sulfur starting complex (*p*-cymene)Ru(μ-S_2)Ru($S_2C_2B_{10}H_{10}$)$_2$.

Table 1 Crystallographic data and structural refinement details of compound **2**

Empirical formula	$C_{22}H_{46}B_{20}ORu_2S_4Se_2$•$H_2O$	*Z*	2
Formula weight	1049.10	ρ_{calc}/(g•cm^{-3})	1.509
Temperature/K	293(2)	Absorp. coeff. (mm^{-1})	2.434
Crystal size/mm	0.23×0.15×0.10	*F*(000)	1032
Crystal system	Triclinic	θ range/(°)	1.72 to 26
a/Å	10.5176(19)	Reflns collected	12236 [*R*(int) =0.0136]
b/Å	13.1714(11)	Indep. reflns	8809
c/Å	18.5995(17)	Refns obs. [$I>2\sigma(I)$]	4633
α/(°)	110.177(2)	Data/restr./paras	8809/0/479
β/(°)	90.217(3)	GOF	1.077
γ/(°)	106.084(2)	$R_1/wR_2[I>2\sigma(I)]$	0.0499/0.1123
Space group	*P*-1	R_1/wR_2 (all data)	0.1251/0.1280
V/Å^3	2309.7(5)	Larg. peak/hole (e•Å^{-3})	0.769/−0.614

3 Conclusions

The Se—Se bridged dinuclear complex (*p*-cymene)-Ru(μ-Se_2)Ru($S_2C_2B_{10}H_{10}$)$_2$ shows reactivity toward alkynyl achohol to give addition products which can lose water under mild conditions to lead to new-type products containing cyclohexenyl unit. Such products can exchange at higher temperature via M—S bond cleavage and re-generation. This reactivity paralells to its sulfur analog.

4 Experimental

4.1 General procedures

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 mol/L in cyclohexane, Aldrich), 1-ethynyl-1-cyclohexanol (Aldrich), other chemicals were used as commercial products without further purification. [(*p*-cymene)$RuCl_2$]$_2$[11] was prepared according to literature. 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 ^{1}H=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. Matrix-assisted laser desorption/ionization (MALDI) in a linear time-of-flight mass spectrometry (MS) was recorded in a Bruker autoflex TOF/TOF equipped with an acquisition operation mode of reflector and signal averaging of 30 laser shots.

4.2 Synthesis of 2 and 3

1-Ethynyl-1-cyclohexanol (126 mg, 1.0 mmol) was added to **1** (91 mg, 0.1 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 18 h at ambient temperature. After removal of the solvent the residue was chromatographed on silica to give **2** and **3** [petroleum ether/CH_2Cl_2 (1∶4)]. Recrystallization from CH_2Cl_2-hexane afforded yellow crystals of **2**.

2: Yield 44.1 mg (42%). m.p. (dec.) 223 ℃. ^{1}H NMR ($CDCl_3$) δ: 0.86, 1.23 (d, J=7.0 Hz, 3H, CH(C**H**$_3$)$_2$ for each), 1.52～2.39 (m, 2H, C**H**$_2$, *cyclo*-C_6H_{10} for each), 2.13 (s, 3H, CH_3), 2.66 (sept, 1H, C**H**(CH_3)$_2$), 3.77 (s, 1H, OH), 4.98, 5.03, 6.05, 6.09 (d, J=6.0 Hz, 1H, C_6H_4 for each), 7.08 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$) δ: 18.35 (C_6H_4-**C**H_3), 22.63, 22.91 (CH(**C**H_3)$_2$), 21.64, 21.91, 22.46, 25.01, 29.66 (CH_2 in *cyclo*-C_6H_{10}), 31.31 (**C**H(CH_3)$_2$), 75.81 (COH), 80.14, 81.35, 81.96, 85.76 (**C**H in *p*-cymene), 90.29, 95.17, 96.78, 99.19, 99.73, 106.78 (*o*-carborane and quaternary C in *p*-cymene), 136.67 (**C**=CH), 159.15 (H**C**=C). ^{11}B{^{1}H} NMR ($CDCl_3$) δ: −0.68, −1.03, −1.92, −4.88, −7.23 (2∶1∶3∶2∶2); IR (KBr): 2581 (ν_{B-H}) cm^{-1}; MALDI-TOF MS (m/z) calcd for $C_{22}H_{46}B_{20}ORu_2S_4Se_2$: 1031.14; found 1032.23 ($[M+H]^+$, 80%). Anal. calcd for $C_{22}H_{46}B_{20}ORu_2S_4Se_2$•$H_2O$: C 25.16, H 4.57; found C 24.83, H 4.69.

3: Yield 44.3 mg (43%). m.p. (dec.) 221 ℃; ^{1}H NMR ($CDCl_3$) δ: 0.87, 1.24 (d, J=7.0 Hz, 3H, CH(C**H**$_3$)$_2$ for each), 1.53～2.39 (m, 2H, C**H**$_2$, *cyclo*-C_6H_{10} for each), 2.12 (s, 3H, CH_3), 2.65 (sept, 1H, C**H**(CH_3)$_2$), 3.76 (s, 1H, OH), 4.99, 5.06, 6.03, 6.08 (d,

J=6.0 Hz, 1H, C_6H_4 for each), 7.07 (s, 1H, HC=C). ^{13}C NMR ($CDCl_3$) δ: 18.37 (C_6H_4-**C**H_3), 22.61, 22.73 (CH(**C**H_3)$_2$), 21.69, 21.93, 22.65, 24.99, 29.61 (CH_2 in *cyclo*-C_6H_{10}), 31.32 (**C**H(CH$_3$)$_2$), 75.76 (COH), 80.11, 81.26, 81.79, 85.43 (**C**H in *p*-cymene), 90.16, 94.91, 96.87, 99.12, 99.71, 106.69 (*o*-carborane and quaternary C in *p*-cymene), 136.57 (**C**=CH), 159.09 (H**C**=C); ^{11}B{^{1}H} NMR ($CDCl_3$) δ: −0.69, −1.05, −1.93, −4.91, −7.26 (2∶1∶3∶2∶2); IR (KBr) ν: 2583 ($\nu_{B—H}$) cm^{-1}. MALDI-TOF MS (m/z) calcd for $C_{22}H_{46}B_{20}ORu_2S_4Se_2$: 1031.14; found 1032.23 ([M+H]$^+$, 80%). Anal. calcd for $C_{22}H_{46}B_{20}ORu_2S_4Se_2$: C 25.61, H 4.46; found C 25.25, H 4.30.

4.3 Synthesis of 4 and 5

The solution of **2** (0.41 g, 0.40 mmol) or **3** (0.41 g, 0.40 mmol) in chloroform (10 mL) was refluxed for 24 h to give a dark yellow solution. After removal of the solvent the residue was chromatographed on silica to give **4** or **5** [petroleum ether/CH_2Cl_2 (1∶2)].

4: Yield 0.33 g (80%). m.p. (dec.) 225 ℃. ^{1}H NMR ($CDCl_3$) δ: 0.86, 1.24 (d, J=7.0 Hz, 3H, CH(C**H**$_3$)$_2$ for each), 1.50～2.45 (m, 2H, C**H**$_2$, *cyclo*-C_6H_9 for each), 2.25 (s, 3H, CH_3), 2.69 (sept, 1H, C**H**(CH$_3$)$_2$), 5.01, 5.08, 6.09, 6.16 (d, J=6.0 Hz, 1H, C_6H_4 for each), 6.70～6.73 (m, 1H, C=C**H**, *cyclo*-C_6H_9), 6.89 (s, 1H, **H**C=C—S); ^{13}C NMR ($CDCl_3$) δ: 18.79 (C_6H_4-**C**H_3), 22.58, 22.71 (CH(**C**H_3)$_2$), 21.23, 22.19, 23.05, 29.72 (CH_2 in *cyclo*-C_6H_9), 31.79 (**C**H(CH$_3$)$_2$), 80.11, 80.86, 83.01, 85.21 (**C**H in *p*-cymene), 90.51, 92.33, 93.73, 99.56, 104.01, 106.78 (*o*-carborane and quaternary C in *p*-cymene), 127.98 (**C**=CH, *cyclo*-C_6H_9), 131.34 (H**C**=C, *cyclo*-C_6H_9), 135.63 (S–**C**=), 151.81 (S–C=**C**H). ^{11}B{^{1}H} NMR ($CDCl_3$) δ: −0.59, −1.16, −1.83, −5.13, −7.26 (2∶1∶3∶2∶2). IR (KBr): 2578 ($\nu_{B—H}$) cm^{-1}; MALDI-TOF MS (m/z): calcd for $C_{22}H_{44}B_{20}Ru_2S_4Se_2$: 1013.12; found 1014.29 ([M+H]$^+$, 75%). Anal. calcd for $C_{22}H_{44}B_{20}Ru_2S_4Se_2$: C 26.05, H 4.34; found C 25.68, H 4.51.

5: Yield 0.32 g (79%). m.p. (dec.) 224 ℃; ^{1}H NMR ($CDCl_3$) δ: 0.88, 1.23 (d, J=7.0 Hz, 3H, CH(C**H**$_3$)$_2$ for each), 1.51～2.46 (m, 2H, C**H**$_2$, *cyclo*-C_6H_9 for each), 2.26 (s, 3H, CH_3), 2.69 (sept, 1H, C**H**(CH$_3$)$_2$), 4.97, 5.11, 6.10, 6.12 (d, J=6.0 Hz, 1H, C_6H_4 for each), 6.71～6.73 (m, 1H, C=C**H**, *cyclo*-C_6H_9), 6.91 (s, 1H, **H**C=C—S); ^{13}C NMR ($CDCl_3$) δ: 18.44 (C_6H_4-**C**H_3), 22.56, 22.70 (CH(**C**H_3)$_2$), 21.23, 22.31, 23.12, 29.88 (CH_2 in *cyclo*-C_6H_9), 31.73 (**C**H(CH$_3$)$_2$), 80.18, 80.82, 82.93, 85.68 (**C**H in *p*-cymene), 91.13, 93.67, 94.34, 99.41, 103.98, 106.86 (*o*-carborane and quaternary C in *p*-cymene), 128.08 (**C**=CH, *cyclo*-C_6H_9), 131.62 (H**C**=C, *cyclo*-C_6H_9), 135.98 (S–**C**=), 151.97 (S–C=**C**H). ^{11}B{^{1}H} NMR ($CDCl_3$) δ: −0.62, −1.19, −1.93, −5.18, −7.43 (2∶1∶3∶2∶2); IR (KBr): 2579 ($\nu_{B—H}$) cm^{-1}; MALDI-TOF MS (m/z): calcd for $C_{22}H_{44}B_{20}Ru_2S_4Se_2$, 1013.12; found 1014.28 ([M+H]$^+$, 75%). Anal. calcd for $C_{22}H_{44}B_{20}Ru_2S_4Se_2$: C 26.05, H 4.34; found C 25.81, H 4.46.

4.4 X-ray structure determinations

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. The structures were solved by direct methods using the SHELXL-97 program.[12] 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 (Table 1).

CCDC-921956 (for **2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) Xie, Z. *Coord. Chem. Rev.* **2006**, *250*, 259; (b) Deng, L.; Xie, Z. *Coord. Chem. Rev.* **2007**, *251*, 2452; (c) Armstronga, A. F.; Valliant, J. F. *Dalton Trans.* **2007**, 4240; (d) Liu, D.; Dang, L.; Sun, Y.; Chan, H. S.; Lin, Z.; Xie, Z. *J. Am. Chem. Soc.* **2008**, *130*, 16103.

[2] (a) Hawthorne, M. F.; Zink, J. I.; Skelton, J. M.; Bayer, M. J.; Liu, C.; Livshits, E.; Baer, R.; Neuhauser, D. *Science* **2004**, *303*, 1849; (b) Wedge, T. J.; Hawthorne, M. F. *Coord. Chem. Rev.* **2003**, *240*, 111; (c) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1; (d) Lee, J. D.; Lee, Y. J.; Son, K. C.; Cheong, M.; Ko, J.; Kang, S. O. *Organometallics* **2007**, *26*, 3374.

[3] (a) Núñez, R.; Tutusaus, O.; Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Organometallics* **2004**, *23*, 2273; (b) Chizhevsky, I. T. *Coord. Chem. Rev.* **2007**, *251*, 1590; (c) Juhasz, M.; Hoffmann, S.; Stoyanov, E.; Kim, K. C.; Reed, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5352.

[4] (a) Meng, X.; Wang, F. S.; Jin, G. X. *Coord. Chem. Rev.* **2010**, *254*, 1260; (b) Liu, S.; Han, Y. F.; Jin, G. X. *Chem. Soc. Rev.* **2007**, *36*, 1543; (c) Jin, G. X. *Coord. Chem. Rev.* **2004**, *248*, 587; (d) Yao, Z. J.; Jin, G. X. *Organometallics* **2011**, *30*, 5365; (e) Zhang, J. S.; Lin, Y. J.; Jin, G. X. *J. Organomet. Chem.* **2009**, *694*, 2069; (f) Yao, Z. J.; Su, G.; Jin, G. X. *Chem. Eur. J.* **2011**, *17*, 13298; (g) Yao, Z. J.; Jin, G. X. *Coord. Chem. Rev.* **2013**, *257*, in press (doi: 10.1016/j.ccr.2013.02.004).

[5] (a) Xu, B. H.; Peng, X. Q.; Li, Y. Z.; Yan, H. *Chem. Eur. J.* **2008**, *14*, 9347; (b) Xu, B. H.; Tao, J. C.; Li, Y. Z.; Li, S. H.; Yan, H. *Organometallics* **2008**, *27*, 334; (c) Li, Y. G.; Jiang, Q. B.; Zhang, X. L.; Li, Y. Z.; Yan, H.; Bregadze, V. I. *Inorg. Chem.* **2010**, *49*, 3911; (d) Ye, H. D.; Ding, G. Y.; Xie, M. S.; Li, Y. Z.; Yan, H. *Dalton Trans.* **2011**, *40*, 2036; (e) Li, Y. G.; Jiang, Q. B.; Li, Y. Z.; Yan, H.; Bregadze, V. I. *Inorg. Chem.* **2010**, *49*, 4.

[6] (a) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *J. Organomet. Chem.* **2000**, *604*, 170; (b) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Angew. Chem. Int. Ed.* **1999**, *38*, 3689; (c) Wang, J. Q.; Cai, S. Y.; Jin, G. X.; Weng, L. H.; Herberhold, M. *Chem. Eur. J.* **2005**, *11*, 7342; (d) Jin, G. X.; Wang, J. Q.; Zhang, C.; Weng, L. H.; Herberhold, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 259; (e) Zhang, J. S.; Lin, Y. J.; Jin, G. X. *Dalton Trans.* **2009**, 111; (f) Wang, J. Q.; Ren, C. X.; Weng, L. H.; Jin, G. X. *Chem. Commun.* **2006**, 162.

[7] (a) Hu, J. R.; Liu, G. F.; Jiang, Q. B.; Zhang, R.; Huang, W.; Yan, H. *Inorg. Chem.* **2010**, *49*, 11199; (b) Hu, J. R.; Wen, J. L.; Wu, D. H.; Zhang, R.; Liu, G. F.; Jiang, Q. B.; Li, Y. Z.; Yan, H. *Organometallics* **2011**, *30*, 298; (c) Hu, J. R.; Tang, X.; Liu, G. F.; Jiang, Q. B.; Duanmu, D. D.; Li, Y. Z.; Yan, H. *J. Organomet. Chem.* **2012**, *721-722*, 36.

[8] (a) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem. Eur. J.* **2000**, *6*, 3026; (b) Herberhold, M.; Yan, H.; Milius, W.; Wrackmeyer, B. *Chem. Eur. J.* **2002**, *8*, 388; (c) Wu, D. H.; Wu, C. H.; Li, Y. Z.; Guo, D. D.; Wang, X. M.; Yan, H. *Dalton Trans.* **2009**, 285; (d) Herberhold, M.; Yan, H.; Milius, W. *J. Organomet. Chem.* **2000**, *598*, 142.

[9] (a) Wu, D. H.; Ji, C.; Li, Y. Z.; Yan, H. *Organometallics* **2007**, *26*, 1560; (b) Wu, D. H.; Xu, B. H.; Li, Y. Z.; Yan, H. *Organometallics*

2007, *26*, 6300.
[10] Wu, D. H.; Li, Y. G.; Han, L.; Li, Y. Z.; Yan, H. *Inorg. Chem.* **2008**, *47*, 6524.
[11] Bennett, M. A.; Huang, T. N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.
[12] *Bruker*, *SMART* (Version 5.0), *SAINT* (Version 6), *SHELXTL* (Version 6.1) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA, **2000**.

(Lu, Y.)

