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Mixed-Valent Diruthenium Half-Sandwich Complexes Containing Two Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dithiolate Ligands: Reactivity towards Phenylacetylene, 1,4-Diethynylbenzene, and Ethynylferrocene

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Treatment of **1a** and **1b** with phenylacetylene, 1,4-diethynylbenzene, and ethynylferrocene affords addition complexes, (p-cymene)Ru(μ-E$_2$)Ru(S$_2$C$_2$B$_{10}$H$_{10}$)$_2$(R$_1$C=CR$_2$), (R$_1$ = Ph (H), R$_2$ = H (Ph), **2a**, **2b**, **3a**, **3b**; R$_1$ = −Ph−C≡CH (H), R$_2$ = H (−Ph−C≡CH), **4a**, **4b**, **5a**, **5b**; R$_1$ = Fc (H), R$_2$ = H (Fc), **6a**, **6b**, **7a**, **7b**). Alkyne addition occurs at sulfur atoms of two different chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligands that leads to a change of 16e Ru(IV) in **1a** and **1b** to 18e Ru(II) in **2a**−**7a** and **2b**−**7b**, respectively. Moreover, the reaction of **1a** with ethynylferrocene produces an unprecedented tetranuclear mixed-valent Ru(IV)Ru(II)$_3$S$_{12}$ cluster (**8a**) consisting of two **1a** and one ethynylferrocene through the cleavage and generation of Ru−S, S−S, and C−S bonds. The complexes were characterized by IR, MS, and NMR spectroscopy and microanalysis. X-ray structural analyses were performed on **1b**, **2a**, **3b**, **5a**, **5b**, **7b**, and **8a**.

Introduction

Research focusing on 1,2-dicarba-*closo*-dodecaborane derivatives has attracted enormous attention because of their unique molecular structures, fundamental properties, and a variety of potential applications in microelectronics, optics, medicines, and material synthesis during the past decades.[1,2] Mononuclear 16e half-sandwich Co, Rh, Ir, Ru, and Os complexes containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand, $[E_2C_2B_{10}H_{10}]^{2-}$ (E = S, Se) have been described extensively.[3,4] These sterically congested, mononuclear coordination compounds are stable starting materials and have exhibited rich reaction chemistries.[3–5] For instance, they can undergo insertion of alkynes to metal-chalcogen bonds that further leads to B−H activation, formation of metal−boron bonds, and functionalization of the carborane cage in B(3)/B(6) positions.[4] Moreover, construction of novel poly carborane molecular architectures using two or more $[S_2C_2(B_{10}H_{10})]^{2-}$ units were described.[6,7] One metalation product, [1-(σ-S)-2-(η^5-C$_5$H$_4$CH(Ph))-1,2-C$_2$B$_{10}$H$_{10}$)]Ti(NMe$_2$)$_2$, was also synthesized where the ap-

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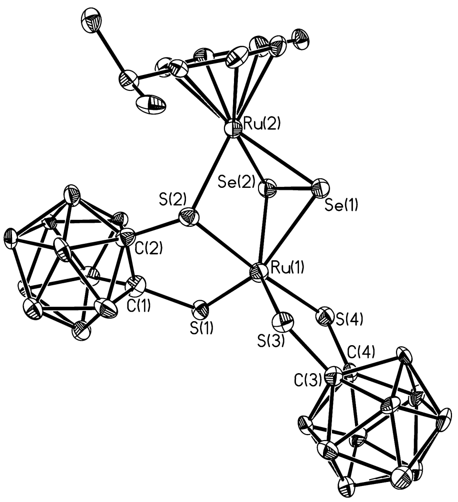


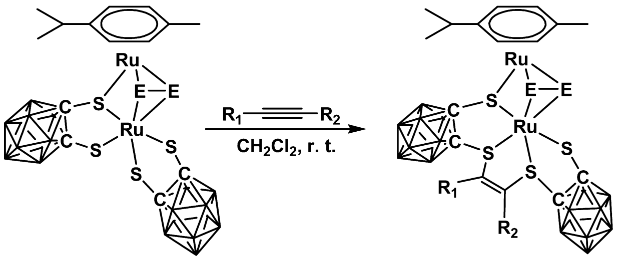
Figure 1. Molecular structure of **1b** with ellipsoids at a 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)−S(1) = 2.2146(18), Ru(1)−S(2) = 2.3976(17), Ru(1)−S(3) = 2.2030(17), Ru(1)−S(4) = 2.3749(18), Ru(1)−Se(1) = 2.5082(9), Ru(1)−Se(2) = 2.5271(9), Ru(2)−S(2) = 2.4327(16), Ru(2)−Se(1) = 2.5036(9), Ru(2)−Se(2) = 2.4954(9), Se(1)−Se(2) = 2.3078(10), C(1)−S(1) = 1.760(7), C(2)−S(2) = 1.831(7), C(3)−S(3) = 1.784(6), C(4)−S(4) = 1.784(6), C(1)−C(2) = 1.696(9), C(3)−C(4) = 1.658(9), Ru(1)···Ru(2) = 3.486; S(1)−Ru(1)−S(3) = 117.28(6), S(1)−Ru(1)−S(4) = 85.62(6), Se(1)−Ru(1)−Se(2) = 54.56(2).

pended carboranyl-thiol unit acts as both a linking and η^1-bonding group.[8] Two mixed-valent diruthenium complexes containing two $[S_2C_2B_{10}H_{10}]^{2-}$ units and one E−E (E = S, Se) bridging ligand and their preliminary reactivity with alkynes were reported by our group.[6] As a continuation of this chemistry, we further report on the reaction chemistries of **1a** and **1b** with phenylacetylene, 1,4-diethynylbenzene, and ethynylferrocene that lead to (*p*-cymene)Ru(μ-E_2)Ru($S_2C_2B_{10}H_{10}$)$_2$($R_1C{=}CR_2$) (R_1 = Ph (H), R_2 = H (Ph), **2a**, **2b**, **3a**, **3b**; R_1 = −Ph−C≡CH (H), R_2 = H (−Ph−C≡CH), **4a**, **4b**, **5a**, **5b**; R_1 = Fc (H), R_2 = H (Fc), **6a**, **6b**, **7a**, **7b**) as well as an unprecedented tetranuclear mixed-valent Ru(IV)Ru(II)$_3$S$_{12}$ cluster (*p*-cymene)$_2$Ru$_4$S$_4$($S_2C_2B_{10}H_{10}$)$_4$-(HC=CFc) (**8a**), containing two *p*-cymene groups, one ferrocenyl unit, and four 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligands.

Results and Discussion

The compounds **1a** and **1b** were previously reported by our group but lack the solid-state structure of **1b**.[6b] Suitable green block crystals of **1b** were lately obtained from CD_2Cl_2 solution at ambient temperature. Its solid-state structure (Figure 1) shows an analogous structure with **1a**, differing in a bridging S−S bond replacement by a Se−Se (2.3078 Å) one. The angles of S(1)−Ru(1)−S(3) and S(1)−Ru(1)−S(4) are 117.28°, 85.62° in **1b** versus 117.30°, 85.22° in **1a**, showing no significant difference. Thus, the large angle of S(1)−Ru(1)−S(3) likewise introduces considerable strain to the structure. However, the angle of Se(1)−Ru(1)−Se(2) (54.56°) in **1b** is larger than S(5)−Ru(1)−S(6) (50.29°) in **1a**. This may reduce the structural strain of **1b** relative to **1a**. Similarly, Ru(1) is electronically unsaturated (16e) with a charge of +4, and Ru(2) is electronically saturated (18e) with a charge of +2 in **1b**. Therefore, the 16e Ru(IV) center and the large angle of S(1)−Ru(1)−S(3) in both **1a** and **1b** predict their reactivity.

Scheme 1. Reactions of **1a**, **1b** with Phenylacetylene, 1,4-Diethynylbenzene



1a (E = S)
1b (E = Se)

2a - 5a (E = S)
2b - 5b (E = Se)

E = S	2a	3a	4a	5a
R_1 =	Ph	H	—Ph—≡CH	H
R_2 =	H	Ph	H	—Ph—≡CH

E = Se	2b	3b	4b	5b
R_1 =	Ph	H	—Ph—≡CH	H
R_2 =	H	Ph	H	—Ph—≡CH

Reaction of 1a or 1b with Phenylacetylene. The reaction of **1a** with PhC≡CH affords two geometrical isomers **2a** and **3a** in a ratio of approximately 1:1 (Scheme 1) on the basis of NMR measurements. Different from the products from the reaction with $HC{\equiv}CCO_2Me$,[6] **2a** and **3a** cannot be separated by chromatography. The solid-state structure of **2a** (Figure 2) indicates that the terminal carbon atom is bonded to S(3) rather than S(1). The alkyne addition selectively occurs at S(1) and S(3) sites to generate an almost planar five-membered RuSCCS ring with a mean deviation from the plane of 0.0421 Å. As a consequence, two saturated Ru(II)/Ru(II) (18e/18e) atoms in **2a** correspond to two mixed-valent Ru(II)/Ru(IV) (18e/16e) ones in **1a**. In **3a** the terminal carbon atom of the alkyne is bonded to S(1) rather than S(3). The experimental results demonstrate that the phenyl group does not significantly affect the regioselectivity of the alkyne addition as observed in $HC{\equiv}CCO_2Me$.[6] Note that the two characteristic olefinic proton signals are observed at 7.18 and 7.24 ppm, but the other ^1H signals are overlapped for **2a** and **3a**. The olefinic carbon signals are recognized as 132.8, 134.4 (H*C*=C) and 133.8, 133.9 (*C*=CH) through 2D $^{13}C/^1H$ HETCOR (HMQC, HMBC) experiments.

In the case of **1b**, the reaction with phenylacetylene leads to two isomers of **2b** and **3b** in a ratio of approximately 1:1 without being separated by chromatography (Scheme 1). The solid-state structure of **3b** (Figure 2) demonstrates that the terminal carbon atom of the alkyne is bonded to S(1) rather than S(3). The two characteristic olefinic proton signals appear at 7.22 and 7.26 ppm, and the rest of the ^1H signals are overlapped for **2b** and **3b**.

Reaction of 1a or 1b with 1,4-Diethynylbenzene. The treatment of **1a** and **1b** with 1,4-diethynylbenzene generates **4a**, **5a** and **4b**, **5b**, respectively, in a ratio of approximate 1:1 without being separated by chromatography (Scheme 1). The solid-state structures of **5a** and **5b** (Figure 3) indicate that the alkyne addition selectively occurs at S(1) and S(3)

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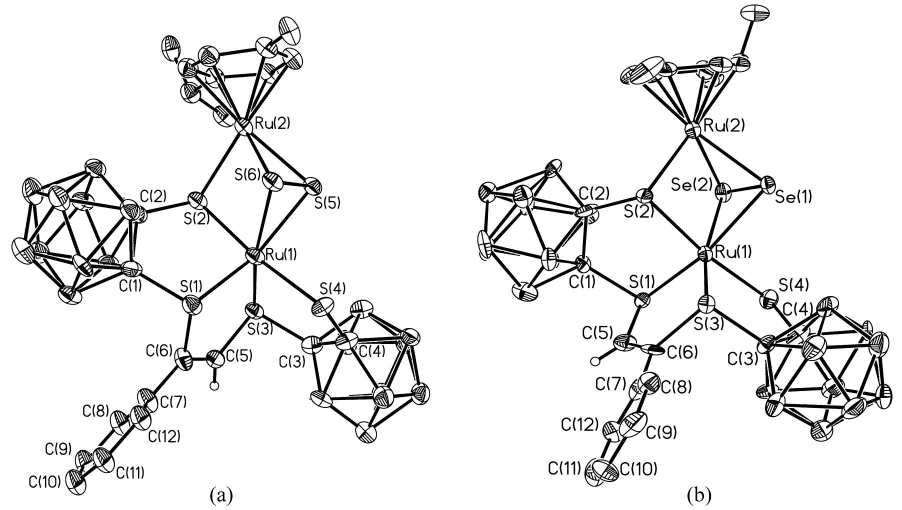


Figure 2. Molecular structures of **2a** (a) and **3b** (b) with ellipsoids at a 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): **2a**: Ru(1)−S(1) = 2.2394(19), Ru(1)−S(2) = 2.3742(19), Ru(1)−S(3) = 2.2692(18), Ru(1)−S(4) = 2.3818(19), Ru(1)−S(5) = 2.3901(17), Ru(1)−S(6) = 2.4062(18), S(5)−S(6) = 2.030(2), C(6)−S(1) = 1.789(7), C(5)−S(3) = 1.734(7), C(5)−C(6) = 1.394(10), Ru(1)···Ru(2) = 3.419; S(1)−Ru(1)−S(3) = 87.35(6), S(1)−Ru(1)−S(4) = 91.41(6), S(5)−Ru(1)−S(6) = 50.08(6). **3b**: Ru(1)−S(1) = 2.2811(17), Ru(1)−S(2) = 2.3903(16), Ru(1)−S(3) = 2.2597(17), Ru(1)−S(4) = 2.3565(17), Ru(1)−Se(1) = 2.5211(9), Ru(1)−Se(2) = 2.5191(8), Se(1)−Se(2) = 2.3192(10), C(5)−S(1) = 1.764(7), C(6)−S(3) = 1.843(7), C(5)−C(6) = 1.317(10), Ru(1)···Ru(2) = 3.480; S(1)−Ru(1)−S(3) = 88.41(6), S(1)−Ru(1)−S(4) = 92.32(6), Se(1)−Ru(1)−Se(2) = 54.79(2).

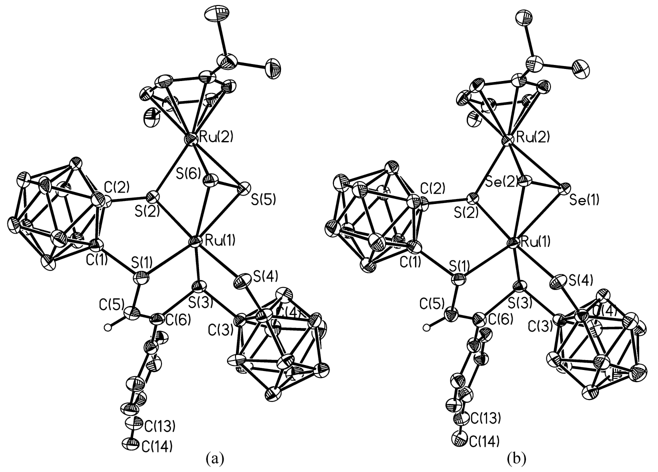


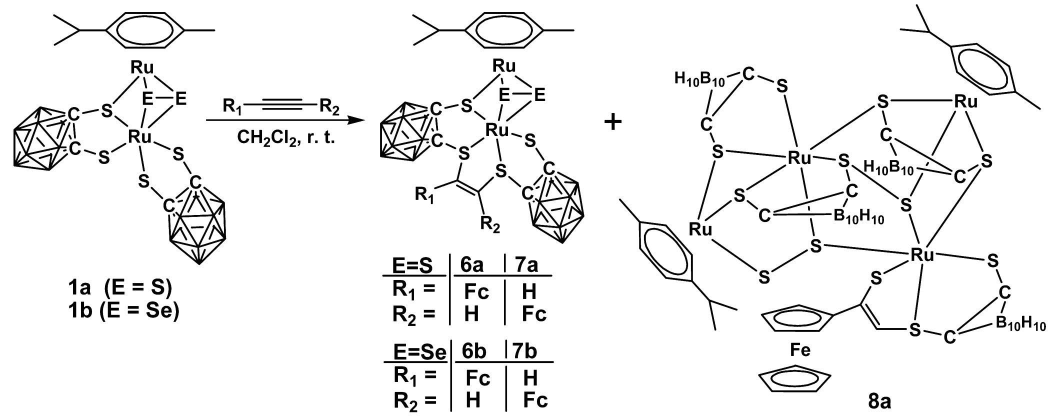
Figure 3. Molecular structures of **5a** (a) and **5b** (b) with ellipsoids at a 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): **5a**: Ru(1)−S(1) = 2.2588(12), Ru(1)−S(2) =2.3759(11), Ru(1)−S(3) = 2.2649(11), Ru(1)−S(4) = 2.3692(12), Ru(1)−S(5) = 2.4066(12), Ru(1)−S(6) = 2.4031(11), S(5)−S(6) = 2.0429(16), C(5)−S(1) = 1.766(5), C(6)−S(3) = 1.814(5), C(5)−C(6) = 1.322(7), C(13)−C(14) = 1.193(8), C(1)−C(2) = 1.696(6), C(3)−C(4) = 1.673(6), Ru(1)···Ru(2) = 3.422; S(1)−Ru(1)−S(3) = 87.32(4), S(1)−Ru(1)−S(4) = 91.04(5), S(5)−Ru(1)−S(6) = 50.27(4). **5b**: Ru(1)−S(1) = 2.3048(12), Ru(1)−S(2) = 2.4254(11), Ru(1)−S(3) = 2.2622(11), Ru(1)−S(4) = 2.3789(12), Ru(1)−Se(1) = 2.5360(6), Ru(1)−Se(2) = 2.5285(6), Se(1)−Se(2) = 2.3157(6), C(5)−S(1) = 1.870(5), C(6)−S(3) = 1.827(5), C(5)−C(6) = 1.337(7), C(13)−C(14) = 1.220(8), C(1)−C(2) = 1.661(6), C(3)−C(4) = 1.656(6), Ru(1)···Ru(2) = 3.510; S(1)−Ru(1)−S(3) = 88.53(4), S(1)−Ru(1)−S(4) = 90.33(5), Se(1)−Ru(1)−Se(2) = 54.418(15).

sites and the terminal carbon atom is bonded to S(1) site. The alkyne addition leads to a Ru(II) (18e) center from a Ru(IV) (16e) one in **1a** or **1b**. In **4a** and **4b** the terminal carbon atom of the alkyne is bonded to S(3) rather than S(1). Apart from the two olefinic proton signals at 7.19 and 7.21 ppm, the other ^{1}H signals are still overlapped in **4a** and **5a**. However, in **4b** and **5b** two sets of discrete^{1}H signals are observed.

Reaction of 1b with Ethynylferrocene. The treatment of **1b** with FcC≡CH leads to **6b** and **7b** in a ratio of approximate 1:1 from the nonregioselective addition of the alkyne (Scheme 2). The two isomers can be well separated on column chromatography. The olefinic proton appears at 7.04 and 7.09 ppm in **6b** and **7b**, respectively. The carbon signals at 125.8 (H*C*=C), 147.8 (*C*=CH) ppm in **6b** and 126.3 (H*C*=C), 149.9 (*C*=CH) ppm in **7b** further show the presence of a C=C bond. The MALDI-TOF MS spectrum demonstrates an intense $[M + H]^+$ peak for both **6b** and **7b**. The solid-state structure of **7b** (Figure 4) further verifies that the alkyne addition is in the same manner as observed in **3b** and **5b**.

Reaction of 1a with Ethynylferrocene. The treatment of **1a** with FcC≡CH leads to **6a** and **7a** in a ratio of approximate 1:1. Analogous to **6b** and **7b**, they can be separated by chromatography. The spectroscopic data along with microanalysis support the proposed structures in Scheme 2. Interestingly, an unprecedented tetranuclear (*p*-cymene)$_2$Ru$_4$S$_4$(S$_2$C$_2$B$_{10}$H$_{10}$)$_4$-(HC=CFc), **8a**, was also isolated from this reaction (Scheme 2). The single-crystal structure (Figure 5) analysis shows a large cluster with a Ru$_4$S$_{12}$ core. Ru(2) is a three-legged piano stool with the ruthenium atom bonded to a *p*-cymene ring in an η^6-fashion, one S atom from the broken S−S bond in **1a**, and two S atoms from one individual 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate ligand. Ru(4) is the other three-legged piano stool with the ruthenium atom bonded to a *p*-cymene ring in an η^6-mode, two S atoms from two chelating $[S_2C_2B_{10}H_{10}]^{2-}$ ligands, and one S atom from a S−S unit. Both Ru(1) and Ru(3) are in slightly distorted octahedral environments defined by six sulfur atoms. Ru(1) is surrounded by three S atoms from two S−S units, and three S atoms from two individual $[S_2C_2B_{10}H_{10}]^{2-}$ ligands, whereas Ru(3) is connected to one S atom from the S−S unit, and five S atoms from three individual $[S_2C_2B_{10}H_{10}]^{2-}$ ligands.

Scheme 2. Reactions of **1a**, **1b** with Ethynylferrocene



The four Ru(1), Ru(2), Ru(3), Ru(4) atoms are almost coplanar with mean deviation from the plane of 0.0676 Å. The Ru···Ru distances of 3.51−5.59 Å preclude any metal−metal interactions owing to the typical Ru−Ru single bond of 2.71−3.02 Å.[9] Each of the twelve S atoms has a charge of −1, thus, the electron counts for Ru(1), Ru(2), and Ru(4) are saturated (18e) with a charge of +2. Ru(3), however, is electron-deficient (16e) with a charge of +4.

Apart from the distorted octahedron around the Ru(1) center that introduces considerable strain to the structure,[6] the S−S bond in **1a** that constructs the constrained triangles of S(5)−Ru(2)−S(6) and S(5)−Ru(1)−S(6) predicts potential reactivity as well. In generation of **8a**, the reaction may initiate attack of the alkyne at the unsaturated Ru center in **1a**, followed by the formation of C−S bonds at the sulfur sites of both $[S_2C_2B_{10}H_{10}]^{2-}$ and S−S units that further leads to the cleavage of the S−S bond. The other S atom of the broken S−S bridge is linked to one new **1a** via S(10)−S(5) bond, and subsequently resulting in more bonds between two molecules of **1a** through Ru−S bonds. Note that the analogous **1b** does not show the same reactivity. Likely, the larger radius of selenium reduces the strain of the triangles of Se(1)Ru(1)Se(2) and Se(1)Ru(2)Se(2) relative to that in **1a**, thus hampering the reactivity of the Se−Se bond. So far ethynylferrocene is the only alkyne that generates a complex structural type of **8a**.

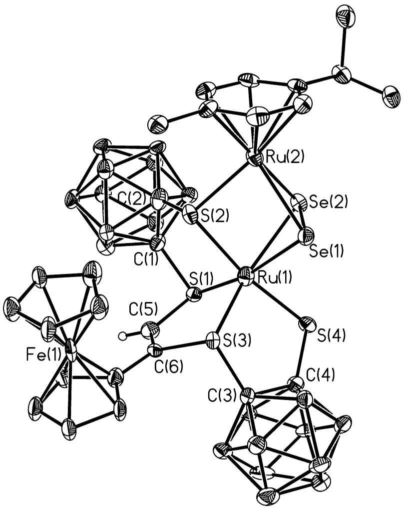


Figure 4. Molecular structure of **7b** with ellipsoids at a 30% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)−S(1) = 2.2676(17), Ru(1)−S(2) = 2.3894(19), Ru(1)−S(3) = 2.2418(18), Ru(1)−S(4) = 2.3828(18), Ru(1)−Se(1) = 2.5111(9), Ru(1)−Se(2) = 2.5542(10), Se(1)−Se(2) = 2.2891(11), C(5)−S(1) = 1.784(7), C(6)−S(3) = 1.804(7), C(5)−C(6) = 1.285(10), C(1)−C(2) = 1.684(10), C(3)−C(4) = 1.657(9), Ru(1)···Ru(2) = 3.484; S(1)−Ru(1)−S(3) = 86.12(6), S(1)−Ru(1)−S(4) = 94.02(6), Se(1)−Ru(1)−Se(2) = 53.72(3).

Formation Mechanism for 1:1 Adducts. The proposed mechanism for the formation of 1:1 adducts is shown in Scheme 3. On the basis of the large angles of S(1)−Ru(1)−S(3) (~117.3°) and the electronically unsaturated (16e) Ru(1) centers in **1a** and **1b**, an alkyne may be first attached to the Ru(1) atom in the perpendicular direction of the S(1)···S(3) vector to generate a 18e species **A**. Then the coordinated C≡C bond rotates to get close to either S(1) or S(3) in an equal probability. The next step is to form a C−S bond that is accompanied by a change from a covalent S−Ru bond to a coordinative S→Ru bond, thus leading to a 17e species **B**. Then, the second C−S bond is formed as the second coordinative S→Ru bond is generated from a covalent S−Ru bond. As a result, the electronically unsaturated Ru(IV) center is changed to electronically saturated Ru(II), and the angle of S(1)−Ru(1)−S(3) is reduced from 117° to close to 90°, generating more stable products **2a**−**7a**, **2b**−**7b**. This may explain the approximate ratio of 1:1 of the two geometrical isomers for either a larger (Fc) or a smaller (COOMe) group in a used terminal alkyne.

Conclusions

The solid-state structures of **1a** and **1b** reveal the 16e Ru(IV) center in a distorted octahedron geometry and the largely strained S(1)−Ru(1)−S(3) angle that destine their reactivity. The reaction with an alkyne takes place at two sulfur atoms of two individual $[S_2C_2B_{10}H_{10}]^{2-}$ ligands opposite to the bridging S−S, or Se−Se unit. The resulting adducts **2a**−**7a**, **2b**−**7b** are more stable owing to the reduced structural strain and the formation of a 18e Ru(II) center. The substituent groups of the used terminal alkynes, phenylacetylene, 1,4-diethynylbenzene, ethynylferrocene, and

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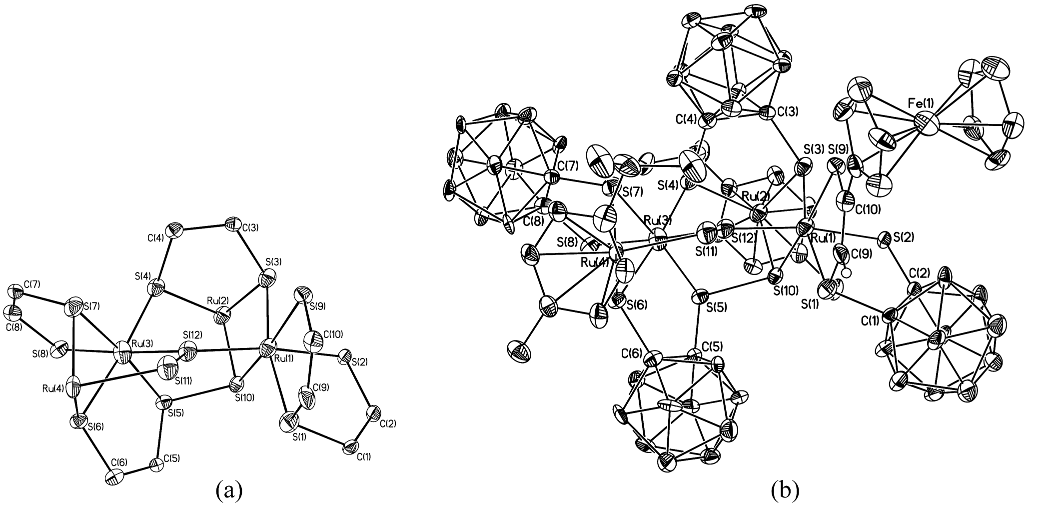


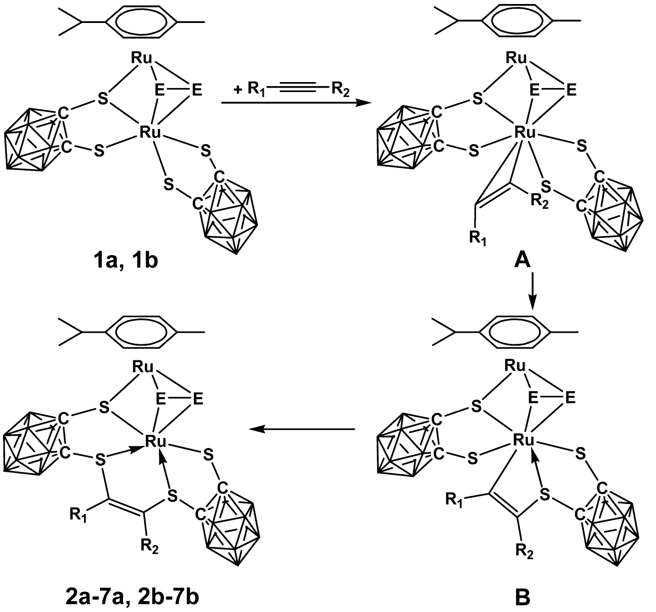
Figure 5. (a) **$Ru_4S_{12}C_{10}$** skeleton in **8a**; (b) Molecular structure of **8a** (30% probability displacement ellipsoids), hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Ru(1)−S(1) = 2.3311(19), Ru(1)−S(2) = 2.4161(15), Ru(1)−S(3) = 2.4486(19), Ru(1)−S(9) = 2.3240(17), Ru(1)−S(10) = 2.4346(18), Ru(1)−S(12) = 2.2110(17), Ru(2)−S(3) = 2.3948(19), Ru(2)−S(4) = 2.4279(17), Ru(2)−S(10) = 2.3720(19), Ru(3)−S(4) = 2.4232(19), Ru(3)−S(5) = 2.2916(17), Ru(3)−S(6) = 2.3276(18), Ru(3)−S(7) = 2.3816(17), Ru(3)−S(8) = 2.4073(18), Ru(3)−S(12) = 2.2137(18), Ru(4)−S(6) = 2.4074(18), Ru(4)−S(7) = 2.486(2), Ru(4)−S(11) = 2.3281(16), S(5)−S(10) = 2.151(2), S(11)−S(12) = 1.998(2), C(9)−C(10) = 1.323(10), C(9)−S(1) = 1.738(7), C(10)−S(9) = 1.779(6), Ru(1)···Ru(2) = 3.645, Ru(2)···Ru(3) = 3.975, Ru(3)···Ru(4) = 3.509, Ru(4)···Ru(1) = 5.590; S(9)−Ru(1)−S(12) = 97.52(6), S(1)−Ru(1)−S(12) = 89.99(7), S(1)−Ru(1)−S(9) = 85.55(6), S(2)−Ru(1)−S(12) = 167.62(6), S(2)−Ru(1)−S(9) = 94.82(6), S(1)−Ru(1)−S(2) = 89.99(6), S(10)−Ru(1)−S(12) = 84.90(6), S(9)−Ru(1)−S(10) = 170.58(6), S(1)−Ru(1)−S(10) = 103.59(6), S(2)−Ru(1)−S(10) = 83.07(6), S(3)−Ru(1)−S(12) = 102.98(6), S(3)−Ru(1)−S(9) = 91.30(6), S(1)−Ru(1)−S(3) = 166.96(6), S(2)−Ru(1)−S(3) = 77.65(6), S(3)−Ru(1)−S(10) = 79.29(6).

methyl propiolate, do not markedly affect the regioselectivity of the alkyne addition, thus, generating approximate 1:1 adducts. However, they significantly affect the reaction rate, for instance, CO_2Me > Fc > Ph ∼ $-Ph-C{\equiv}CH$. A structural change from a S−S bond to a Se−Se one decreases alkyne addition. The reaction of **1a** with ethynylferrocene leads to an extra novel cluster (*p*-cymene)$_2$$Ru_4S_4(S_2C_2B_{10}H_{10})_4$-(HC=CFc) (**8a**) with the alkyne addition at both S−S bond and $[S_2C_2B_{10}H_{10}]^{2-}$ ligand in **1a**.

Experimental Section

General Information. *n*-Butyllithium (2.0 M in cyclohexane, Aldrich), *o*-carborane (Katchem, Czech), phenylacetylene (Alfa Aesar), and 1,4-diethynylbenzene (Aldrich) were used as commercial products without further purification. The starting material ethynylferrocene[10] and $[(p\text{-cymene})RuCl_2]_2$[11] were prepared according to the literature. All manipulations were performed under argon using standard Schlenk techniques. 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 an elementar vario EL *III* 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 $^1H = 5.32$, 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 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.[12]

Scheme 3. Formation Mechanism for 1:1 Adducts



Synthesis of 2a and 3a. Phenylacetylene (0.1 mL, 1 mmol) was added to **1a** (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 on silica to give **2a** and **3a** (petroleum ether/CH_2Cl_2 (1:4)). Suitable crystals were obtained from petroleum ether/CH_2Cl_2. **2a** and **3a**: yield 73 mg (80%). mp 238 °C dec Anal. Calcd for $C_{22}H_{40}B_{20}Ru_2S_6$: C, 28.87; H, 4.40. Found: C, 28.29; H, 4.01. MALDI-TOF MS (*m*/*z*): calcd for

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Table 1. Crystallographic Data and Structural Refinement Details of **2a**, **5a**, and **8a**

	2a	**5a**	**8a**
chemical formula	$C_{22}H_{40}B_{20}Ru_2S_6$	$2(C_{24}H_{40}B_{20}Ru_2S_6)\cdot H_2O$	$C_{40}H_{78}B_{40}FeRu_4S_{12}\cdot 3H_2O$
crystal size(mm)	0.30 × 0.24 × 0.22	0.28 × 0.24 × 0.20	0.36 × 0.34 × 0.28
formula weight	915.24	1896.66	1890.45
temperature(K)	298(2)	291(2)	291(2)
radiation	Mo Kα(0.71073Å)	Mo Kα(0.71073Å)	Mo Kα(0.71073Å)
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	11.722(5)	14.2417(12)	16.6027(11)
b (Å)	13.909(5)	18.6394(16)	16.9671(16)
c (Å)	13.911(5)	17.3441(15)	17.283(2)
α (deg)	117.938(4)	90.00	96.638(3)
β (deg)	98.632(5)	108.5790(10)	117.232(2)
γ (deg)	90.543(6)	90.00	91.548(3)
V (Å^3) Z	1972.6(13) 2	4364.2(6) 2	4282.3(7) 2
ρ_{calc} (g·cm^{-3})	1.541	1.443	1.466
absorp. coeff.(mm^{-1})	1.103	1.001	1.182
F(000)	912	1892	1884
θ range (deg)	2.31−21.19	2.19−23.22	2.38−27.97
reflns collected	10449 (R_{int} = 0.031)	23428 (R_{int} = 0.043)	23416 (R_{int} = 0.026)
indep. reflns	7557	8436	16471
refns obs.[$I > 2\sigma(I)$]	5000	6812	11252
data /restr./paras	7557/0/439	8436/0/487	16471/0/956
GOF	1.000	1.051	1.039
$R_1/wR_2[I > 2\sigma(I)]$	0.0639/0.1366	0.0501/0.1196	0.0691/0.1793
R_1/wR_2 (all data)	0.1016/0.1447	0.0631/0.1235	0.0948/0.1869
larg.peak/hole (e·Å^{-3})	1.054/−1.385	0.412/−0.634	1.574/−2.631

Table 2. Crystallographic Data and Structural Refinement Details of **1b**, **3b**, **5b**, and **7b**

	1b	**3b**	**5b**	**7b**
chemical formula	$C_{14}H_{34}B_{20}Ru_2S_4Se_2$	$C_{22}H_{40}B_{20}Ru_2S_4Se_2\cdot H_2O$	$4(C_{24}H_{40}B_{20}Ru_2S_4Se_2)\cdot 4H_2O$	$2(C_{26}H_{44}B_{20}FeRu_2S_4Se_2)\cdot H_2O$
crystal size(mm)	0.30 × 0.26 × 0.22	0.30 × 0.24 × 0.22	0.30 × 0.26 × 0.24	0.32 × 0.28 × 0.26
formula weight	906.95	1027.10	4204.47	2252.03
temperature(K)	291(2)	291(2)	291(2)	291(2)
radiation	Mo Kα(0.71073Å)	Mo Kα(0.71073Å)	Mo Kα(0.71073Å)	Mo Kα(0.71073Å)
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	13.1350(18)	10.2036(10)	14.3260(16)	13.201(3)
b (Å)	10.0121(14)	13.8240(13)	18.683(2)	13.2007(18)
c (Å)	25.638(4)	15.1766(15)	17.465(2)	13.669(2)
α (deg)	90.00	85.1170(10)	90.00	73.480(3)
β (deg)	98.073(2)	83.179(3)	108.784(2)	73.480(2)
γ (deg)	90.00	88.259(2)	90.00	86.334(3)
V (Å^3) Z	3338.2(8) 4	2117.4(4) 2	4425.6(9) 1	2189.0(7) 1
ρ_{calc} (g·cm^{-3})	1.805	1.611	1.578	1.708
absorp. coeff.(mm^{-1})	3.348	2.652	2.539	2.887
F(000)	1752	1004	2056	1102
θ range (deg)	2.39−28.19	2.47−17.63	2.46−25.58	2.23−28.19
reflns collected	17192 (R_{int} = 0.041)	11725 (R_{int} = 0.031)	23130 (R_{int} = 0.038)	11701(R_{int} = 0.024)
indep. reflns	6561	8170	8685	8368
refns obs.[$I > 2\sigma(I)$]	4906	5825	7034	6043
data /restr./paras	6561/0/380	8170/0/481	8685/0/508	8368/0/505
GOF	1.093	1.060	1.065	1.014
$R_1/wR_2[I > 2\sigma(I)]$	0.0548/0.1208	0.0577/0.1321	0.0439/0.1044	0.0593/0.1470
R_1/wR_2 (all data)	0.0745/0.1250	0.0806/0.1378	0.0535/0.1068	0.0801/0.1527
larg.peak/hole (e·Å^{-3})	1.405/−1.138	0.638/−2.485	0.447/−0.608	1.526/−1.687

$C_{22}H_{40}B_{20}Ru_2S_6$, 915.156; found, 916.218 ([M + H]$^+$, 85%). ^{1}H NMR ($CDCl_3$): *δ* 1.24 (d, *J* = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.37 (d, *J* = 7.0 Hz, 6H, $CH(CH_3)_2$), 2.23 (s, 6H, CH_3), 2.71 (sept, *J* = 7.0 Hz, 2H, $CH(CH_3)_2$), 5.05 (d, *J* = 6.0 Hz, 2H, C_6H_4), 5.12 (d, *J* = 6.0 Hz, 2H, C_6H_4), 6.13 (d, *J* = 6.0 Hz, 2H, C_6H_4), 6.15 (d, *J* = 6.0 Hz, 2H, C_6H_4), 7.18 (s, 1H, HC=C), 7.24 (s, 1H, HC=C), 7.49 (m, 6H, Ph), 7.64 (m, 4H, Ph). ^{13}C NMR ($CDCl_3$): *δ* 18.5 (C_6H_4-$\mathit{C}H_3$), 22.6, 22.9 ($CH(\mathit{C}H_3)_2$), 31.4 ($\mathit{C}H(CH_3)_2$), 80.1, 80.2, 81.0, 82.1, 85.2, 85.4 (*C*H in *p*-cymene), 90.7, 91.1, 92.2, 92.4 (quaternary C in *p*-cymene), 92.5, 92.9, 99.4, 100.3, 100.4, 101.5, 106.9, 107.0 (*o*-carborane), 127.9, 128.3, 129.5, 129.6, 130.9, 131.0 (phenyl group), 132.8, 134.4 (H*C*=C), 133.8, 133.9 (*C*=CH), 149.8, 151.6 (quaternary C in phenyl group). ^{11}B {^{1}H} NMR ($CDCl_3$): *δ* −6.8, −4.4, −2.2 (4:2:4). IR (KBr, cm^{-1}): *ν* 2581 (ν_{B-H}).

Synthesis of 2b and 3b. Phenylacetylene (0.1 mL, 1 mmol) was added to **1b** (91 mg, 0.1 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 48 h at ambient temperature. After removal of the solvent the residue was isolated by column chromatography to give **2b** and **3b** (petroleum ether/CH_2Cl_2 (1:3)). Suitable crystals were obtained from petroleum ether/CH_2Cl_2. **2b** and **3b**: yield 81 mg (80%). mp 239 °C dec Anal. Calcd for $C_{22}H_{40}B_{20}Ru_2S_4Se_2\cdot H_2O$: C, 25.73; H, 4.12. Found: C, 25.18; H, 3.91. MALDI-TOF MS (*m*/*z*): calcd for $C_{22}H_{40}B_{20}Ru_2S_4Se_2$, 1009.093; found, 1009.346 (M$^+$, 45%). ^{1}H NMR ($CDCl_3$): *δ* 1.22 (d, *J* = 7.0 Hz, 6H, $CH(CH_3)_2$), 1.35 (d, *J* = 7.0 Hz, 6H, $CH(CH_3)_2$), 2.24 (s, 6H, CH_3), 2.74 (sept, *J* = 7.0 Hz, 2H, $CH(CH_3)_2$), 5.02 (d, *J* = 6.0 Hz, 2H, C_6H_4), 5.10 (d, *J* = 6.0 Hz, 2H, C_6H_4), 6.10 (d, *J* = 6.0 Hz, 2H, C_6H_4), 6.11 (d, *J* = 6.0 Hz, 2H, C_6H_4), 7.22 (s, 1H, HC=C), 7.26

(s, 1H, HC=C), 7.49 (m, 6H, Ph), 7.64 (m, 4H, Ph). ^{13}C NMR (CDCl$_3$): 18.7 (C$_6$H$_4$-*C*H$_3$), 22.6, 23.3 (CH(*C*H$_3$)$_2$), 31.5 (*C*H(CH$_3$)$_2$), 77.2, 78.4, 80.2, 80.3, 80.5, 84.6 (*C*H in *p*-cymene), 91.2, 91.9, 92.8, 93.1 (quaternary C in *p*-cymene), 96.3, 97.8, 98.5, 99.1, 102.4, 106.5, 107.1 (*o*-carborane), 127.9, 128.2, 129.3, 129.6, 130.9, 131.0 (phenyl group), 134.1, 134.7 (H*C*=C), 133.1, 133.3 (*C*=CH), 149.6, 150.9 (quaternary C in phenyl group). ^{11}B {^{1}H} NMR (CDCl$_3$): δ −9.5, −6.7, −4.6 (6:1:3). IR (KBr, cm^{-1}): ν *2580* ($\nu_{\mathrm{B-H}}$).

Synthesis of 4a and 5a. 1,4-Diethynylbenzene (25 mg, 0.2 mmol) was added to **1a** (81 mg, 0.1 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred for 7 d. After removal of the solvent the residue was isolated by column chromatography to give **4a** and **5a** (petroleum ether/CH$_2$Cl$_2$ (1:1)). Suitable crystals were obtained from petroleum ether/CH$_2$Cl$_2$. **4a** and **5a**: yield 66 mg (70%). mp 234 °C dec Anal. Calcd for C$_{24}$H$_{40}$B$_{20}$Ru$_2$S$_6$: C, 30.69; H, 4.29. Found: C, 30.02; H, 4.66. MALDI-TOF MS (*m*/*z*): calcd for C$_{24}$H$_{40}$B$_{20}$Ru$_2$S$_6$, 939.324; found, 940.288 ([M + H]$^+$, 65%). ^{1}H 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$_3$)$_2$), 2.23 (s, 3H, CH$_3$), 2.71 (sept. *J* = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 3.24 (s, 1H, C≡CH), 5.05 (d, *J* = 6.0 Hz, 2H, C$_6$H$_4$), 5.12 (d, *J* = 6.0 Hz, 2H, C$_6$H$_4$), 6.14 (d, *J* = 6.0 Hz, 2H, C$_6$H$_4$), 6.15 (d, *J* = 6.0 Hz, 2H, C$_6$H$_4$), 7.19 (s, 1H, HC=C), 7.21 (s, 1H, HC=C), 7.18 (4H, C$_6$H$_4$), 7.60 (4H, C$_6$H$_4$). ^{11}B {^{1}H} (CDCl$_3$): δ −10.1, −7.2, −5.5 (5:1:4). IR (KBr, cm^{-1}): ν 2581 ($\nu_{\mathrm{B-H}}$).

Synthesis of 4b and 5b. 1,4-Diethynylbenzene (25 mg, 0.2 mmol) was added to **1b** (91 mg, 0.1 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred for 10 d. After removal of the solvent the residue was isolated by column chromatography to give **4b** and **5b** (petroleum ether/CH$_2$Cl$_2$ (1:2)). Suitable crystals were obtained from petroleum ether/CH$_2$Cl$_2$. **4b** and **5b**: yield 88 mg (85%). mp 238 °C dec Anal. Calcd for C$_{24}$H$_{40}$B$_{20}$Ru$_2$S$_4$Se$_2$: C, 27.90; H, 3.90. Found: C, 28.48; H, 4.46. MALDI-TOF MS (*m*/*z*): calcd for C$_{24}$H$_{40}$B$_{20}$Ru$_2$S$_6$, 1033.114; found, 1034.239 ([M + H]$^+$, 75%). ^{1}H NMR (CDCl$_3$): δ 1.22 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 1.23 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 1.33 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 1.35 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 2.24 (s, 6H, CH$_3$), 2.73 (sept. *J* = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 2.74 (sept. *J* = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 3.25 (s, 1H, C≡CH), 3.26 (s, 1H, C≡CH), 5.03 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.10 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.15 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.18 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.98 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.02 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.10 (d, *J* = 6.0 Hz, 2H, C$_6$H$_4$), 7.25 (s, 1H, HC=C), 7.31 (s, 1H, HC=C), 7.51~7.73 (8H, Ph). ^{11}B {^{1}H} (CDCl$_3$): δ −11.5, −7.8, −4.9 (5:1:4). IR (KBr, cm^{-1}): ν 2568 ($\nu_{\mathrm{B-H}}$).

Synthesis of 6a, 7a, and 8a. Ethynylferrocene (0.154 g, 1 mmol) was added to **1a** (81 mg, 0.1 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred for 18 h. After removal of the solvent the residue was isolated by column chromatography to give deep-red **6a** (petroleum ether/CH$_2$Cl$_2$ (1: 2)), **7a** (petroleum ether/CH$_2$Cl$_2$ (1:5)), and gray-purple **8a** (petroleum ether/CH$_2$Cl$_2$ (1:3)). Suitable gray-purple block crystals were obtained from petroleum ether/CH$_2$Cl$_2$. **6a**: yield 20 mg (20%). mp 254 °C dec Anal. Calcd for C$_{26}$H$_{44}$B$_{20}$FeRu$_2$S$_6$: C, 30.52; H, 4.33. Found: C, 30.07; H, 4.68. MALDI-TOF MS (*m*/*z*): calcd for C$_{26}$H$_{44}$B$_{20}$FeRu$_2$S$_4$Se$_2$, 1023.223; found, 1024.452 ([M + H]$^+$, 80%). ^{1}H NMR (CDCl$_3$): δ 1.26 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 1.38 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 2.25 (s, 3H, CH$_3$), 2.71 (sept., *J* = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 4.36 (s, 5H, Cp), 4.56 (1H), 4.59 (1H), 4.65 (1H), 4.86 (1H) (Fc), 5.06 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.12 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.11 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.12 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 7.06 (s, 1H, HC=C−Fc). ^{13}C NMR (CDCl$_3$): δ 18.7 (C$_6$H$_4$−*C*H$_3$), 22.7, 23.1 (CH(*C*H$_3$)$_2$), 31.5 (*C*H(CH$_3$)$_2$), 69.7 (CH in Fc), 70.2 (CH in Fc), 70.4 (Cp in Fc), 70.9 (CH in Fc), 71.6 (CH in Fc), 81.0 (quaternary C in Fc), 80.2, 80.2, 82.0, 84.6 (CH in *p*-cymene), 90.9, 91.0 (quaternary C in *p*-cymene), 94.2, 99.2, 106.1, 106.9 (*o*-carborane), 125.9 (H*C*=C), 147.8 (*C*=CH). ^{11}B {^{1}H} (CDCl$_3$): δ −14.9, −13.2, −9.1, (4:2:4). IR (KBr, cm^{-1}): ν 2579 ($\nu_{\mathrm{B-H}}$). **7a**: yield 21 mg (21%). mp 244 °C dec Anal. Calcd for C$_{26}$H$_{44}$B$_{20}$FeRu$_2$S$_6$: C, 30.52; H, 4.33. Found: C, 30.98; H, 4.75. MALDI-TOF MS (*m*/*z*): calcd for C$_{26}$H$_{44}$B$_{20}$FeRu$_2$S$_4$Se$_2$, 1023.223; found, 1024.452 ([M + H]$^+$, 80%).^{1}H NMR (CDCl$_3$): δ 1.20 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 1.33 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 2.16 (s, 3H, CH$_3$), 2.68 (sept., *J* = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 4.32 (s, 5H, Cp), 4.60 (2H), 4.66 (1H), 4.94 (1H) (Fc), 5.05 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.06(d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.13 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.14 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 7.09 (s, 1H, HC=C−Fc). ^{13}C NMR (CDCl$_3$): δ 18.4 (C$_6$H$_4$−*C*H$_3$), 22.7, 22.8 (CH(*C*H$_3$)$_2$), 31.4 (*C*H(CH$_3$)$_2$), 70.1 (Cp in Fc), 70.3 (CH in Fc), 70.6 (CH in Fc), 71.1 (CH in Fc), 71. Seven (CH in Fc), 80.4 (quaternary C in Fc), 79.9, 82.0, 82.2, 84.9 (CH in *p*-cymene), 90.5, 94.4 (quaternary C in *p*-cymene), 95.9, 99.4, 99.9, 107.3 (*o*-carborane), 126.2 (H*C*=C), 150.2 (*C*=CH). ^{11}B {^{1}H} (CDCl$_3$): δ −14.7, −12.7, −10.8, (4:2:4). IR (KBr, cm^{-1}): ν 2574 ($\nu_{\mathrm{B-H}}$). **8a**: yield 57 mg (30%). mp 286 °C dec Anal. Calcd for C$_{40}$H$_{78}$B$_{40}$FeRu$_4$S$_{12}$·3H$_2$O: C, 25.41; H, 4.48. Found: C, 25.88; H, 4.76. MALDI-TOF MS (*m*/*z*): calcd for C$_{40}$H$_{78}$B$_{40}$FeRu$_4$S$_{12}$, 1836.392; found, 1837.416 ([M + H]$^+$, 85%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.07 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.18 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.43 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.52 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 2.49 (s, 3H, CH$_3$), 2.52 (s, 3H, CH$_3$), 2.70 (sept. *J* = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 3.31 (sept. *J* = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 4.35 (s, 5H, Cp), 4.46 (2H), 4.80 (1H), 4.87 (1H) (Fc), 5.38 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.56 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.64 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.79 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.87 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.93 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.03 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.08 (s, 1H, *H*C=C−Fc), 6.44 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$). ^{13}C NMR (CD$_2$Cl$_2$): δ 19.4, 19.5(CH$_3$), 21.1, 22.4, 23.8, 24.6 (CH(*C*H$_3$)$_2$), 31.2, 32.8 (*C*H(CH$_3$)$_2$), 69.2, 70.0, 70.4, 70.5 (CH in Fc), 70.9 (Cp in Fc), 82.9 (quaternary C in Fc), 83.0, 85.9, 89.3, 90.5, 90.8, 93.0, 93.4, 101.5 (CH in *p*-cymene), 87.3, 89.6, 91.3, 91.9 (quaternary C in *p*-cymene), 93.2, 93.7, 96.4, 99.1, 103.6, 106.9, 107.3, 115.9 (*o*-carborane), 179.4 (*C*=CH), 206.7 (*C*=*C*H). ^{11}B {^{1}H} NMR (CD$_2$Cl$_2$): δ −9.8, −6.4, −3.5 (3: 3:4). IR (KBr, cm^{-1}): ν 2584 ($\nu_{\mathrm{B-H}}$).

Synthesis of 6b and 7b. Ethynylferrocene (0.154 g, 1 mmol) was added to **1b** (91 mg, 0.1 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred for 18 h. After removal of the solvent the residue was isolated by column chromatography to give deep-red **6b** (petroleum ether/CH$_2$Cl$_2$ (1:2)) and **7b** (petroleum ether/CH$_2$Cl$_2$ (1: 4)). Suitable red block crystals were obtained from petroleum ether/CH$_2$Cl$_2$. **6b**: yield 50 mg (45%). mp 252 °C dec Anal. Calcd for C$_{26}$H$_{44}$B$_{20}$FeRu$_2$S$_4$Se$_2$: C, 27.96; H, 3.97. Found: C, 27.31; H, 4.46. MALDI-TOF MS (*m*/*z*): calcd for C$_{26}$H$_{44}$B$_{20}$FeRu$_2$S$_4$Se$_2$, 1117.013; found, 1118.347 ([M + H]$^+$, 85%). ^{1}H NMR (CDCl$_3$): δ 1.25 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 1.37 (d, *J* = 7.0 Hz, 3H, CH(CH$_3$)$_2$), 2.27 (s, 3H, CH$_3$), 2.74 (sept., *J* = 7.0 Hz, 1H, CH(CH$_3$)$_2$), 4.37 (s, 5H, Cp), 4.57 (1H), 4.59 (1H), 4.65 (1H), 4.88 (1H) (Fc), 5.07 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 5.09 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.07 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 6.08 (d, *J* = 6.0 Hz, 1H, C$_6$H$_4$), 7.04 (s, 1H, HC=C−Fc). ^{13}C NMR (CDCl$_3$): δ 19.0 (C$_6$H$_4$−*C*H$_3$), 22.8, 23.3 (CH(*C*H$_3$)$_2$), 31.5 (*C*H(CH$_3$)$_2$), 69.5 (CH in Fc), 70.1 (CH in Fc), 70.5 (Cp in Fc), 70.9 (CH in Fc), 71.6 (CH in Fc), 80.4 (quaternary C in Fc), 78.5, 80.2, 80.6, 83.7 (CH in *p*-cymene), 90.6, 91.4 (quaternary C in *p*-cymene), 97.9, 98.8, 106.1, 106.8 (*o*-carborane), 125.8 (H*C*=C), 147.8 (*C*=CH). ^{11}B {^{1}H} (CDCl$_3$): δ

−7.6, −6.0, −4.9, −2.1 (4:1:1:4). IR (KBr, cm^{-1}): ν 2569 ($\nu_{\text{B-H}}$). **7b**: yield 39 mg (35%). mp 258 °C dec Anal. Calcd for $C_{26}H_{44}B_{20}FeRu_2S_4Se_2 \cdot H_2O$: C, 27.73; H, 4.03. Found: C, 27.05; H, 4.48. MALDI-TOF MS (*m/z*): calcd for $C_{26}H_{44}B_{20}FeRu_2S_4Se_2$, 1117.013; found, 1118.347 ($[M + H]^+$, 65%). ^1H NMR ($CDCl_3$): δ 1.18 (d, $J = 7.0$ Hz, 3H, $CH(CH_3)_2$), 1.31 (d, $J = 7.0$ Hz, 3H, $CH(CH_3)_2$), 2.17 (s, 3H, CH_3), 2.71 (sept., $J = 7.0$ Hz, 1H, $CH(CH_3)_2$), 4.34 (5H), 4.61 (2H), 4.67 (1H), 4.96 (1H) (Fc), 4.99 (d, $J = 6.0$ Hz, 1H, C_6H_4), 5.06(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), 7.09 (s, 1H, HC=C−Fc). ^{13}C NMR ($CDCl_3$): δ 18.6 (C_6H_4-CH_3), 22.7, 22.9 ($CH(CH_3)_2$), 31.2 ($CH(Me)_2$), 69.8 (CH in Fc), 70.1 (Cp in Fc), 70.6 (CH in Fc), 71.1 (CH in Fc), 71.7 (CH in Fc), 80.5 (quaternary C in Fc), 77.9, 80.3, 81.7, 84.0 (CH in *p*-cymene), 93.9, 95.4 (quaternary C in *p*-cymene), 96.1, 99.1, 99.2, 107.5 (*o*-carborane), 126.3 (H*C*=C), 149.9 (*C*=CH). ^{11}B {^1H} ($CDCl_3$): δ −7.4, −5.1, −3.3, −1.8 (4:1:1:4). IR (KBr, cm^{-1}): ν 2573 ($\nu_{\text{B-H}}$).

X-ray Data Collection, Processing, and Structure Analysis and Refinement. Diffraction data were collected on a Bruker SMART Apex II CCD diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ 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.[13] The structures were solved by direct methods using the SHELXL-97 program.[14] 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 **2a**, **5a**, **8a**; **1b**, **3b**, **5b**, and **7b** are given respectively in Table 1 and Table 2.

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Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of compounds **1b**, **2a**, **3b**, **5a**, **5b**, **7b**, and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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