Reactivity of Cp*Rh 16e Half-Sandwich Complexes Containing a Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolato Ligand. Intermediates in the Catalyzed Trimerization of Methyl Acetylene Carboxylate and Phenylacetylene

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Reactions of the 16-electron (16e) half-sandwich complexes Cp*Rh[$E_2C_2(B_{10}H_{10})$] [E = S (**1S**), Se (**1Se**)] with methyl acetylene carboxylate and phenylacetylene were studied in order to obtain information on both the primary addition products and the potential catalyzed oligomerization of the alkynes as a function of reaction conditions. Both rhodium complexes **1S** and **1Se** reacted with HC≡C−CO_2Me under mild conditions to give in low yield the dimers **2S** and **2Se**, of which **2Se** could be characterized by X-ray structural analysis. Both **1S** and **1Se** act as catalysts for the cyclotrimerization of HC≡C−CO_2Me and HC≡C−Ph to give the respective 1,3,5- and 1,2,4-trisubstituted benzenes in a 1:1 ratio, if the reaction is carried out at 70 °C in toluene. In boiling chloroform or at room temperature in dichloromethane, trimerization is of minor importance. In the case of **1Se** and methyl acetylene carboxylate, an intermediate **3Se**, formed in the course of the trimerization process, could be characterized by X-ray structural analysis. The dimer **2Se** catalyzes trimerization in the same way as **1Se**. In the absence of HC≡C−CO_2Me, **2Se** rearranges upon heating in toluene at 70 °C completely into the known carborane-substituted complex **8Se**. One of the final products of the reaction of **1S** with HC≡C−CO_2Me, the 16e complex **4S**, also catalyzes the trimerization of HC≡CCO_2Me.

Introduction

Although numerous transition metal complexes containing chalcogenolato ligands have been prepared by various routes, only a few aspects of their chemistry have been explored so far.[1] The reactivity of the 16e half-sandwich complexes Cp*Rh[$E_2C_2(B_{10}H_{10})$] **1S** and **1Se**, and of related compounds of iridium, ruthenium, and osmium, deserve particular attention considering the accumulation of reactive sites around the metal center.[2] We have already shown that reactions take place with methyl acetylene carboxylates[3−5] and phenylacetylene[6] leading to new complexes as the result of consecutive steps, in which the metal center and the metal−chalcogen bonds are involved as well as the B(3,6)−H bonds of the *o*-carborane cage by metal-induced B−H activation.[7] Thus, the complexes **4S**−**7S**, **8Se**, and **9S** (Scheme 1) have been isolated and structurally characterized.[3−6]

In the cases of the reactions of both **1S** and **1Se** with methyl acetylene carboxylate (HC≡C−CO_2Me), carried out under mild conditions in dichloromethane at room temperature, we have noted that small amounts of rather insoluble complexes **2S** and **2Se** were formed in addition to other well-defined products. It had been assumed that these complexes are dimers of the initial addition products.[4,5] Furthermore, it had been found that the reactions of **1S** or **1Se** with both HC≡C−CO_2Me and HC≡C−Ph, under mild conditions, produce small amounts of organic compounds that do not contain rhodium and are most likely oligomers of the alkynes.

In the present work, we report the hitherto unknown molecular structure of the rhodium complexes **2**, and we have changed the reaction conditions in order to find out about the potential catalytic activity of **1S** and **1Se** in the oligomerization of the alkynes HC≡C−CO_2Me and HC≡C−Ph.

Results and Discussion

Reaction of Cp*Rh[$S_2C_2(B_{10}H_{10})$] (1S) with Methyl Acetylene Carboxylate. The results of this reaction

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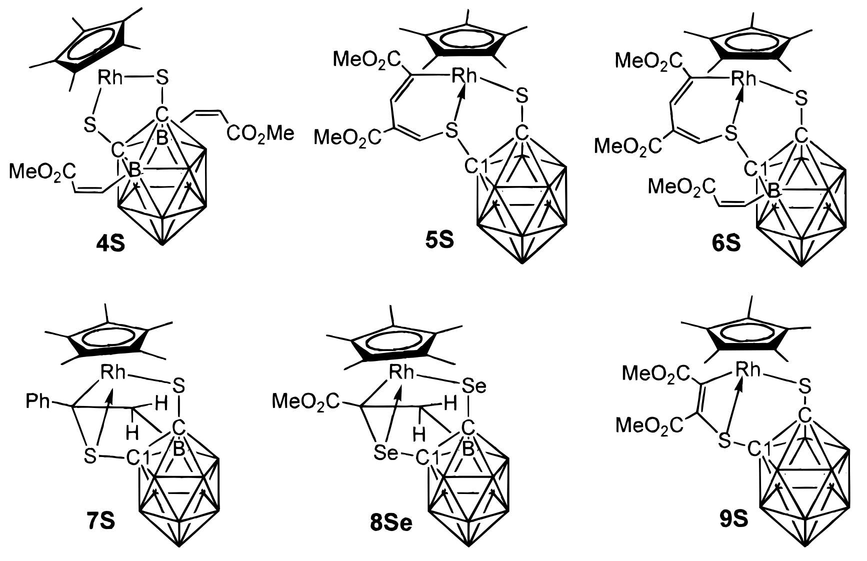
Scheme 1



carried out in dichloromethane at room temperature have been described,[3,4] and the products **4S**, **5S**, and **6S** have been fully characterized. A dimer **2S** (vide infra) of a first addition product had been proposed on the basis of the field desorption (FD) MS spectra, but there had been insufficient other data for a reliable structural assignment. The formation of **4S** requires metal-induced B−H activation[7] and ortho-metalation (see also the reaction of CpCo[$S_2C_2(B_{10}H_{10})$] with alkynes[8]) in order to arrive finally at the B(3/6)-disubstituted carborane cage.[3,4] The complexes **5S** and **6S** could be considered as intermediates in the trimerization of HC≡C−CO_2Me. When the reaction of **1S** with an excess of HC≡C−CO_2Me was performed in toluene at 70 °C, none of these products could be isolated. Instead, the alkyne was converted into the isomeric trimers, the 1,3,5- and 1,2,4-trisubstituted benzenes in a 1:1 ratio, and **1S** was left unchanged. Under the same conditions, the 16e complex **4S** reacted with HC≡C−CO_2Me to give the benzene derivatives. It is likely that the dimer **2S** (vide infra) as well as the complexes **5S** and **6S** are intermediates, which can be isolated only under mild conditions. When **2S** was isolated and then heated in toluene at 70°, the major product was **1S** along with traces of organic material. Under the same conditions, in the presence of an excess of HC≡C−CO_2Me, trimerization of the alkyne took place, and the formation of **1S** was observed as well. Similarly, the reaction of **5S**[4] with an excess of HC≡C−CO_2Me leads cleanly to the 1,3,5- and 1,2,4-trisubstituted benzenes (ratio 1:1). The influence of the solvent is remarkable, since the reaction of **1S** with an excess of HC≡C−CO_2Me in boiling chloroform leads in high yield to the complex **4S**,[3] and benzene derivatives are formed only in a small amount.

Reaction of Cp*Rh[$Se_2C_2(B_{10}H_{10})$] (1Se) with Methyl Acetylene Carboxylate. The reaction of **1Se** with HC≡C−CO_2Me under mild conditions leads to products that differ in their structures considerably from those that were obtained starting from **1S**.[5] Thus, **8Se** is a final product, whereas **8S** was not even detected in the reaction mixtures. Furthermore, selenium complexes with a Rh−B bond could be isolated (again in contrast with the sulfur case), and there are selenium complexes such as **3Se** (similar to **5S**), which, however, differ from the sulfur analogues in the substituent pattern at the C=C bond.[5] A product **2Se**, analogous to **2S**, had not been well characterized except by a FD MS spectrum indicating the presence of a dinuclear complex.[5] This product **2Se** could now be crystallized and its molecular structure determined (Figure 1). It is assumed that the structure of **2S** is similar to that of **2Se**. In contrast, the products of the reactions of **1S** or **1Se** with dimethyl acetylene dicarboxylate, $MeO_2C-C\equiv C-CO_2Me$, are mononuclear complexes,[3−5] for which the molecular structure has been established in the case of **9S**[3] (Scheme 1).

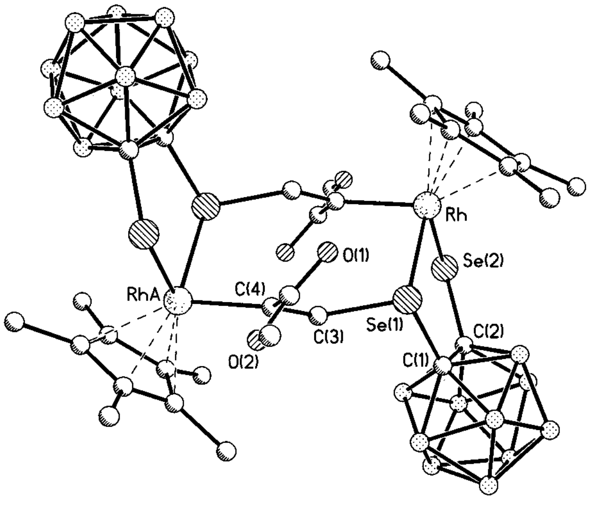


Figure 1. Molecular geometry of the dinuclear rhodium complex **2Se**. Selected bond lengths [pm] and angles [deg]: Rh−ring centroid 190.8, Rh−C(4) 205.7(4), Rh−Se(1) 248.48(5), Rh−Se(2) 247.13(5), Se(1)−C(3) 192.2(3), Se(1)−C(1) 196.5(3), Se(2)−C(2) 193.8(4), C(1)−C(2) 165.5(5), C(3)−C(4) 133.2(5), C(4)RhSe(1) 90.44(10), Se(1)RhSe(2) 90.749(16), C(3)Se(1)Rh 104.38(10), C(1)Se(1)Rh 103.78(11), C(2)Se(2)Rh 103.12(11), C(3)C(4)Rh 120.2(3), Se(1)C(3)C(4) 123.2(2), C(3)C(4)C(5) 119.0(3), C(5)C(4)Rh 120.5(2), Se(1)RhSe(2)/Se(1)C(1)C(2)Se(2) 159.2.

Heating the pure dimer **2Se** in toluene solution at 70 °C led exclusively to the known complex **8Se**[5] as a result

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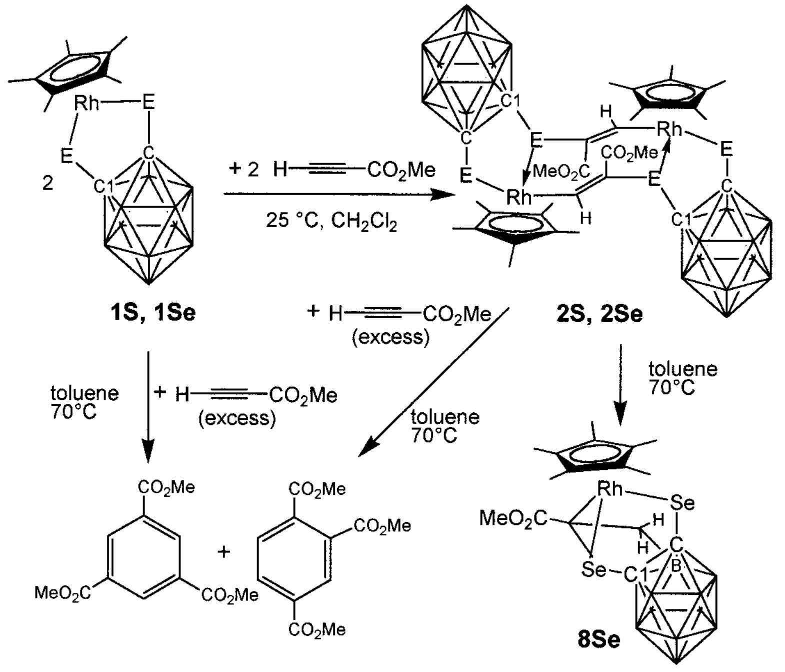
Scheme 2



of metal-induced B−H activation followed by a number of additional steps. Heating of **2Se** under the same conditions in the presence of an excess of HC≡C−CO_2Me afforded the isomeric trisubstituted benzene derivatives in a 1:1 ratio together with the starting complex **1Se**. When **1Se** was treated with an excess of HC≡C−CO_2Me in toluene at 70 °C, again the benzene derivatives were formed, and **8Se** or precursors were not detected. These results are summarized in Scheme 2.

Another product, isolated from the reaction of **1Se** with HC≡C−CO_2Me under mild conditions, is the complex **3Se**, for which the structure had been proposed on the basis of NMR data.[5] By repeated crystallization of **3Se** suitable crystals for X-ray diffraction analysis were obtained, and the molecular structure is shown in Figure 2, confirming the previous NMR spectroscopic evidence. By heating of **3Se** in the presence of an excess of HC≡C−CO_2Me in toluene at 70 °C, clean formation of the trimethyl-1,3,5- and trimethyl-1,2,4-benzenetricarboxylates (ratio 1:1) was observed together with the parent complex **1Se** (Scheme 3).

When a mixture of **8Se** and HC≡C−CO_2Me (excess) is heated in toluene at 70 °C, the 1,3,5- and 1,2,4-trisubstituted benzenes are also formed in a 1:1 ratio. This is accompanied by decomposition of **8Se** into unidentified products. The molecular structure of **8Se** (Scheme 1) shows that a coordinative Se→Rh bond is present as part of a three-membered ring.[5] Opening of this bond would lead to a 16e complex which can be considered as an active catalyst in the trimerization.

It appears that complexes such as **3Se**, **5S**, and **6S** must be regarded as intermediates in the process of alkyne cyclotrimerization, and the same is true for **2S** and **2Se**. The catalyst in each case is the 16e complex **1S** or **1Se**, which is formed once the intermediates react with the alkyne. Again, in the case of **1Se**, the influence of the solvent is noteworthy: in boiling chloroform, the reaction of **1Se** with an excess of HC≡C−CO_2Me affords mainly **8Se** and **3Se**.

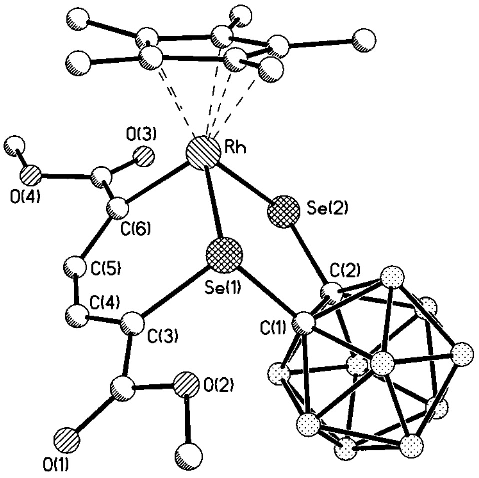
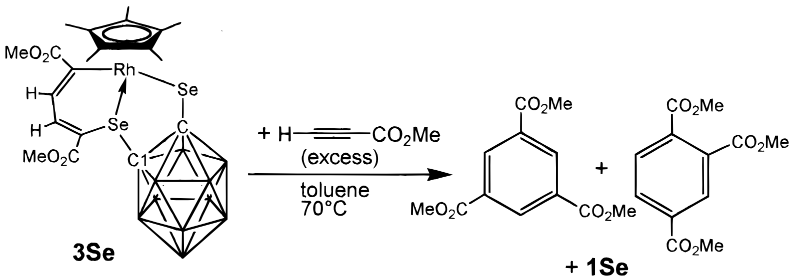


Figure 2. Molecular geometry of the rhodium complex **3Se**. Selected bond lengths [pm] and angles [deg]: Rh−ring centroid 186.5, Rh−C(6) 203.6(4), Rh−Se(1) 238.33(5), Rh−Se(2) 247.06(6), Se(1)−C(3) 190.0(4), Se(1)−C(1) 197.4(4), Se(2).C(2) 194.5(4), C(1)−C(2) 165.3(5), C(3)−C(4) 134.0(6), C(4)−C(5) 143.8(6), C(5)−C(6) 135.0(5), C(6)RhSe(1) 93.15(11), C(6)RhSe(2) 86.59(11), Se(1)-RhSe(2) 93.002(18), C(3)Se(1)C(1) 101.07(16), C(3)Se(1)-Rh 109.54(12), C(1)Se(1)Rh 106.51(11), C(2)Se(2)Rh 102.68(12), Se(1)EhSe(2)/Se(1)C(1)C(2)Se(2) 172.3, Se(1)-RhC(6)/C(3)C(4)C(5) 158.3.

Reaction of Cp*Rh[$E_2C_2(B_{10}H_{10})$] (1S, 1Se) with Phenylacetylene. The reaction of **1S** with an excess of HC≡C−Ph under mild conditions has been described.[6] In addition to complexes with rhodium−boron bonds, the rhodium complex **7S** (analogous to **8Se**) is one of the final products (Scheme 1). None of these products was obtained when the reaction of **1S** with an excess of HC≡C−Ph was carried out in toluene at 70 °C. The products were the 1,3,5- and 1,2,4-triphenylbenzenes, and **1S** remained in the mixture. The same result was obtained by heating of a mixture of **7S** and HC≡C−Ph (excess) in toluene at 70 °C; this reaction was accompanied by decomposition of **7S**. Cyclotrimer-

Scheme 3



ization of HC≡C−Ph proved to be already prominent in the reaction of **1Se** with an excess of HC≡C−Ph under mild conditions. In toluene at 70 °C, the trimerization of the alkyne was the only active process.

Mechanistic Implications. The mechanism proposed previously for the reactions of some half-sandwich 16e metal *o*-carboranedichalcogenolato complexes with methyl acetylene carboxylates[3−5] or phenylacetylene[6] is confirmed and complemented by the present results. The alternative to metal-induced B−H activation turns out to be the catalytic cyclotrimerization of the alkynes, a well-known process homogeneously or heterogeneously catalyzed by many transition metal complexes.[9−15] In the present cases, for both alternatives, the primary step of the reactions is the addition of the alkyne to the 16e metal center,[13−15] followed by insertion[16] into one of the Rh−E bonds. In contrast with the mononuclear complexes **9** obtained with $MeO_2C-C{\equiv}C-CO_2Me$ (see Scheme 1 for the structure of **9S**), it proved possible, in the case of $HC{\equiv}C-CO_2Me$ under mild conditions, to isolate dinuclear complexes of type **2**, of which **2Se** could be characterized both by X-ray analysis in the solid state and by ^{77}Se NMR in solution. The effective catalysts for trimerization of the alkynes are 16e complexes such as **1S** or **1Se**. Catalytic effectivity appears to be a general function of these 16e complexes since **4S** (Scheme 1) is also active. The dinuclear complexes **2**, in which already two alkene units bridge the rhodium and one of the chalcogen atoms, are intermediates in the trimerization of the alkynes.

NMR Spectroscopic Results. The NMR data of the complexes shown in Scheme 1 have been reported previously[3−6] and served efficiently to establish the presence or absence of these species in the reactions of **1S** or **1Se** with $HC{\equiv}C-CO_2Me$ and HC≡C−Ph under different conditions (boiling $CHCl_3$ or toluene at 70 °C). It was important to obtain the ^{77}Se NMR spectrum[17] of the sparingly soluble **2Se** in solution in order to prove its dimeric nature or to find evidence for monomer−dimer equilibria. The ^{77}Se NMR spectrum shows deceptively simple splittings into a doublet (δ^{77}Se 469.3) and a triplet (δ^{77}Se 695.7), respectively. The "doublet" is assigned to Se(2) as the A-part of an AXX′ spin-system with $^{1}J(^{103}\mathrm{Rh(X)},^{77}\mathrm{Se(2)}) \approx 46.0$ Hz and negligibly small coupling constants $J(^{103}\mathrm{Rh(X')},\mathrm{Se(2)})$ and $J(^{103}\mathrm{Rh(X)},^{103}\mathrm{Rh(X')})$. The "triplet" belongs to Se(1), again as the A-part of an AXX′ spin-system with $^{1}J(^{103}\mathrm{Rh(X)},^{77}\mathrm{Se(1)})$, nonnegligible magnitude of $^{3}J(^{103}\mathrm{Rh(X')},^{77}\mathrm{Se(1)})_{trans}$ $[\Sigma(^{1}J) + (^{3}J) = 29.0$ Hz], and a negligibly small coupling constant $J(^{103}\mathrm{Rh(X)},^{103}\mathrm{Rh(X')})$. Thus, the dimeric structure of **2Se**, determined for the solid state, is retained in solution.

X-ray Structural Analyses of the Rhodium Complexes 2Se and 3Se. The molecular structures of the rhodium complexes **2Se** and **3Se** are shown in Figures 1 and 2, respectively. The eight-membered ring in **2Se** adopts a steplike structure, in which the four atoms C(3), Se(1), Rh, C(4A) [and because of symmetry also C(4), Rh(A), Se(1A), C(3A)] form a plane within experimental error. According to the bond angles at the C=C bonds, the *E*-configuration does not induce significant strain. In **3Se**, the five-membered ring Se(1)RhSe(2)C(2)C(1) is less folded than in **2Se**. The six-membered ring Se(1)RhC(6)C(5)C(4)C(3) in **3Se** deviates markedly from a planar arrangement. In both complexes **2Se** and **3Se**, the carborane cage appears to be hardly distorted, as shown by the bond lengths $d_{C(1)C(2)}$ 165.5(5) and 165.3(5) Å, which are in the range typical of *o*-carborane derivatives.[18] The prominent structural features of **3Se** are very similar to those of the related sulfur complexes **5S** and **6S**.[4]

Experimental Part

General and Starting Materials. The starting complex $[Cp^*RhCl_2]_2$[19] and the 16e complexes $Cp^*Rh[E_2C_2(B_{10}H_{10})]$ [E

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= S (**1S**), Se (**1Se**)] were obtained as described.[2] Methyl acetylene carboxylate and phenylacetylene were used as commercial products without further purification. NMR measurements: Bruker ARX 250 and DRX 500 spectrometers; chemical shifts are given with respect to $CHCl_3/CDCl_3$ (δ^1H = 7.24; $\delta^{13}C$ = 77.0) or $CDHCl_2$ (δ^1H = 5.33, $\delta^{13}C$ = 53.8), external Et_2O-BF_3 ($\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 MHz), external Me_2Se ($\delta^{77}Se$ = 0 for $\Xi(^{77}Se)$ = 19.071523 MHz). Mass spectra: VARIAN MAT CH7 for EI-MS (70 eV), direct inlet; VARIAN MAT 311A for FD-MS. IR spectra: Perkin-Elmer 983 G. Melting or decomposition points are uncorrected.

Synthesis of 2S. Methyl acetylene carboxylate (0.38 mL, 4.5 mmol) was added to the green solution of **1S** (200 mg, 0.45 mmol) in CH_2Cl_2 (30 mL), and the mixture was stirred for 3 days at ambient temperature to give a brown solution. After removing the solvent, chromatography of the residue on silica gel (Merck, Kieselgel 60) with elution by CH_2Cl_2 gave **2S** as an orange-red solid (11.9 mg, 5%; mp = 190 °C (dec)). ^1H NMR ($CDCl_3$): δ 1.71 (s, 15H, Cp*), 3.61 (s, 3H, OMe), 5.11 (s, 1H, CH). ^{11}B NMR ($CDCl_3$): δ −9.5, −5.4. ^{13}C NMR ($CDCl_3$): δ 9.6 (Cp*), 51.4 (OMe), 91.8 and 94,9 ($C_2B_{10}H_{10}$), 101.3 ($^1J(^{103}Rh,^{13}C)$ = 5.7 Hz, Cp*), 117.1 (C−S), 168.8 ($^1J(^{103}Rh,^{13}C)$=37.0 Hz, C−Rh), 171.9 (C=O). IR (KBr) [cm^{-1}]: ν_{B-H} = 2572, 2593, ν_{COOMe} = 1698. EI-MS (70 eV): 613 (4%, M^+ − ($Cp^*Rh(S_2C_2B_{10}H_{10})$)), 529 (25%, 1/2 M^+), 444 (100%, $[Cp^*Rh(S_2C_2B_{10}H_{10})]^+$.

Synthesis of 2Se. Methyl acetylene carboxylate (0.32 mL, 3.7 mmol) was added to the suspension of **1Se** (200 mg, 0.37 mmol) in CH_2Cl_2 (30 mL). Within several hours at ambient temperature the mixture changed to a red solution. After the solvent had been removed, the residue was chromatographed on a column of silica gel. Elution with hexane/CH_2Cl_2 (4:3) gave **2Se** as an orange-red solid (23 mg, 10%; mp = 182 °C (dec)). ^1H NMR ($CDCl_3$): δ 1.76 (s, 15H, Cp*), 3.60 (s, 3H, OMe), 5.46 (s, 1H, CH). ^{11}B NMR (80.1 MHz, $CDCl_3$): δ −7.6, −4.4. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 9.7 (Cp*), 51.6 (OMe), 100.4 ($^1J(^{103}Rh,^{13}C)$ = 4.7 Hz, Cp*), 115.1 (C−Se), 172.5 (C=O). IR (KBr) [cm^{-1}]: ν_{B-H} = 2592, ν_{COOMe} = 1687. EI-MS (70 eV): 707 (5%, $[M - Cp^*Rh(Se_2C_2B_{10}H_{10})]^+$, 622 (18%, 1/2 M^+), 539 (100%, $[Cp^*Rh(Se_2C_2B_{10}H_{10})]^+$).

Reactions of 1S and 1Se with Methyl Acetylene Carboxylate in Boiling $CHCl_3$. Methyl acetylene carboxylate (0.5 mL, 5.9 mmol) was added to 0.05 mmol of **1S** (22.2 mg) or **1Se** (27 mg) in $CHCl_3$ (20 mL). Then the mixtures were heated at reflux for 24 h. After removing the solvent and unreacted methyl acetylene carboxylate, the compositions of the residues were checked by ^1H NMR. For the reaction with **1S**, the residue contained **4S**, trimethyl-1,2,4-benzenetricarboxylate, and trimethyl-1,3,5-benzenetricarboxylate in a ratio of 2.5:1:0.8. For the reaction with **1Se**, the residue contained **8Se**, **3Se**, trimethyl-1,2,4-benzenetricarboxylate, and trimethyl-1,3,5-benzenetricarboxylate in a ratio of 15:5:1:1. ^1H NMR (250 MHz, $CDCl_3$): δ^1H 8.39 (d, J(H,H) 1.6 Hz, 1H, C(3)−H), 8.17 (dd, J(H,H) 1.6 and 8.0 Hz, 1H, C(5)−H), 7.72 (d, J(H,H) = 8.0 Hz, 1H, C(6).H), 3.93 (s, 3H, OMe), 3.90 (s, 6H, OMe), 1,2,4-isomer; 8.82 (s, 3H, CH), 3.95 (s, 9H, OMe) 1,3,5-isomer. The identification of **4S**,[3] **3Se**, and **8Se**[5] was based on the comparison of NMR data.

Reactions of 1S and 1Se with Methyl Acetylene Carboxylate in Toluene at 70 °C. Methyl acetylene carboxylate (0.5 mL, 5.9 mmol) was added to 0.05 mmol of **1S** (22.2 mg) or of **1Se** (27 mg) in toluene (15 mL). Then the mixtures were heated at 70 °C for 24 h, and the color of the solutions turned dark red. After removing the solvent the residues were checked by ^1H NMR. The residues contained the trimethyl-1,2,4- and trimethyl-1,3,5-benzenetricarboxylates in a ratio close to 1:1, and the respective 16e complex **1S** or **1Se**, respectively, was still present (identified by the typical ^1H NMR signal of the Cp* group). EI-MS showed the molecular ion peak at m/e = 252.

Heating of 2S and 2Se in Toluene at 70 °C. Suspensions of the complexes **2S** (10.6 mg, 0.01 mmol) or **2Se** (12.4 mg, 0.01 mmol) in toluene (15 mL) were heated at 70 °C for 24 h. In the case of **2S** a green solution was obtained, and the ^1H NMR spectrum indicated the presence of the 16e complex $Cp^*Rh[S_2C_2(B_{10}H_{10})]$ (**1S**) as the main component. In the case of **2Se**, a deep brown solution was obtained, and after removing the solvent a product was left for which the NMR spectra showed complete agreement with known data for **8Se**.[5]

Heating of 2S, 2Se with Methyl Acetylene Carboxylate in Toluene at 70 °C. The complex **2S** (5.3 mg, 5×10^{-3} mmol) or **2Se** (6.2 mg, 5×10^{-3} mmol) was added to a solution of methyl acetylene carboxylate (0.5 mL, 5.9 mmol) in toluene (15 mL). Then the mixtures were heated at 70 °C for 24 h. The resulting deep-brown solutions were evaporated under reduced pressure until viscous residues were left. ^1H NMR spectra showed these to consist of a mixture of trimethyl-1,2,4- and trimethyl-1,3,5-benzenetricarboxylates in an approximate ratio of 1:1, along with a small amount of the corresponding 16e complex **1S** or **1Se**, respectively.

Reaction of 4S with Methyl Acetylene Carboxylate in Toluene at 70 °C. The complex **4S**[3] (12.2 mg, 0.02 mmol) was dissolved in toluene (15 mL), and methyl acetylene carboxylate (0.5 mL, 5.9 mmol) was added. The mixture was heated for 24 h at 70 °C until it turned to a deep-red solution, which was evaporated to give a viscous residue. The ^1H NMR spectra showed the presence of a mixture of trimethyl-1,2,4- and trimethyl-1,3,5-benzenetricarboxylates in an approximate ratio of 1:1. The $^1H(Cp^*)$ NMR signal of **4S** was still detectable, although it was very weak, indicating that decomposition of **4S** occurred to some extent in the course of the reaction.

Reactions of 3Se and 5S with Methyl Acetylene Carboxylate in Toluene at 70 °C. The complex **5S**[4] (15.3 mg, 0.025 mmol) or **3Se**[5] (15.6 mg, 0.025 mmol) was added to a solution of methyl acetylene carboxylate (0.5 mL, 5.9 mmol) in toluene (15 mL). Then the mixtures were heated at 70 °C for 24 h. The resulting dark-red solutions were evaporated to give a viscous residue. The ^1H NMR spectra showed the presence of trimethyl-1,2,4- and trimethyl-1,3,5-benzenetricarboxylates in 1:1 ratio and also the complexes **1S** and **1Se**, respectively.

Reactions of 7S with Phenylacetylene and of 8Se with Methyl Acetylene Carboxylate in Toluene at 70 °C. Toluene solutions (15 mL) of **7S**[6] (10.9 mg, 0.02 mmol) and phenylacetylene (0.5 mL, 4.6 mmol) or **8Se**[5] (12.4 mg, 0.02 mmol) and methyl acetylene carboxylate (0.5 mL, 5.9 mmol), respectively, were heated at 70 °C for 24 h. The resulting dark-red solutions were evaporated to give viscous residues. ^{13}C NMR showed in the case of **7S** that a mixture of 1,2,4-triphenylbenzene and 1,3,5-triphenylbenzene was present (ratio close to 1:1). ^{13}C NMR (62.9 MHz, $CDCl_3$, 22 °C; all 8 signals for quaternary carbon atoms are resolved and 12 of 16 signals for the *o*-, *m*, and *p*-CH carbon atoms): $\delta^{13}C$ 142.3, 141,4, 141.0, 141.1, 140.9, 140.5, 140.3, 139.5 (quaternary C); 131.1, 129.82, 129.84, 129.4, 128.6, 128.3, 127.85, 127.89, 127.4, 126.6, 126.5, 126.1 (*o*-, *m*, *p*-CH). In the case of **8Se**, a mixture of trimethyl-1,2,4- and trimethyl-1,3,5-benzenetricarboxylates was present in an approximate ratio of 1:1.

Reactions of 1S and 1Se with Phenylacetylene in Toluene at 70 °C. Phenylacetylene (0.5 mL, 4.6 mmol) was added to **1S** (22.2 mg; 0.05 mmol) or **1Se** (27 mg, 0.05 mmol) in toluene (15 mL), and the mixtures were heated at 70 °C for 17 h to give dark-red solutions. After removing the solvent in vacuo, viscous residues were left. According to the ^{13}C NMR spectra, the residues contained 1,2,4- and 1,3,5-triphenylbenzenes in an approximate ratio of 1:1, a small amount of unreacted phenylacetylene, and the respective 16e complex. The EI-MS showed the molecular ion peak at *m*/*e* 306 (100%).

Crystal Structure Analyses of 2Se and 3Se. The reflection intensities were collected on a Siemens P4 diffractometer (Mo Kα radiation, λ = 71.073 pm, graphite monochromated).

Structure solution and refinements were carried out with the program package SHELXTL-PLUS V.5.1. The temperature for all structure determinations was 296 K. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms at the boron atoms were located from difference Fourier syntheses. The remaining hydrogen atoms are on calculated positions. All hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

Crystal structure of 2Se: $C_{32}H_{58}B_{20}O_4Se_4Rh_2$, red plate with dimensions 0.18 × 0.15 × 0.08 mm crystallizes in the triclinic space group $P\bar{1}$ with the lattice parameters a = 1154.19(6), b = 1162.08(8), c = 1319.05(8) pm, α = 104.643(5)°, β = 105.382(4)°, γ = 113.184(4)°, V = 1435.06(15) × 10^6 pm^3, $Z = 1$, $\mu = 3.427$ mm^{-1}; 5639 reflections collected in the range 3° ≤ 2ϑ ≤ 50°, 4850 reflections independent, 4156 assigned to be observed [$I > 2\sigma(I)$], full-matrix least-squares refinement against F^2 with 314 parameters converged at R1/wR2 values of 0.028/0.073; empirical absorption correction (Ψ-scans) resulted in min./max. transmission factors of 0.7147/0.9985, the max./min. residual electron density was 0.59/−0.46 10^{-6} e pm^3.

Crystal Structure of 3Se: $C_{20}H_{33}B_{10}O_4Se_2Rh$, dark-red prism with dimensions 0.18 × 0.13 × 0.10 mm crystallizes in the monoclinic space group $P2_1/n$ with the lattice parameters a = 960.99(9), b = 3057.47(14), c = 991.38(8) pm, β = 91.076(7)°, V = 2912.4(4) 10^6 pm^3, $Z = 4$, $\mu = 3.112$ mm^{-1}; 6316 reflections collected in the range 3° ≤ 2ϑ ≤ 50°, 5101 reflections independent, 3958 assigned to be observed [$I > 2\sigma(I)$], full-matrix least-squares refinement against F^2 with 335 parameters converged at R1/wR2 values of 0.032/0.073, empirical absorption correction (Ψ-scans) resulted in min./max. transmission factors of 0.2324/0.2721, the max./min. residual electron density was 0.507/-0.285 10^{-6} e pm^{-3}.

Supporting Information Available: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-142272 (**2Se**) and CCDC-142271 (**3Se**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat.): +44 (0)1223/336033; e-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: Details about the X-ray crystal structures, including tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **2Se** and **3Se**, are available free of charge via the Internet at http://pubs.acs.org.

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