Metal-Induced B–H Activation: Addition of Methyl Acetylene Carboxylates to Cp*Rh-, Cp*Ir-, (*p*-cymene)Ru-, and (*p*-cymene)Os Half-Sandwich Complexes Containing the Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dithiolate Ligand

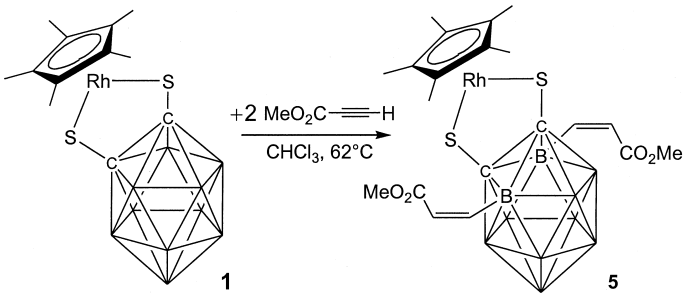
Max Herberhold,* Hong Yan, Wolfgang Milius, and Bernd Wrackmeyer*[a]

Abstract: The reactions of the 16e half-sandwich complexes [Cp*M{S_2C_2-($B_{10}H_{10}$)}] (**1**: M = Rh; **2**: M = Ir) and [η^6-(4-isopropyltoluene)M{S_2C_2-($B_{10}H_{10}$)] (**3**: M = Ru; **4**: M = Os) with both methyl acetylene monocarboxylate and dimethyl acetylene dicarboxylate were studied in order to obtain more evidence for B–H activation, *ortho*-metalation, and B(3,6)-substitution of the carborane cluster. In the case of rhodium, the reaction of **1** with methyl acetylene monocarboxylate led to new complexes after twofold insertion into one of the Rh–S bonds (**7**), and twofold insertion together with B-substitution at the carborane cage (**8**). In the case of iridium, the reactions of **2** with methyl acetylene monocarboxylate gave two geometrical isomers **10** and **11**, in which the alkyne is inserted into one of the Ir–S bonds, followed by hydrogen transfer from the carborane via the metal to the former alkyne and formation of an Ir–B bond. Only one type each (**12** and **13**) of these isomers was obtained from the reactions of the ruthenium and osmium half-sandwich complexes **3** and **4**. The 16e starting materials **1**–**4** reacted with dimethyl acetylene dicarboxylate at room temperature to give the complexes **14**–**17**, respectively, which are formed by addition of the C≡C bond to the metal center and insertion into one of the metal–sulfur bonds. The proposed structures in solution were deduced from NMR data (^{1}H, ^{11}B, ^{13}C, ^{103}Rh NMR), and X-ray structural analyses were carried out for the rhodium complexes **7** and **8**.

Keywords: B–H activation · carboranes · insertions · sulfur · transition metals

Introduction

Although numerous organothiolato complexes of transition metals have been reported, and in some cases their chemistry has been studied,[1] the chelating 1,2-dicarba-*closo*-dodecaborane(1,2)-dithiolate ligand has received only scant attention. In the 16e half-sandwich complexes [Cp*M{$S_2C_2(B_{10}H_{10})$}] [M = Rh (**1**),[2] Ir (**2**)[3, 4]] and [(*p*-cymene)M{$S_2C_2(B_{10}H_{10})$}] [M = Ru (**3**), Os (**4**)],[5] the metal centers, the metal–sulfur bonds, and the B(3,6)–H bonds of the *o*-carborane cage are reactive sites for interactions with unsaturated substrates. We have shown recently that the reaction of **1** with methyl acetylene monocarboxylate can be controlled to give selectively a 3,6-disubstituted *o*-carborane derivative (Scheme 1).[6] This reaction must follow a fairly complex pathway, for example involving not only addition[7] of the C≡C bond to the metal center, insertion of the C≡C unit[8] into the metal–sulfur bond, and B–H activation,[9] but also formation and cleavage of a metal–B bond, and therefore further studies were indicated. Insertion of the C≡C unit was found in the case of the reaction of **1** with dimethyl acetylene dicarboxylate,[6] and analogous products have been obtained from the reaction of [CpCo{$S_2C_2(B_{10}H_{10})$}] with alkynes.[10] Bearing in mind that selective B-substitution of the *o*-carborane cage is still a challenge,[11] and that the concept of transition metal induced activation of element–hydrogen bonds is of considerable interest,[12] we have tried to obtain more information on the reaction of **1** with methyl acetylene monocarboxylate (Scheme 1), and we have also studied the



Scheme 1. Reaction of **1** with methyl acetylene monocarboxylate to give **5**.

[a] M. Herberhold, B. Wrackmeyer, H. Yan, W. Milius
Laboratorium für Anorganische Chemie der Universität Bayreuth
95440 Bayreuth (Germany)
Fax: (+49) 921-55-2157
E-mail: Max.Herberhold@uni-bayreuth.de
B.Wrack@uni-bayreuth.de

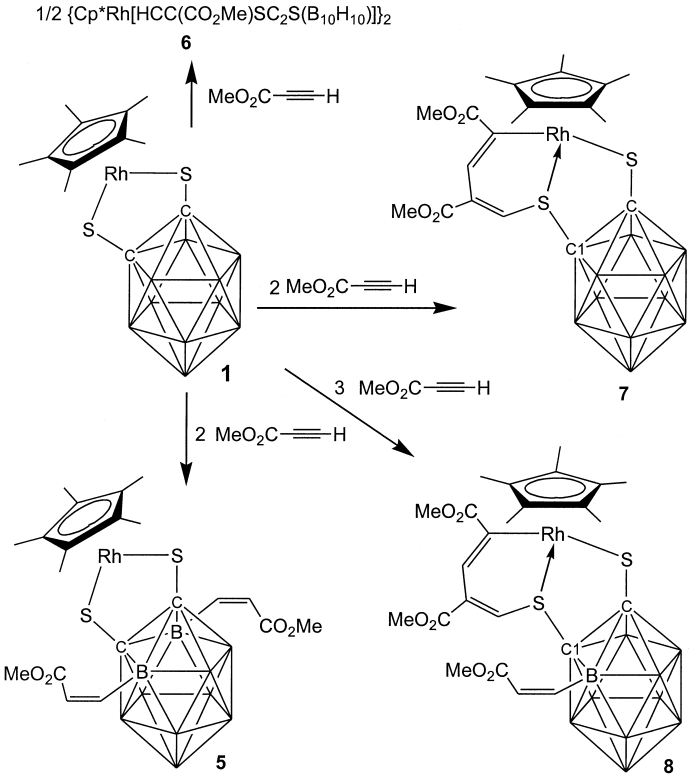
0947-6539/00/0616-3026 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 16

behavior of other comparable 16e half-sandwich complexes of iridium (**2**), ruthenium (**3**), and osmium (**4**) towards methyl acetylene carboxylates.

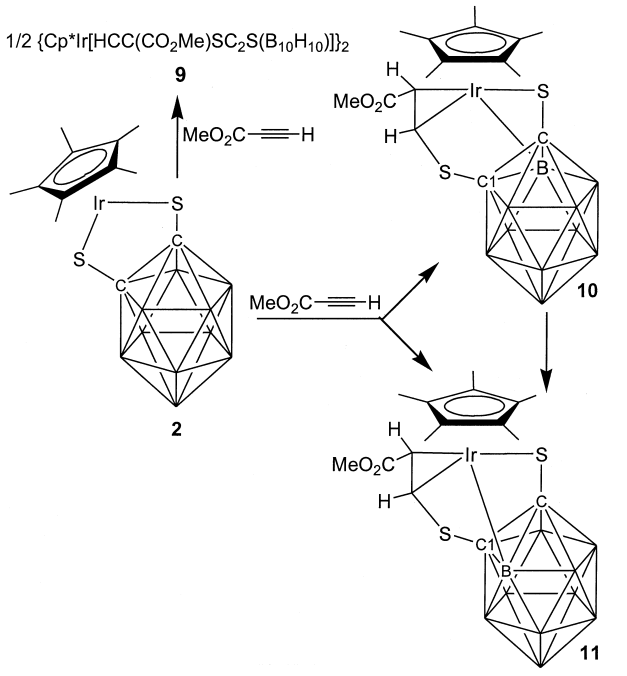
Results and Discussion

Reaction of 1 with methyl acetylene monocarboxylate: The results are summarized in Scheme 2. If the reaction of **1** with $MeO_2C{-}C{\equiv}CH$ is carried out in boiling chloroform, the main product is **5**, as reported previously.[6] However, the same reaction in CH_2Cl_2 at room temperature affords several products of which three (**5**, **7**, **8**) could now be isolated and fully characterized. A minor product **6** is almost insoluble, and so far we have failed to obtain suitable crystals for X-ray structural analysis. The molecular ion of **6** in the FD mass spectrum suggests that it should be the dimer of the 1:1 reaction. However, the ^1H and ^{13}C NMR data of diluted solutions are also consistent with a monomeric complex which has a structure analogous to that established for the complexes **14**–**17**[6] (vide infra). In the cases of the two major products, **7** and **8**, NMR spectroscopy indicates that the molecular structures, as determined by X-ray diffraction in the solid state, are retained in solution.

Reactions of 2 with methyl acetylene monocarboxylate: The iridium complex **2** reacts with $MeO_2C{-}C{\equiv}CH$ as shown in Scheme 3. There is again a fairly insoluble product **9**,



Scheme 2. Reactions of **1** with methyl acetylene monocarboxylate.



Scheme 3. Reactions of **2** with methyl acetylene monocarboxylate.

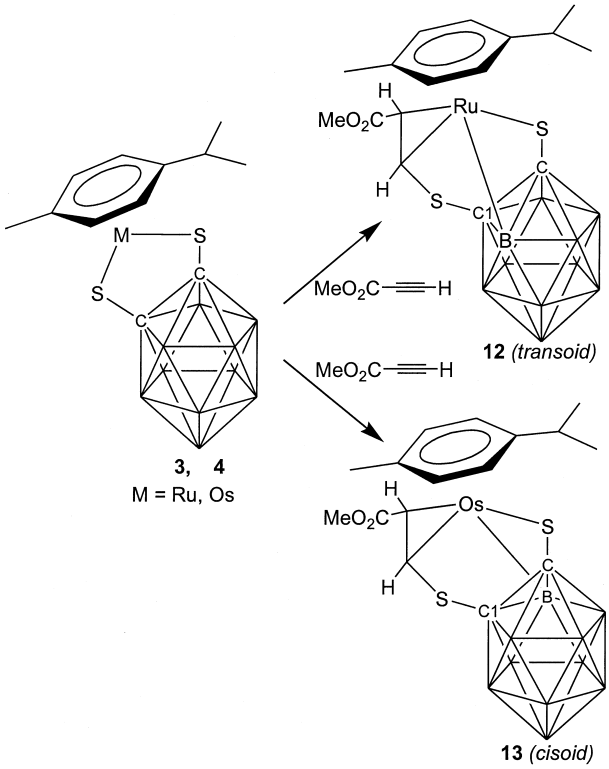
analogous to **6**. A labile complex **10** was isolated in a mixture with the more stable **11**. According to the NMR data (see Table 1) these complexes are geometrical isomers with the same structural units. However, there is a *cisoid* structure in **10** and a *transoid* structure in **11** (*cisoid* and *transoid*: the η^2-(S)CH=CH and the B–C(1) bonds in the coordination sphere of the metal point into the same (*cisoid*) or into opposite

Abstract in German: *Die Reaktionen der 16e Halbsandwichkomplexe [Cp*M{$S_2C_2(B_{10}H_{10})$}] (**1**, M = Rh, **2**, M = Ir) und [η^6-(4-Isopropyltoluol)M{$S_2C_2(B_{10}H_{10})$}] (**3**, M = Ru, **4** M = Os) mit Acetylenmonocarbonsäure-methylester und Acetylendicarbonsäure-dimethylester wurden untersucht, um weitere Hinweise auf B-H-Aktivierung, ortho-Metallierung and B(3,6)-Substitution des Carboran-Clusters zu erhalten. Im Fall von Rhodium führte die Reaktion von **1** mit Acetylenmonocarbonsäure-methylester zu neuen Komplexen nach zweifacher Insertion in eine der Rh-S Bindungen (**7**), bzw. nach zweifacher Insertion und zusätzlicher B-Substitution am Carboran-Gerüst (**8**). Im Fall von Iridium ergaben die Reaktionen von **2** mit Acetylenmonocarbonsäure-methylester zwei geometrische Isomere **10** und **11**, in denen jeweils die C≡C-Bindung in eine der Ir-S Bindungen insertiert, ein Wasserstoff vom Carboran über das Metall zu dem ehemaligen Alkin-Kohlenstoffatom übertragen, und eine Ir-B Bindung ausgebildet worden war. Nur jeweils ein Typ (**12** bzw. **13**) dieser Isomere wurde bei den analogen Reaktionen der Ruthenium- (**3**) und Osmium Halbsandwichkomplexe (**4**) erhalten. Alle 16e Edukte **1**–**4** reagierten mit Acetylendicarbonsäure-dimethylester schon bei Raumtemperatur zu den Komplexen **14**–**17**, die unter Addition der C≡C-Bindung an das Metall und Insertion in eine der Metall-Schwefel Bindungen entstanden waren. Die vorgeschlagenen Strukturen in Lösung beruhen auf NMR Daten (^1H, ^{11}B, ^{13}C, ^{103}Rh NMR), und für die Rhodiumkomplexe **7** und **8** wurden Röntgenstrukturanalysen durchgeführt.*

  0947-6539/00/0616-3027 $ 17.50+.50/0

directions (*transoid*)). Both complexes **10** and **11** possess an Ir–B bond, and a hydrogen atom has been transferred from boron to the olefinic carbon atom which had been attached to the iridium center in the first insertion product (see Scheme 6). This hydrogen transfer is stereoselective. The stereochemistry of the insertion is the same as that which must be assumed for the analogous reaction of **1**, taking into account the structures of **5**,[6] **7** and **8**. However, in the case of the reaction of **1** with $MeO_2C{-}C{\equiv}CH$, we have failed to detect such complexes with Rh–B bonds, although rhodium complexes of this type are formed if other alkynes (e.g. phenylacetylene[4]) are used. It is also noteworthy that there is no further reaction of either **10** or **11** with $MeO_2C{-}C{\equiv}CH$, in contrast to the situation for **1**. The derivative **11** with the *transoid* arrangement of the η^2-EC(H)=C(H)CO_2Me and the B–C(1) bond is the final product. NMR spectra of solutions containing **10** and **11** show a steadily decrease in the signal intensities for **10**, and the signal intensities for **11** increase. It is not quite clear as yet how **10** is converted into **11**.[13] Further intramolecular rearrangements were not observed.

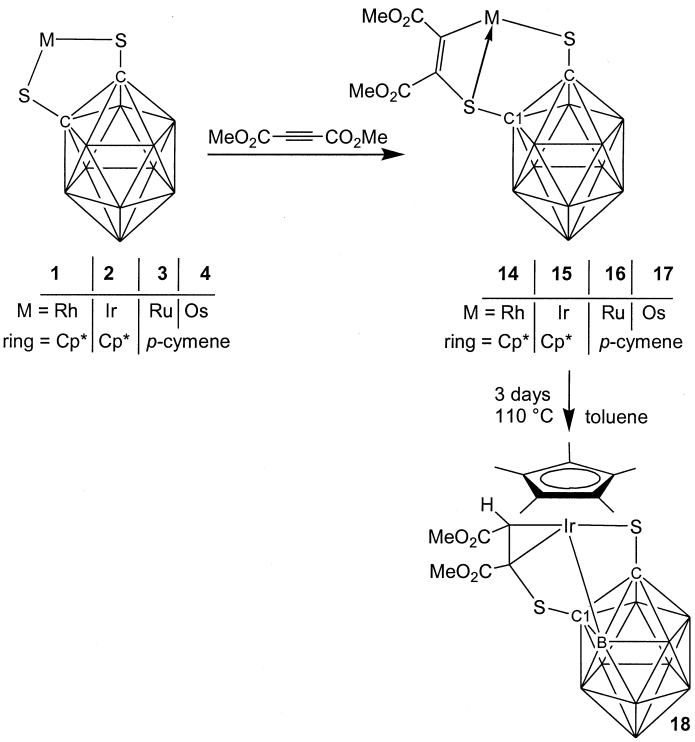
Reactions of 3 and 4 with methyl acetylene monocarboxylate: The ruthenium and osmium complexes **3** and **4** react with $MeO_2C{-}C{\equiv}CH$ in the same way as **2** to give the complexes **12** and **13**, each with a M–B bond (Scheme 4). The ^{13}C NMR data



Scheme 4. Reactions of **3** and **4** with methyl acetylene monocarboxylate.

(Table 1) suggest that a *transoid* structure is present in **12** and a *cisoid* structure in **13**. In contrast to the case of **10** and **11**, there were no further rearrangements observed for **13** after prolonged time at room temperature or after heating at 60 °C in $CDCl_3$ solution.

Reactions of 1–4 with dimethyl acetylene dicarboxylate: Although there is no firm evidence so far, it must be assumed that the first product in all reactions of **1–4** with $MeO_2C{-}C{\equiv}CH$ arises from oxidative addition of the C≡C bond to the 16e metal center, followed by insertion into one of the metal–sulfur bonds. Such a product **14** was indeed obtained from the reaction of **1** with $MeO_2C{-}C{\equiv}C{-}CO_2Me$,[6] and we have found now that the analogous addition/insertion products **15–17** are the result of the reactions of $MeO_2C{-}C{\equiv}C{-}CO_2Me$ with the 16e complexes **2–4** (Scheme 5). These complexes are fairly stable with respect

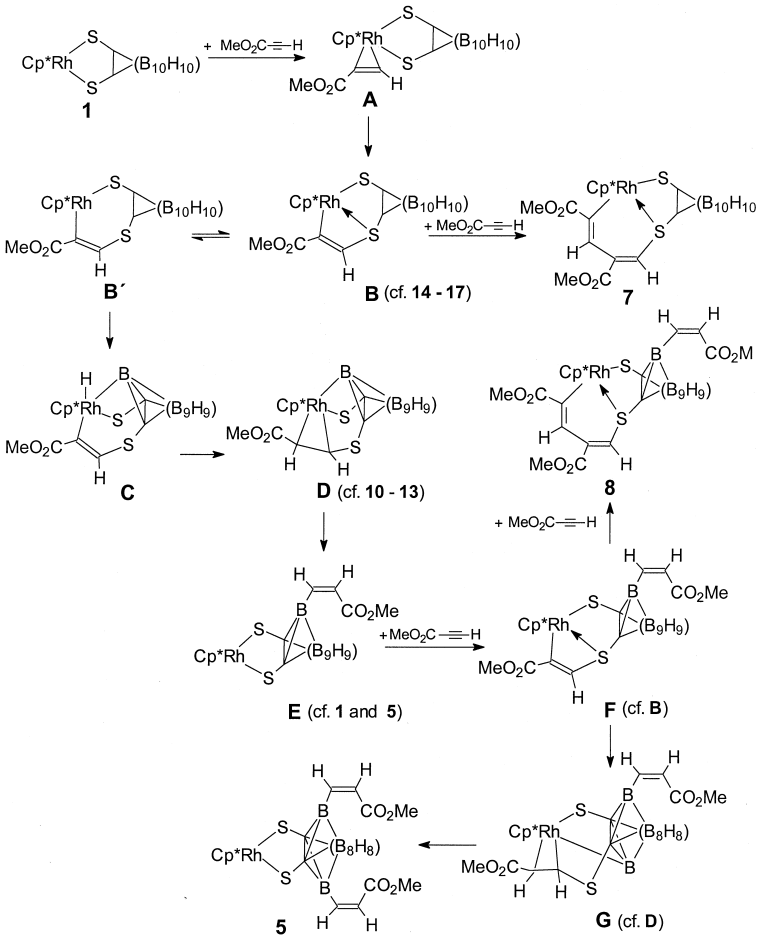


Scheme 5. Reactions of **1–4** with dimethyl acetylene dicarboxylate.

to further rearrangements. Thus, heating in boiling toluene for three days was necessary to enforce the conversion of **15** into **18**. The progress of the reaction could be monitored by ^{11}B NMR spectroscopy, and the appearance of a new ^{11}B NMR signal at $\delta = -24$, typical of the carborane cage Ir–B bond, indicated the rearrangement.

Mechanistic implications: The reaction pathway leading from **1** to **5**—as had been suggested in part previously[6]—is summarized in Scheme 6. Although there are still a few gaps with respect to isolated intermediates, most of the types of complexes shown in Scheme 6 have been identified or even characterized by X-ray structural analysis (exceptions are **A** and **C**). The equilibrium between **B** and **B′** is assumed in order to explain B–H activation, since the structure **B** appears to be fairly rigid, and the rhodium atom cannot come close to the B(3)–H or B(6)–H positions of the carborane cage. In the structure **B′** the rhodium atom would be more mobile than in **B**, and therefore can approach reactive sites at the carborane cage in order to take over a hydrogen atom as shown in **C**. The

0947-6539/00/0616-3028 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 16



Scheme 6. Mechanism proposed for the reaction of [Cp*Rh{$S_2C_2(B_{10}H_{10})$}] (**1**) with methyl acetylene monocarboxylate (complexes assigned to capital letters were not isolated).

hydrogen atom is passed stereoselectively to the olefinic carbon atom to give complex **D** which has a structure comparable to that of **10**–**13**. Apparently, the insertion of a second alkyne (from **B** to **7**) competes with the pathway from **B** to **E**, and in **7** the strength of the coordinative S → Rh bond may be increased, hampering further reactions. In the complexes **14**–**17**, the presence of a second carboxylate substituent may also cause an increase in the strength of the respective coordinative S → M bond, since these derivatives are exceptionally stable examples of type **B**. It can be expected that the 16e complex **E** reacts with the alkyne to give the addition/insertion product **F**. If a second insertion takes place, the complex **8** is formed as another stable product, for the same reasons as discussed for **7**. However, in competition, the analogous intramolecular rearrangements as from **B** to **E** will transform **F** into the 16e complex **5**, in which both the B(3) and B(6) positions are substituted. This twofold substitution then helps to protect the 16e complex **5** against further reactions with the alkyne.

NMR spectroscopic results: The ^{13}C NMR data are given in the Tables 1 and 2, whereas ^{1}H, ^{11}B and ^{103}Rh NMR data are listed in the Experimental Section. In all cases, the NMR spectroscopic results are in support of the proposed structures in solution. Both ^{1}H and ^{13}C NMR spectra (see Figure 2) indicate that the complexes

Table 1. ^{13}C NMR data[a] of the complexes **6** and **9**–**17**.

	$E_2C_2B_{10}H_{10}$	Cp* or *p*-cymene	C–E	C–M	C=O	Me-O
6	91.8, 94.9	9.6, 101.3 [5.7]	117.1	168.8 [37.0]	171.9	51.4
9	90.2, 92.4	8.9, 95.7	118.8	151.9	172.5	51.2
10	94.1, 97.5	8.8, 103.8	58.9	29.6	174.4	51.6
11	101.3,105.7	8.9, 100.6	53.7	50.0	171.7	51.6
12[b]	105.8, 105.9	17.6, 20.9, 25.3, 31.5, 95.9, 98.2, 102.1, 103.4, 105.9, 120.4	67.4	56.1	175.8	52.1
	105.4, 106.1	19.2, 21.3, 24.5, 30.5, 96.2, 98.4, 101.9, 102.5, 112.4, 113.9	67.7	55.3	176.2	52.3
13	93.3, 100.3	18.5, 23.3, 23.6, 30.9, 90.7 (broad), 95.1 (broad), 97.8, 98.6	57.8	28.9	179.1	51.9
14	77.7, 97.2	9.3, 100.3 [5.8]	123.0	182.2 [28.4]	158.5 [2.0], 168.5	52.0, 52.7
15	73.3, 94.6	9.0, 94.8	129.4	169.5	162.4, 165.4	51.9, 52.4
16	76.1, 94.6	19.0, 22.8, 30.8, 88.3, 88.5, 88.9, 91.5, 105.1, 107.6	122.8	187.5	157.5, 172.9	52.0, 52.2
17	72.5, 94.0	18.9, 23.0, 23.3, 30.8, 80.3, 80.9, 84.5, 98.2, 99.2	129.7	172.6	161.6, 171.0	51.9, 52.0

[a] The complexes **6** and **9**–**13** were measured in $CDCl_3$, **14**–**17** in CD_2Cl_2, at 22 °C; $J(^{103}Rh,^{13}C)$ (±0.5 Hz) in brackets; (broad) denotes signals broadened by dynamic processes. [b] Measured at −30 °C; two isomers (ratio ≈1.6:1) as a result of hindered rotation of the *p*-cymene ring.

Table 2. ^{13}C NMR data[a] of the complexes **5**,[b] **7**, and **8.**

	$E_2C_2B_{10}H_{10}$	Cp*	C–E	C–C–E	C–C–Rh	C–Rh	=C–B	C=C–B	C=O	Me–O
5	99.4	10.3,99.5 [7.4]	–	–	–	–	138.2 (br)	132.6	167.1	51.0
7	93.9, 100.0	9.0,103.1 [5.1]	125.8	145.3 [2.7]	107.9	165.6 [36.0]	–	–	165.6, 172.8	52.1, 53.1
8	91.5 [1.2], 95.4 [1.7]	8.9, 103.3 [5.2]	128.0 [1.7]	145.5 [2.8]	105.6	162.8 [36.0]	139.0 (br)	133.5	165.1, 166.6, 172.8 [0.6]	50.9, 52.2, 52.9

[a] In $CDCl_3$, at 22 °C; $J(^{103}Rh,^{13}C)$ (±0.5 Hz) in brackets; (br) denotes signals broadened by partially relaxed $^{13}C-^{11}B$ coupling. [b] Data from reference [6].

12 and **13** are fluxional with respect to rotation of the *p*-cymene ligand about the metal-ring-centroid axis. All ^{11}B NMR spectra show the typical pattern of signals for *o*-carborane derivatives, [14] and the ^{11}B NMR signal of the boron atom linked to the metal is readily identified by comparison of ^{1}H coupled and ^{1}H decoupled ^{11}B NMR spectra. The ^{13}C NMR spectra are particularly instructive (cf. Figures 1 and 2) for structural assignments. By inspection of the data sets available for related complexes, together with direct structural information,[4, 15] the $\delta(^{13}C)$ data can be used to distinguish between *cisoid* and *transoid* structures (see e.g. the data for **10**/**11** and **12**/**13**): there are significant changes in the ^{1}H NMR data (see Experimental Section), and both in the $\delta(^{13}C)$(carborane) and in the $\delta(^{13}C)$ values of the terminal carbon atom of the coordinated C=C bond. Chemical shifts $\delta(^{103}Rh)$ were determined by heteronuclear $^{1}H\{^{103}Rh\}$ double-resonance experiments,[16] which also allowed one to differentiate between coupling constants $J(^{1}H,^{1}H)$ and $J(^{103}Rh,^{1}H)$. The $\delta(^{103}Rh)$ values of **7** ($+439\pm1$) and **8** ($+462\pm1$) are similar, in agreement with the comparable structural features in the vicinity of the rhodium atom.

X-ray structural analyses of the complexes 7 and 8: The molecular structures of the rhodium complexes **7** and **8** are shown in the Figures 3 and 4, respectively. In each case, the rhodium atom is part of a bicyclic ring system fused at the Rh–S(1) bond with angles close to 90°. Both the five- and the six-membered rings are nonplanar. The arrangements of the carborane cages are different in **7** and **8** with respect to B(3) and (B6). In **7**, the rhodium atom is tilted owing to the nonplanar five-membered ring into the direction of B(6) and a similar tilt is observed in the case of **8** towards B(3), B(6) being already substituted. In both complexes, the coordinative S(1) → Rh bond is somewhat shorter (8–9 pm) than the Rh–S(2) bond. Clearly, if this coordinative bond would be sufficiently weak, the rhodium atom could approach more easily the site of B(6)–H (in **7**) or B(3)–H (in **8**). The bond length C(1)–C(2) in the 16e complex **5** is shorter (by 4–5 pm) than in the 18e complexes **7** and **8**. Otherwise, the structural features of the carborane cages in **5**, **7**, and **8** remain unchanged. There is a rather large bond angle C(12)-C(11)-B(6) (132.6°), similar to the analogous data for **5** with the 3,6-disubstituted carborane cage.

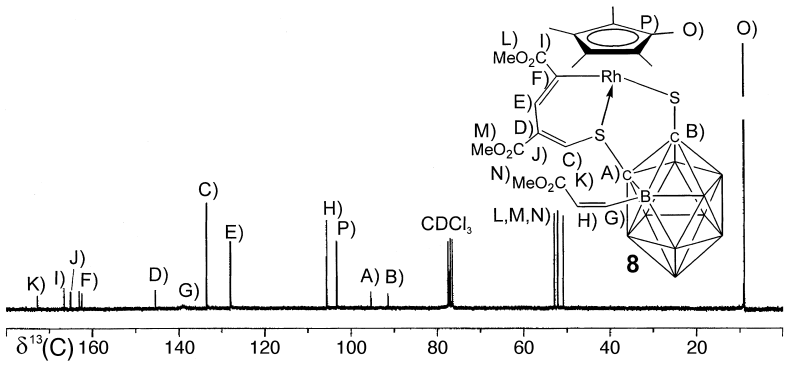


Figure 1. 62.9 MHz $^{13}C\{^{1}H\}$ NMR spectrum of the rhodium complex **8** in $CDCl_3$ measured at 22 °C. All sixteen ^{13}C resonances are visible. The $^{13}C(1,2)$ carborane signals, marked (A) and (B), are somewhat broader and less intense than the other signals of quaternary carbon atoms, and there is the typical broad signal of the olefinic carbon atom (G) linked to boron by a two-center, two-electron (2c/2e) bond. The $^{13}C(F)$ resonance signal is observed as a doublet with $^{1}J(^{103}Rh,^{13}C) = 36.0$ Hz.

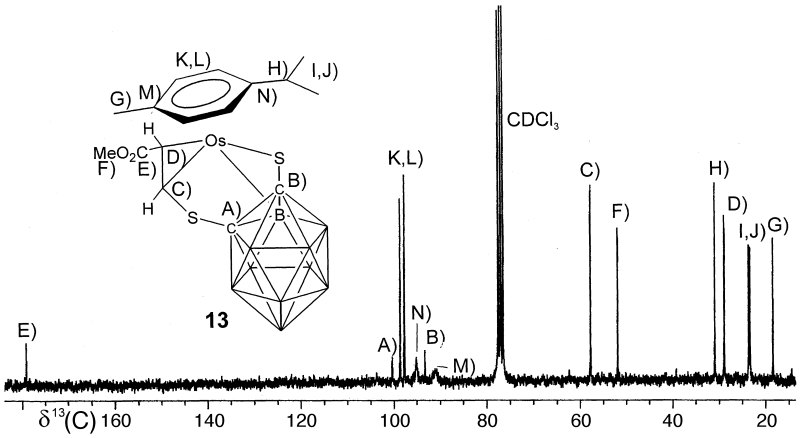


Figure 2. 62.9 MHz $^{13}C\{^{1}H\}$ NMR spectrum of the osmium complex **13** in CD_2Cl_2 at 22 °C. All ^{13}C NMR signals are observed. Note the broad signals (N) and (M) for the quaternary carbon atoms of the *p*-cymene ring, indicating slow rotation of this ring about the Os-ring-center axis.

Conclusion

In the course of the reactions of the 16e half-sandwich complexes **1**–**4** with methyl acetylene carboxylates firm evidence of metal-induced B–H activation is provided by the identification of the iridium, ruthenium, and osmium complexes **10**–**13** and **18**, in which a metal–boron bond is present. Although the analogous rhodium complexes could not be detected, the structures of the products, in particular those of **5** and **8**, leave no doubt that the mechanistic proposals are correct and consistent. Both, the alkyne insertion reaction and the hydrogen transfer proceed with remarkable stereoselectivity. Geometrical isomers, as in the case of **10** and **11**, arise from the orientation of the C(1)-C(2)-B plane at the metal center. It is not clear at present why the *transoid* complexes are sometimes favored (e.g. **11**, **12**) and sometimes not (**13**). However, it is beyond doubt that further intramolecular rearrangements leading to substitution of the carborane cage cannot take place readily in the *transoid* complexes.

0947-6539/00/0616-3030 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 16

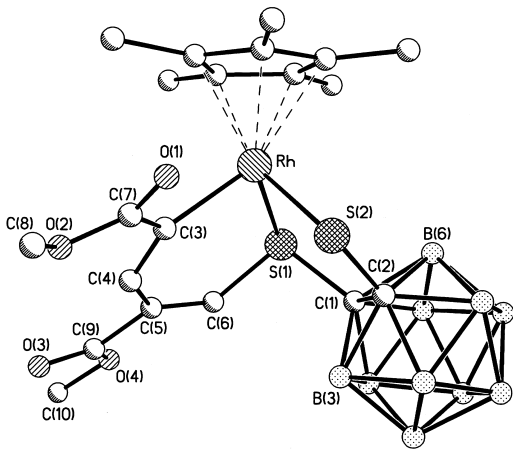


Figure 3. Molecular geometry of the rhodium complex **7**. Selected bond lengths [pm] and angles [°]: Rh–C(3) 204.3(3), Rh–ring centroid 186.9, Rh–S(1) 228.47(10), Rh–S(2) 236.40(10), S(1)–C(6) 175.2(4), S(1)–C(1) 180.8(4), S(2)–C(2) 177.6(4), C(1)–C(2) 167.9(5), C(3)–C(4) 134.5(6), C(4)–C(5) 144.9(6), C(5)–C(6) 135.5(5), C(3)–C(7) 150.5(6), C(5)–C(9) 150.4(6), C(1)–B(6) 171.8(5), C(2)–B(3) 174.5(6); C(3)-Rh-S(1) 92.23(12), C(3)-Rh-S(2) 86.08(12), S(1)-Rh-S(2) 91.02(4), C(6)-S(1)-Rh 114.48(13), C(6)-S(1)-C(1) 104.24(18), C(1)-S(1)-Rh 107.95(12), C(2)-S(2)-Rh 104.07(12), C(4)-C(3)-Rh 127.7(3), C(3)-C(4)-C(5) 129.6(4), C(4)-C(5)-C(6) 128.6(4), C(5)-C(6)-S(1) 122.6(2), S(1)-C(1)-C(2) 114.6(2), S(2)-C(2)-C(1) 119.7(2); S(1)-Rh-S(2)/S(1)-C(1)-C(2)-S(2) 165.3, S(1)-Rh-C(3)/C(3)-C(4)-C(5)-C(6)-S(1) 162.4, S(1)-Rh-C(3)/S(1)-Rh-S(2) 93.9.

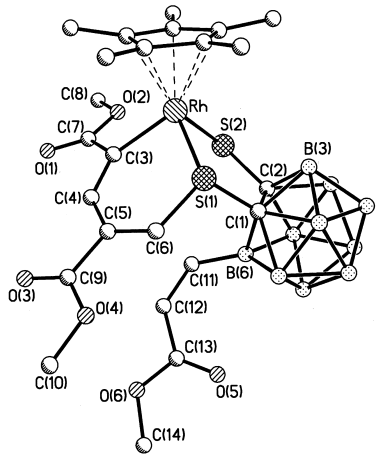


Figure 4. Molecular geometry of the rhodium complex **8**. Selected bond lengths [pm] and angles [°]: Rh–C(3) 203.6(3), Rh–ring centroid 187.3, Rh–S(1) 228.99(7), Rh–S(2) 237.95(8), S(1)–C(6) 175.8(3), S(1)–C(1) 182.1(3), S(2)–C(2) 177.6(3), C(1)–C(2) 166.9(4), C(3)–C(4) 134.6(4), C(4)–C(5) 143.9(5), C(5)–C(6) 134.3(4), C(3)–C(7) 150.2(4), C(5)–C(9) 151.8(4), C(1)–B(6) 176.3(4), C(2)–B(3) 173.9(4), B(6)–C(11) 155.3(5), C(11)–C(12) 134.0(5), C(12)–C(13) 145.6(5); C(3)-Rh-S(1) 91.30(9), C(3)-Rh-S(2) 88.85(9), S(1)-Rh-S(2) 90.78(3), C(6)-S(1)-Rh 115.03(11), C(6)-S(1)-C(1) 103.85(13), C(1)-S(1)-Rh 107.64(9), C(2)-S(2)-Rh 103.89(9), C(4)-C(3)-Rh 129.2(2), C(3)-C(4)-C(5) 129.7(3), C(4)-C(5)-C(6) 128.6(3), C(5)-C(6)-S(1) 123.0(2), S(1)-C(1)-C(2) 115.00(18), S(2)-C(2)-C(1).119.57(18), C(12)-C(11)-B(6) 132.6(3), C(11)-C(12)-C(13) 127.5(4); S(1)-Rh-S(2)/S(1)-C(1)-C(2)-S(2) 164.8, S(1)-Rh-C(3)/C(3)-C(4)-C(5)-C(6)-S(1) 165.4, S(1)-Rh-C(3)/S(1)-Rh-S(2) 91.1.

Experimental Section

General and starting materials: The preparative work was carried out by observing all precautions to exclude air and moisture. The starting complexes $[\{Cp^*MCl_2\}_2]$ (M = Rh, Ir[17]) and $[\{(p\text{-cymene})MCl_2\}_2]$ (M = Ru[18], Os[19]) were prepared according to established procedures; *n*-butyllithium (1.6 M in hexane), *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, and the methyl acetylene carboxylates were used as commercial products without further purification. The 16e complexes $[Cp^*M\{S_2C_2(B_{10}H_{10})\}]$ (M = Rh[3], Ir[4, 20]) and $[(p\text{-cymene})M\{S_2C_2(B_{10}H_{10})\}]$[5] (M = Ru, Os) were obtained as described. NMR measurements: Bruker ARX 250 and DRX 500 spectrometers, using 5 mm tubes with solutions in $CDCl_3$ or CD_2Cl_2 at 20–23 °C (see also Tables 1, 2); chemical shifts are given with respect to $CHCl_3$/$CDCl_3$ ($\delta(^1H) = 7.24$; $\delta(^{13}C) = 77.0$) or $CDHCl_2$ $\delta(^1H) = 5.33$, $\delta(^{13}C) = 53.8$), external $Et_2O \cdot BF_3$ ($\delta(^{11}B) = 0$ for $\Xi(^{11}B) = 32.083971$ MHz), and $\delta(^{103}Rh) = 0$ for $\Xi(^{103}Rh) = 3.16$ 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.

Synthesis of 5–8: Methyl acetylene carboxylate (0.38 mL, 4.5 mmol) was added to the green solution of **1** (200 mg, 0.45 mmol) in CH_2Cl_2 (30 mL). The solution was stirred for three days at ambient temperature to give a brown solution. After removal of the solvent, chromatography of the residue on silica gel (Merck, Kieselgel 60) gave **6** (orange), **7** (red), and **5** (green) by elution with CH_2Cl_2. Further elution with CH_2Cl_2/THF (50:1) afforded **8** as a red zone.

5: Yield 25%; m.p. 202 °C (decomp); $C_{20}H_{33}B_{10}O_4RhS_2$: calcd: C 39.21, H 5.43, B 17.65; found: C 38.87, H 5.35, B 18.10. Spectroscopic data as reported previously.[6]

6: Yield 5%; m.p. 190 °C (decomp); ^1H NMR ($CDCl_3$): $\delta = 1.71$ (s, 15H; Cp*), 3.61 (s, 3H; OMe), 5.11(s, 1H; CH); ^{11}B NMR ($CDCl_3$): $\delta = -9.5$, -5.4 (5:5); IR (KBr) [cm^{-1}]: $\tilde{\nu} = 2572$, 2593 (B-H); 1698 (COOMe); EI-MS (70 eV): *m*/*z* (%): 613 (4, $[M^+ - [Cp^*Rh(S_2C_2B_{10}H_{10})]$), 529 (25, $1/2[M]^+$), 444 (100, $[Cp^*Rh(S_2C_2B_{10}H_{10})]$).

7: Yield 50%; m.p. 232 °C (decomp); $C_{20}H_{33}B_{10}O_4RhS_2$: calcd: C 39.21, H 5.43, B 17.65; found: C 38.31, H 5.35, B 18.20; ^1H NMR ($CDCl_3$): $\delta = 1.63$ (s, 15H; Cp*), 3.69 (s, 3H; OMe), 3.88 (s, 3H; OMe), 6.73 (d, $J_{Rh,H} = 2.7$ Hz, 1H; CH), 7.54 (d, $J_{Rh,H} = 0.8$ Hz, 1H; S-CH); ^{11}B NMR ($CDCl_3$): $\delta = -12.7$, -10.2, -7.5, -5.3 (1:3:3:3); ^{103}Rh NMR ($CDCl_3$): $\delta = 439 \pm 1$; IR (KBr) [cm^{-1}]: $\tilde{\nu} = 2566$, 2592, 2602, 2611 (B–H); 1693, 1702, 1723 (COOMe); EI-MS (70 eV): *m*/*z* (%): 613 (25, $[M^+]$).

8: Yield 10%; m.p. 260 °C (decomp); ^1H NMR ($CDCl_3$): $\delta = 1.62$ (s, 15H; Cp*), 3.66 (s, 3H; OMe), 3.75 (s, 3H; OMe), 3.80 (s, 3H; OMe), 6.13 (d, $J_{H,H} = 15.0$ Hz, 1H; B–CH=, br.), 6.23 (d, $J_{H,H} = 15.0$ Hz, 1H; CH=), 6.56 (d, $J_{Rh,H} = 2.6$ Hz, 1H; CH), 7.55 (d, $J_{Rh,H} = 0.9$ Hz, 1H; S–CH); ^{11}B NMR ($CDCl_3$): $\delta = -13.4$, -9.3, -8.0, -5.6, -3.8 (1:3:1:3:2; the broad $B(CH_2)$ signal overlaps with the resonances at $\delta = -3.8$ and -5.6); ^{103}Rh NMR ($CDCl_3$): $\delta = 462 \pm 1$; IR (KBr) [cm^{-1}]: $\tilde{\nu} = 2589$ (B-H); 1702, 1729 (COOMe); EI-MS (70 eV): *m*/*z* (%): 697 (41, $[M]^+$).

Synthesis of 9–11: The complex **2** (106 mg; 0.2 mmol) and methyl acetylene carboxylate (0.18 mL, 2.0 mmol) were dissolved in CH_2Cl_2 (20 mL). The mixture was stirred for three days at ambient temperature. The color changed slowly from purple (**2**) to yellow. The products were isolated by chromatography (Merck, Kieselgel 60) using hexane/CH_2Cl_2 (1:1) as eluent.

9: Yield 15%; m.p. 233 °C (decomp); ^1H NMR ($CDCl_3$): $\delta = 1.75$ (s, 15H; Cp*), 3.62 (s, 3H; OMe), 5.08 (s, 1H; CH); ^{11}B NMR ($CDCl_3$): $\delta = -9.8$, -4.9 (5:5); IR (KBr) [cm^{-1}]: $\tilde{\nu} = 2575$, 2593 (B–H); 1699 (COOMe); FD-MS: *m*/*z* (%): 1235 (100, $[M]^+$).

10: Yield, 30% (in mixture with **11**). ^1H NMR ($CDCl_3$): $\delta = 1.82$ (s, 15H; Cp*), 3.68 (d, $J_{H,H} = 8.4$ Hz, 1H; CH), 3.74 (s, 3H; OMe), 5.39 (d, $J_{H,H} = 8.4$ Hz, 1H; CH); ^{11}B NMR ($CDCl_3$): $\delta = -27.7$ (Ir–B; all other signals overlap with those of **11**); IR (KBr) [cm^{-1}]: $\tilde{\nu} = 2581$ (B–H); 1720 (COOMe); EI-MS (70 eV): *m*/*z* (%): 618 (100, $[M]^+$).

11: Yield 50%; m.p. 176 °C (decomp); ^1H NMR ($CDCl_3$): $\delta = 1.83$ (s, 15H; Cp*), 3.75 (s, 3H; OMe), 4.40 (d, $J_{H,H} = 8.6$ Hz, 1H; CH), 5.30 (d, $J_{H,H} = 8.6$ Hz, 1H; CH); ^{11}B NMR ($CDCl_3$): $\delta = -23.9$ (Ir–B), -11.2, -8.5, -7.1, -6.0, -4.0 (1:3:1:2:1:2); IR (KBr) [cm^{-1}]: $\tilde{\nu} = 2579$ (B–H); 1718 (COOMe); EI-MS (70 eV): *m*/*z* (%): 618 (100, $[M]^+$).

Synthesis of 12, 13: The complexes **3** (88.4 mg; 0.2 mmol) or **4** (106.4 mg; 0.2 mmol) and methyl acetylene carboxylate (0.18 mL, 2.0 mmol) were dissolved in CH_2Cl_2 (20 mL). The solution was stirred for 2 h (for **12**) or 2 days (for **13**) at ambient temperature. The color changed from blue (**3**) or from purple (**4**) to brown-red. Column chromatography on silica gel (Merck, Kieselgel 60) gave **12** or **13** by elution with hexane/CH_2Cl_2 (1:2).

12: Yield 75 %; m.p. 150 °C (decomp). Two isomers in solution (ca. 1.6:1 at 243 K) due to hindered rotation of the *p*-cymene ligand: ^{1}H NMR ($CDCl_3$, 243 K): $\delta = 1.22$ (d, $J_{H,H} = 6.7$ Hz, 3H; $CH(CH_3)_2$), 1.32 (d, $J_{H,H} = 6.7$ Hz, 3H; $CH(CH_3)_2$), 2.27 (s, 3H; CH_3), 2.88 (sept. $J_{H,H} = 6.7$ Hz, 1H; $CH(CH_3)_2$), 3.75 (s, 3H; OMe), 4.01 (d, $J_{H,H} = 8.9$ Hz, 1H; CH), 4.42 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4), 5.22 (d, $J_{H,H} = 8.9$ Hz, 1H; CH), 5.45 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4), 6.02 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4), 6.37 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4); minor isomer: ^{1}H NMR ($CDCl_3$, 243 K): $\delta = 1.07$ (d, $J_{H,H} = 6.5$ Hz, 3H; $CH(CH_3)_2$), 1.19 (d, $J_{H,H} = 6.5$ Hz, 3H; $CH(CH_3)_2$), 2.45 (s, 3H; CH_3), 2.88 (sept. $J_{H,H} = 6.7$ Hz, 1H; $CH(CH_3)_2$), 3.75 (s, 3H; OMe), 4.01 (d, $J_{H,H} = 8.9$ Hz, 1H; CH), 4.49 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4), 5.34 (d, $J_{H,H} = 8.9$ Hz, 1H; CH), 5.70 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4), 5.95 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4), 6.37 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4); the following data are for the mixture of the two isomers: ^{11}B NMR ($CDCl_3$, 243 K): $\delta = -6.5$ (broad); ^{11}B NMR ($CDCl_3$, 293 K): $\delta = -11.5, -9.3, -8.3, -7.0, -6.2, -4.2, -2.8$ (overlapping signals without assignment of Ru–B); IR (KBr) [cm^{-1}]: $\tilde{\nu} =$ 2582 (B–H); 1705 (COOMe); EI-MS (70 eV): *m*/*z* (%): 526 (82 %, $[M]^+$).

13: Yield, 85 %; m.p. 173 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta = 1.22$ (d, $J_{H,H} = 6.7$ Hz, 3H; $CH(CH_3)_2$), 1.24 (d, $J_{H,H} = 6.7$ Hz, 3H; $CH(CH_3)_2$), 2.64 (s, 3H; CH_3), 2.74 (sept. $J_{H,H} = 6.7$ Hz, 1H; $CH(CH_3)_2$), 3.73 (s, 3H; OMe), 3.23 (d, $J_{H,H} = 8.1$ Hz, 1H; CH), 4.92 (d, $J_{H,H} = 5.4$ Hz, 1H; C_6H_4), 5.38 (broad 1H; C_6H_4), 5.55 (broad, H; C_6H_4), 5.55 (d, $J_{H,H} = 8.1$ Hz, 1H; CH), 6.13 (d, $J_{H,H} = 5.4$ Hz, 1H; C_6H_4); ^{11}B NMR ($CDCl_3$): $\delta = -19.1$ (Os–B), $-14.2, -12.6, -11.2, -4.8$ (1:1:1:2:5); IR (KBr) [cm^{-1}]: $\tilde{\nu} =$ 2570, 2588 (B–H); 1712 (COOMe); EI-MS (70 eV): *m*/*z* (%): 615 (72, $[M]^+$).

Synthesis of 14–17: Dimethyl acetylene dicarboxylate (0.13 mL, 1 mmol) was added to a solution of **1–4** (0.2 mmol) in CH_2Cl_2 (20 mL) at room temperature. The color of the mixture turned red immediately. Evaporation of the solvent under reduced pressure gave a red residue which was recrystallized from a mixture of CH_2Cl_2/hexane. In the cases of **16** and **17**, the product mixture was first purified (before recrystallization) by chromatography on silica gel (Merck, Kieselgel 60) using CH_2Cl_2 as the eluent.

14: Yield 80 % (red needles), m.p. 187 °C (decomp); ^{1}H NMR (CD_2Cl_2): $\delta = 1.68$ (s, 15H; Cp*), 3.75 (s, 3H; OMe), 3.78 (s, 3H; OMe); ^{11}B NMR (CD_2Cl_2): $\delta = -11.0, -9.2, -7.8, -5.8, -5.3, -4.0$ (3:1:1:2:2:1); ^{103}Rh NMR (CD_2Cl_2): $\delta = 1049 \pm 2$; IR (KBr) [cm^{-1}]: $\tilde{\nu} =$ 2558, 2575, 2589, 2632 (B–H); 1702, 1721 (COOMe); EI-MS (70 eV): *m*/*z* (%): 587 (5, $[M]^+$), 444 (13, $[Cp^*Rh(S_2C_2B_{10}H_{10})]^+$).

15: Yield 85 % (orange needles), m.p. 185 °C (decomp); ^{1}H NMR (CD_2Cl_2): $\delta = 1.77$ (s, 15H; Cp*), 3.74 (s, 3H; OMe), 3.78 (s, 3H; OMe); ^{11}B NMR (CD_2Cl_2): $\delta = -12.4, -10.9, -9.1, -7.9, -5.3, -4.0$ (1:2:1:1:4:1); IR (KBr) [cm^{-1}]: $\tilde{\nu} =$ 2576, 2592, 2584, 2631 (B–H); 1703, 1720 (COOMe); EI-MS: *m*/*z* (%): 676 (28, $[M^+]$), 534 (88, $[Cp^*Ir(S_2C_2B_{10}H_{10})]^+$).

16: Yield 76 % (red needles), m.p. 150 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta =$ 1.10 (d, $J_{H,H} = 6.8$ Hz, 6H; $CH(CH_3)_2$), 2.19 (s, 3H; CH_3), 2.64 (sept, $J_{H,H} =$ 6.8 Hz, 1H; $CH(CH_3)_2$), 3.72 (s, 3H; OMe), 3.81 (s, 3H; OMe), 5.37 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4), 5.42 (d, $J_{H,H} = 6.3$ Hz, 1H; C_6H_4), 5.48 ($J_{H,H} =$ 6.3 Hz, 1H; C_6H_4), 5.61 (d, $J_{H,H} = 6.0$ Hz, 1H; C_6H_4); ^{11}B NMR ($CDCl_3$): $\delta = -11.1, -9.2, -7.5, -5.1, -4.0$ (3:1:2:3:1); IR (KBr) [cm^{-1}]: $\tilde{\nu} =$ 2565, 2583, 2590, 2606, 2617, 2633 (B–H); 1714 (COOMe); EI-MS (70 eV): *m*/*z* (%): 584 (75, $[M]^+$), 442 (100, $[(p\text{-cymene})Ru(S_2C_2B_{10}H_{10})]^+$).

17: Yield 80 % (orange powder), m.p. 125 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta =$ 1.12 (d, $J_{H,H} = 6.8$ Hz, 3H), 1.14 (d, $J_{H,H} = 6.8$ Hz, 3H; $CH(CH_3)_2$), 2.32 (s, 3H; CH_3), 2.61 (sept, $J_{H,H} = 6.8$ Hz, 1H; $CH(CH_3)_2$), 3.73 (s, 3H; OMe), 3.79 (s, 3H; OMe), 5.43 (d, $J_{H,H} = 5.7$ Hz, 1H), 5.50 (d, $J_{H,H} = 6.0$ Hz, 1H), 5.46 (d, $J_{H,H} = 6.0$ Hz, 1H), 5.76 (d, $J_{H,H} = 5.7$ Hz, 1H; C_6H_4); ^{11}B NMR ($CDCl_3$): $\delta = -12.0, -10.8, -9.0, -7.5, -5.0$ (1:2:1:2:4); IR (KBr) [cm^{-1}]: $\tilde{\nu} =$ 2584 (B–H); 1709 (COOMe); EI-MS (70 eV): *m*/*z* (%): 673 (8, $[M]^+$), 531 (29, $[(p\text{-cymene})Os(S_2C_2B_{10}H_{10})]^+$).

Crystal structures of 7 and 8: Intensity data collections were carried out on a Siemens P4 diffractometer with $Mo_{K\alpha}$ radiation ($\alpha = 71.073$ pm, graphite monochromator) at room temperature. The hydrogen atoms of the carborane cage were located by difference Fourier syntheses. The remaining hydrogen atoms are in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

7: $C_{20}H_{33}B_{10}O_4S_2Rh$, red platelet of dimensions $0.36 \times 0.16 \times 0.06$ mm, crystallizes monoclinically, space group $P2_1/c$; $a = 1021.74(13)$, $b = 2038.5(3)$, $c = 1374.1(3)$ pm, $\beta = 96.596(12)°$, $Z = 4$, $\mu = 0.774$ mm^{-1}; 8012 reflections collected in the range $2° - 27.5°$ in θ, 6514 reflections independent, 5127 reflections assigned to be observed ($I > 2\sigma(I)$); full-matrix least-squares refinement with 335 parameters, $R1/wR2$ values 0.0452/0.1236, absorption correction (Ψ scans), min/max transmission factors 0.4051/0.4598; max/min residual electron density $1.72/-0.84$ e 10^{-6} pm^{-3}.

8: $C_{24}H_{37}B_{10}O_6S_2Rh$, red plate of dimensions $0.30 \times 0.18 \times 0.10$ mm, crystallizes monoclinically, space group $P2_1/c$; $a = 1039.90(8)$, $b = 2125.7(2)$, $c = 1465.85(15)$ pm, $Z = 4$, $\mu = 0.696$ mm^{-1}; 7051 reflections collected in the range $2° - 25°$ in θ, 5661 reflections independent, 5041 reflections assigned to be observed ($I > 2\sigma(I)$); full-matrix least-squares refinement with 390 parameters, $R1/wR2$ values 0.0341/0.1019, absorption correction (Ψ scans), min/max transmission factors 0.2429/0.2681; max/min residual electron density $0.82/-0.57$ e 10^{-6} pm^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-139453 (**7**) and CCDC-139454 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

[1] a) J. Arnold, *Progr. Inorg. Chem.* **1995**, *43*, 353–417; b) J. R. Dilworth, J. Hu, *Adv. Inorg. Chem.* **1993**, *40*, 411–459.
[2] M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *Eur. J. Inorg. Chem.* **1999**, 873–875.
[3] M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **1999**, *587*, 252–257.
[4] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **2000**, in press.
[5] M. Herberhold, H. Yan, W. Milius, *J. Organomet. Chem.* **2000**, *598*, 142–149.
[6] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, *Angew. Chem.* **1999**, *111*, 3888–3890; *Angew. Chem. Int. Ed.* **1999**, *38*, 3689–3691.
[7] a) J. P. Collman, W. R. Roper, *Adv. Organomet. Chem.* **1968**, *7*, 53–94; b) J. Halpern, *Acc. Chem. Res.* **1970**, *3*, 386–392; c) M. F. Lappert, W. P. Lednor, *Adv. Organomet. Chem.* **1976**, *14*, 345–399.
[8] I. Beletskaya, C. Moberg, *Chem. Rev.* **1999**, *99*, 3435–3461.
[9] a) V. N. Kalinin, A. V. Usatov, L. I. Zakharkin, *Proc. Indian Sci. Acad.* **1989**, *55*, 293–317; b) L. I. Zakharkin, V. V. Kobak, G. G. Zhigareva, *Russ. Chem. Rev.* **1986**, *55*, 531–545.
[10] D.-H. Khim, J. Ko, K. Park, S. Cho, S. O. Kang, *Organometallics* **1999**, *18*, 2738–2740.
[11] V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209–223.
[12] Reviews for element-H activation: H-H activation: G. J. Kubas, *Comments Inorg. Chem.* **1988**, *7*, 17–40; C–H and Si–H activation: J. J. Schneider, *Angew. Chem.* **1996**, *108*, 1132–1139; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1069–1075; Sn–H activation: U. Schubert, *Adv. Organomet. Chem.* **1990**, *30*, 151–187.
[13] M. L. McKee in *The Borane, Carborane, Carbocation Continuum* (Ed.: J. Casanova), Wiley, New York, **1997**, pp. 259–288, and references therein.
[14] A. R. Siedle, *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 205–314.
[15] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, unpublished results.
[16] B. Mann in *Transition Metal Nuclear Magnetic Resonance Spectroscopy* (Ed.: S. Pregosin), Elsevier, Amsterdam, **1991**, pp. 177–215.
[17] C. White, A. Yates, P. M. Maitlis, *Inorg. Synth.* **1992**, *29*, 228–234.
[18] M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.* **1982**, *21*, 74–78.
[19] H. Werner, K. Zenkert, *J. Organomet. Chem.* **1988**, *345*, 151–156.
[20] J.-Y. Bae, Y.-I. Park, J. Ko, K.-I. Park, S.-I. Cho, S. O. Kang, *Inorg. Chim. Acta* **1999**, *289*, 141–148.

Received: January 20, 2000 [F2246]

