Metal-Induced B–H Activation: Addition of Acetylene, Propyne, or 3-Methoxypropyne to Rh(Cp*), Ir(Cp*), Ru(*p*-cymene), and Os(*p*-cymene) Half-Sandwich Complexes Containing a Chelating 1,2-Dicarba-*closo*-dodecaborane-1,2-dichalcogenolato Ligand

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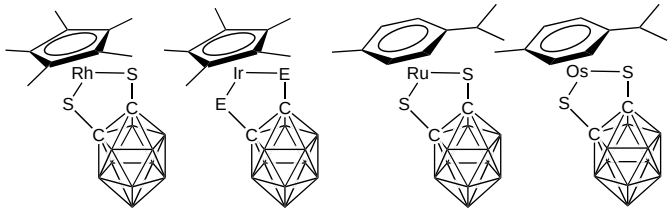
Dedicated to Professor Walter Siebert on the occasion of his 65th birthday

Abstract: The addition reactions of the 16 e half-sandwich complexes $[M(\eta^5\text{-Cp*})\{E_2C_2(B_{10}H_{10})\}]$ (Cp* = pentamethylcyclopentadienyl: **1S**: E = S, M = Rh; **2S**: E = S; M = Ir; **2Se**: E = Se, M = Ir) and $[M(\eta^6\text{-}p\text{-cymene})\{S_2C_2(B_{10}H_{10})\}]$ (*p*-cymene = 4-isopropyltoluene; **3S**: M = Ru; **4S**: M = Os), with acetylene, propyne, and 3-methoxypropyne lead to the 18 e complexes **5**–**19** with a metal–boron bond in each case. The reactions start with an insertion of the alkyne into one of the metal–chalcogen bonds, followed by B–H activation, transfer of one hydrogen atom from the carborane via the metal to the terminal carbon of the alkyne, and concomitant *ortho*-metalation of the carborane. The E-η^2-CC and the C(1)B units are arranged either *cisoid* or *transoid* at the metal. X-ray structural analyses are reported for one of the starting 16 e complexes (**4S**), the *cisoid* complex **12S** (from **2S** and HC≡C-CH_3), and the *transoid* complexes **9S** and **14S** (from **1S** and HC≡C-CH_2OMe, and from **3S** and HC≡CH, respectively). All new complexes **5**–**19** were characterized by NMR spectroscopy (^{1}H, ^{11}B, ^{13}C, and ^{77}Se and ^{103}Rh NMR spectroscopy when appropriate).

Keywords: carboranes · chalcogens · iridium · osmium · rhodium · ruthenium · structure elucidation

Introduction

The ability of voluminous ring ligands such as pentamethylcyclopentadienyl (Cp*) or 4-isopropyltoluene (*p*-cymene) to screen a metal center is well known.[1] Together with the bulky chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligand, $[(B_{10}H_{10})C_2E_2]^{2-}$ (E = S, Se), 16-electron half-sandwich complexes such as **1**–**4** are stabilized as monomeric species.[2–5] These sterically congested, mononuclear coordination compounds can be stored conveniently and be used for further transformations in a controlled way under various conditions.



1S **2S, 2Se** **3S** **4S**

We have shown that the complexes **1**–**4** react with various activated alkynes, such as methyl acetylene carboxylate, (HC≡C-COOMe),[6–9] dimethyl acetylene dicarboxylate (MeO_2C-C≡C-CO_2Me),[6, 7] phenylacetylene (HC≡C-Ph),[10] or ferrocenylacetylene, (HC≡C-Fc),[11] in a number of ways, depending upon the metal, the chalcogen, and the conditions used. The range of reactions observed turned out to be rather wide, from catalytic cyclotrimerization[12] or dimerization of the alkyne[11] to stepwise carborane B(3,6)-substitution,[6, 7, 9] and numerous intermediates have been isolated.[7–9, 12] Particularly intriguing are the structures of those complexes that may be active intermediates in catalytic processes[7, 12] or possess a reactive metal–boron bond. Many of the latter have been detected by NMR spectroscopy in solution but only a few of them have been fully characterized.[9, 10, 13] The intention of the present work was, therefore, to use alkynes of moderate reactivity in order to prevent possible side reactions and to increase the lifetime of intermediates with metal–boron bonds. Thus, we have studied the reactions of acetylene (HC≡CH), propyne (HC≡C-Me), and 3-methoxypropyne (HC≡C-CH_2OMe) with the same 16 e complexes **1**–**4**, which had already been used in comparable reactions with methyl acetylene carboxylate[7] and phenylacetylene.[10]

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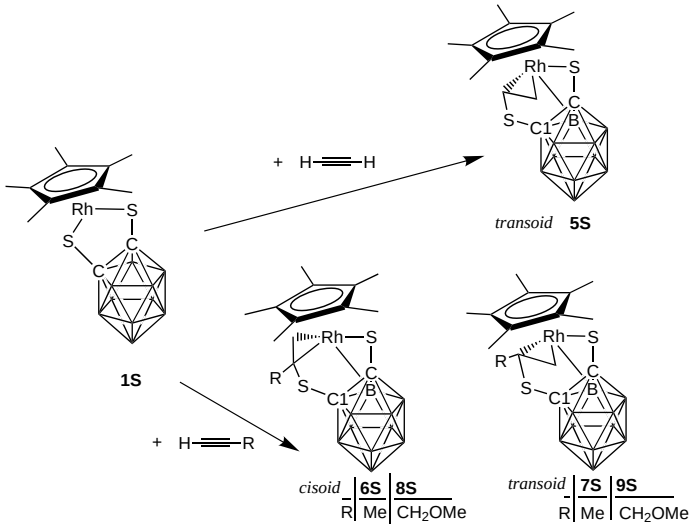
Results and Discussion

The 16 e half-sandwich complexes 1–4: The syntheses of the starting materials **1**–**4** have been optimised previously. The molecular structure of the Ir(Cp*) complex **2Se** is known,[2] and we now report on the crystal structure of the Os(*p*-cymene) complex **4S** (see below).

Reactions of the 16 e rhodium complex 1S with acetylene, propyne, and 3-methoxypropyne: The rhodium complex **1S** reacts readily with all three alkynes at room temperature (Scheme 1). In the case of acetylene, a single product **5S** was isolated in quantitative yield. Its NMR spectroscopic data (Table 1) indicate a *transoid* arrangement of the η^2-S-C=C and the B-C(1) units. In contrast, mixtures of complexes with *cisoid* and *transoid* structures were formed in the reactions of **1S** with either propyne (**6S**, **7S**) or 3-methoxypropyne (**8S**, **9S**). Fortunately, these mixtures could be separated by column chromatography, and the crystal structure of the *transoid* complex **9S** was determined by X-ray analysis (see below).



Scheme 1.

Abstract in German: *Die Additionsreaktionen der 16 e-Halbsandwich-Komplexe [M(η⁵-Cp*){E₂C₂(B₁₀H₁₀)}] (**1S**: E = S, M = Rh; **2S**: E = S; M = Ir; **2Se**: E = Se, M = Ir) und [M(η⁶-p-cymene){S₂C₂(B₁₀H₁₀)}] (p-cymene = 4-isopropyltoluol; **3S**: M = Ru; **4S**: M = Os), mit Acetylen, Propin und 3-Methoxypropin führen zu 18 e-Komplexen **5**–**19**, wobei sich in allen Fällen eine Metall-Bor-Bindung ausbildet. Die Reaktionen beginnen mit einer Einschiebung des Alkins in eine der Metall-Chalkogen Bindungen, dann folgen B–H Aktivierung, Übertragung eines H-Atoms vom Carboran über das Metall zum terminalen Kohlenstoff des Alkins und damit gleichzeitig ortho-Metallierung des Carborans. Die E-η²-CC-Gruppierung des Alkins und die C(1)B Bindung des Carborans können am Metall entweder cisoid oder transoid zueinander angeordnet sein. Es wurden Röntgenstrukturanalysen durchgeführt an einem der 16 e-Ausgangskomplexe (**4S**), an dem cisoid-Komplex **12S** (aus **2S** und HC≡C-CH₃) und den transoid-Komplexen **9S** und **14S** (aus **1S** und HC≡C-CH₂OMe bzw. aus **3S** und HC≡CH). Alle neuen Additionsverbindungen **5**–**19** wurden durch Multikern-magnetische Resonanz-Spektroskopie (¹H-, ¹¹B-, ¹³C-, und ⁷⁷Se- und ¹⁰³Rh-NMR, wo angebracht) charakterisiert.*

Reactions of the 16 e iridium complexes 2S and 2Se with acetylene, propyne, and 3-methoxypropyne: The 16 e iridium complex **2S** is much less reactive than its rhodium analogue **1S**, whereas **2Se** appears to be slightly more reactive than the sulfur analogue **2S**. This also applies to the products formed in the reactions of the iridium complexes with alkynes (Scheme 2). Thus, mixtures of *cisoid* and *transoid* complexes (**10S**, **11S** and **10Se**, **11Se**) are formed in the reactions with acetylene. In the reactions with propyne a single product was obtained in each case (**12S** and **12Se**), with a *cisoid* structure according to the NMR data (Table 1); this was confirmed by X-ray structural analysis in the case of **12S** (see below). Complex **2S** did not react with 3-methoxypropyne, whereas **2Se** reacted to give a single product **13Se**, again with a *cisoid* structure, as shown by the NMR data in solution.

Reactions of the 16 e ruthenium and osmium complexes 3S and 4S with acetylene and propyne: The reactivity of the 16 e ruthenium and osmium half-sandwich complexes **3S** and **4S** towards alkynes appears to be somewhat higher than that of **2S**, close to that of the rhodium complex **1S**. In the reactions of **3S** and **4S** with acetylene (Scheme 3) only the *transoid* complexes **14S** and **17S** were detected and isolated, of which the ruthenium complex **14S** was characterized by an X-ray structural analysis (see below). From the reactions of **3S** and **4S** with propyne, mixtures of *cisoid* (**15S**, **18S**) and *transoid* complexes (**16S**, **19S**) were obtained. In these cases, it was possible to monitor the slow rearrangement of *cisoid* into *transoid* complexes in solution. Apparently, the formation of the *cisoid* arrangement is kinetically controlled, whereas the *transoid* structure results from thermodynamic control.

NMR spectroscopic results: The ^{13}C NMR data (Table 1) and all other NMR data (see Experimental Section) of the complexes **5**–**19** are in agreement with the proposed structures and confirm that the relevant features of the solid-state structures of **9S**, **12S** and **14S** are retained in solution. The ^{11}B NMR spectra show strongly overlapping broad signals in the region typical of *ortho*-carborane derivatives.[14, 15] The $^{11}B(M,B)$ NMR signals were assigned by comparison of ^{1}H decoupled and non-decoupled ^{11}B NMR spectra. In the case of the heavy metals Ir and Os, these ^{11}B NMR signals are shifted to lower frequency, and can be easily recognized (cf. [16]).

Figure 1 shows the $^{13}C\{^{1}H\}$ NMR spectrum of **9S**, which is typical of the complexes studied. The ^{13}C NMR signals of the carbon atoms linked directly to rhodium are doublets according to $^{1}J(^{103}Rh,^{13}C)$, and all other signals are singlets. The signals for C(1) and C(2) of the carborane are readily identified owing to lower intensity and broadening by partially relaxed scalar $^{13}C-^{11}B$ coupling.[17] The magnitude of the coupling constants $|^{1}J(^{103}Rh,^{13}C(3))|$ is significantly

Table 1. ^{13}C NMR data[a] of complexes **1**–**19**.

	HC≡CR R	Carborane	Ring	C(4) M–CH_2	C(3) M–CH	C(3) M–C	CH_2O	Me
M = Rh			Cp*					
1S[3]		94.1	10.6, 99.3	–				
5S	H (*transoid*)	n.o.	9.4; 102.4	68.7	76.1			
			(4.4)	(8.6)	(13.5)			
6S	Me (*cisoid*)	96.4; 102.8	9.7; 105.3	52.7		95.8		25.2
			(3.4)	(9.4)		(8.9)		
7S	Me (*transoid*)	106.0; 107.03	9.9; 103.0	69.8		91.5		29.5
		(4.2)	(8.5)		(14.0)			
8S	CH_2OMe (*cisoid*)	95.8; 100.6	9.7; 105.3	53.0		94.9	78.4	58.1
			(3.3)	(9.2)		(9.7)		
9S[b]	CH_2OMe (*transoid*)	104.3; 106.4	9.9; 103.0	68.5		90.8	77.0	58.6
			(4.1)	(8.6)		(14.7)		
M = Ir			Cp*					
2S[10]		92.8	10.1; 91.8					
2Se[2]		72.8	10.6; 90.7					
10S	H (*cisoid*)	95.8; 100.2	8.7; 100.7	32.1	57.1			
10Se	H (*cisoid*)	76.8; 88.3	9.0; 100.3	33.9	48.2			
11S	H (*transoid*)	n. o.	8.8; 97.0	48.9	58.1			
11Se	H (*transoid*)	95.3; 96.6	8.9; 98.3	46.9	50.2			
12S	Me (*cisoid*)	97.8; 102.0	9.1; 101.4	34.4		74.0		24.5
12Se	Me (*cisoid*)	78.3; 90.7	9.4; 101.2	36.8		67.6		26.0
13Se	CH_2OMe (*cisoid*)	76.8; 88.4	9.6; 100.9	36.7		70.0	80.1	58.3
M = Ru			*p*-cymene					
3S[4]		93.7	20.2; 23.1; 31.9; 79.4; 81.3; 93.8; 104.1					
14S	H (*transoid*)	108.1; 108.7	18.2; 22.1; 24.1; 31.6; 95.7; 96.3; 97.4; 101.3; 106.7; 116.5	50.3	68.6			
15S	Me (*cisoid*)	95.5; 103.9	19.3; 21.2; 21.8; 32.2; 98.1; 98.9; 99.6; 104.6; 107.7; 119.7	42.6		88.4		30.6
16S	Me (*transoid*)	107.7; 109.3	18.1; 21.2; 25.3; 32.0; 94.4; 96.9; 99.0; 103.7; 104.7; 119.5	54.7		85.4		33.1
M = Os			*p*-cymene					
4S[4]		95.9	20.7; 23.4; 32.4; 72.5; 74.9; 87.6; 97.5					
17S	H (*transoid*)	105.8; 106.4	17.7; 21.8; 24.2; 30.8; 88.8; 88.9; 89.8; 92.0; 102.4; 108.8	35.5	55.0			
18S	Me (*cisoid*)	97.4; 103.7	18.8; 22.7; 23.5; 31.7; 91.4; 91.7; 93.9; 97.8; 103.5; 113.5	30.3		71.4		30.6
19S	Me (*transoid*)	106.0; 106.1	17.7; 20.8; 25.6; 31.3; 86.0; 89.6; 93.3; 95.7; 99.0; 111.0	41.7		70.8		34.1

[a] Coupling constants, $^1J(^{103}Rh,^{13}C)$, in parentheses. [b] See Figure 1.

increased ($\geq 50\,\%$) in complexes with a *transoid* structure. There appears to be a remarkable relationship between the magnitude of $|^1J(^{103}Rh,^{13}C(3))|$ and the bond lengths Rh–C(3) determined in the solid state, which are always shorter in the *transoid* with respect to the *cisoid* arrangement (vide infra). These structural changes in the vicinity of the metal also affect the ^{13}C nuclear shielding, in particular that of C(3), C(4), and also the carborane $^{13}C(1,2)$ nuclei. The $^{13}C(3)$ shielding increases slightly in the *transoid* complexes, whereas the $^{13}C(4)$ as well as the carborane $^{13}C(1,2)$ shieldings are reduced. There are small changes in the ^{13}C NMR parameters of the Cp* rings related to *cisoid* and *transoid* arrangement: the shielding of the quaternary ^{13}C nuclei is slightly increased in all complexes with *transoid* structure.

The ^{77}Se NMR spectra[18] of the iridium complexes have been measured, and the expected pattern of two signals for single isomers, or four signals for mixtures of complexes with *cisoid* and *transoid* arrangement was observed. Figure 2 shows for the complex **12Se** how the signals can be assigned. By polarization transfer (INEPT, refocused, with ^1H decoupling[19]) from the methyl or the CH_2 protons to ^{77}Se, only the ^{77}Se nuclei respond which have scalar $^{77}Se-^1H$ coupling across three bonds. The $^{77}Se(2)$ nucleus cannot have appreciable scalar coupling with any of the protons in the molecule. There is a significant influence of the structure on ^{77}Se nuclear shielding. In the *transoid* complexes both ^{77}Se NMR signals are shifted to high frequencies (>60 ppm). This makes the assignment straightforward, even in 1:1 mixtures.

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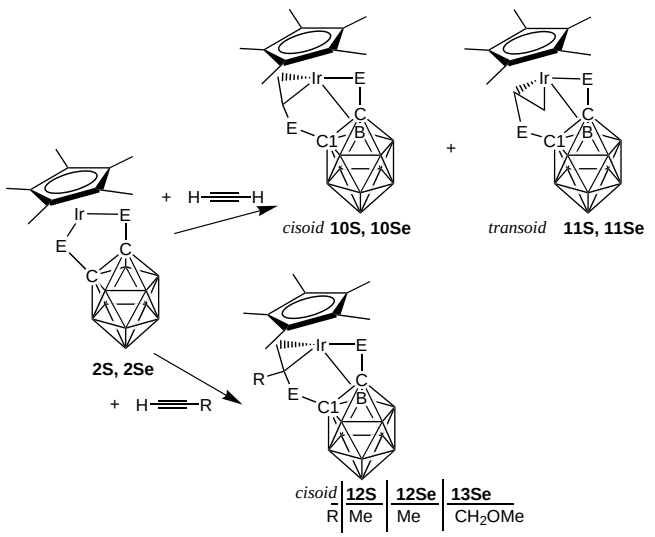


Scheme 2.

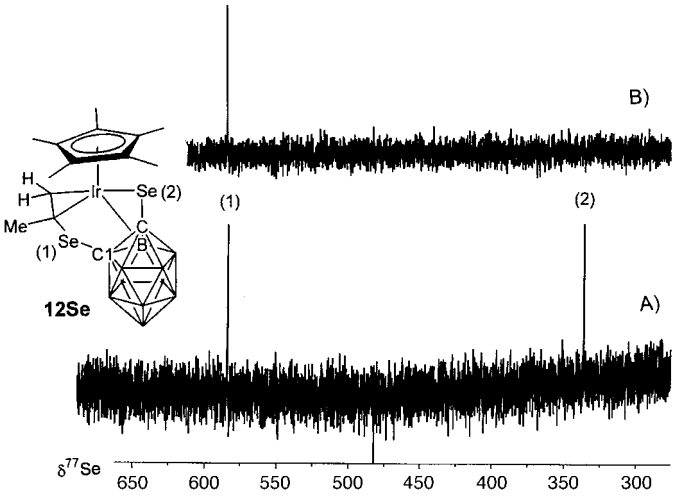
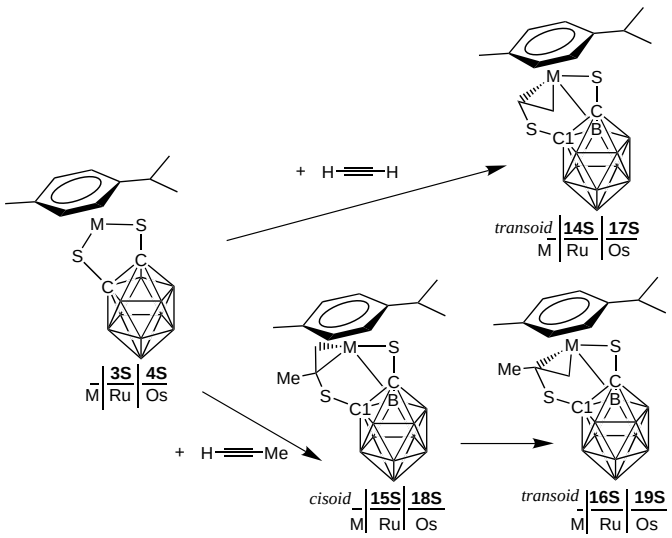


Figure 2. 95.4 MHz ^{77}Se NMR spectra of **12Se** (saturated in $CDCl_3$ at 22 ± 1 °C). A) ^{77}Se{^{1}H} NMR spectrum, recorded by single pulse technique. B) ^{77}Se NMR spectrum, recorded by INEPT[19] (based on $^3J(^{77}Se,^1H) \approx$ 12 Hz; refocused, with ^{1}H decoupling).



Scheme 3.

The ^{103}Rh NMR signals were detected by heteronuclear ^{1}H{^{103}Rh} double-resonance experiments, taking advantage of the coupling constant $^2J(^{103}Rh,^1H)$. As expected, ^{103}Rh nuclear shielding is very sensitive to changes in the surroundings of the rhodium atom.[20] For the pairs of *cisoid* and *transoid* complexes **6S/7S** ($\delta^{103}Rh = -243, +77$) and **8S/9S** ($\delta^{103}Rh = -361, -176$), the ^{103}Rh nuclei are more shielded in the complexes with *cisoid* arrangement.

EI (70 eV) mass spectra: All addition compounds formed with acetylene contain the molecular ion in their electron impact mass spectra. Under comparable conditions, the addition compounds formed with propyne and 3-methoxypropyne have a stronger tendency to lose the alkyne.

X-ray structural analyses of the complexes 4S, 9S, 12S, and 14S: The molecular structures of the four complexes are shown in the Figures 3–6, respectively, together with selected bond lengths and bond angles.

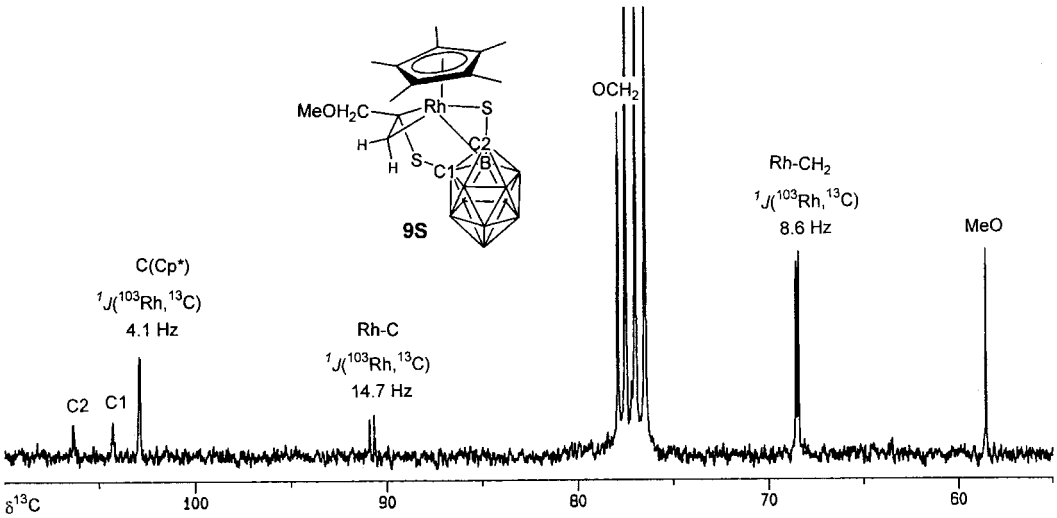


Figure 1. 62.9 MHz ^{13}C{^{1}H} NMR spectrum of **9S**.

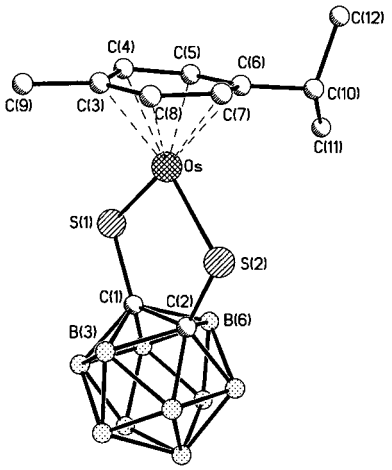


Figure 3. Molecular geometry of **4S**. Selected bond lengths [pm] and angles [°]: Os–S(1) 226.70(13), C(1)–C(2) 163.3(7), Os–S(2) 226.47(14), C(3)–C(4)141.0(9), S(1)–C(1) 178.3(5), C(4)–C(5) 141.6(8), S(2)–C(2) 179.3(5). C(5)–C(6) 141.7(8), Os–C(3) 220.2(5), C(6)–C(7) 143.2(10), Os–C(4) 225.0(5), C(7)–C(8) 139.0(9), Os–C(5) 216.4(5) C(3)–C(8) 144.0(8) Os–C(6) 218.8(5), C(3)–C(9) 150.4(9), Os–C(7) 222.4(5), C(6)–C(11) 153.5(9), Os–C(8) 217.2(6), C(10)–C(11) 151.1(12), Os–Z 168.4, C(10)–C(12) 153.0(9); S(1)-Os-S(2) 91.74(5), Os-S(1)-C(1) 107.12(16), Os-S(2)-C(2) 107.26(16), S(1)-C(1)-C(2) 117.3(3), S(2)-C(2)-C(1) 116.5(3).

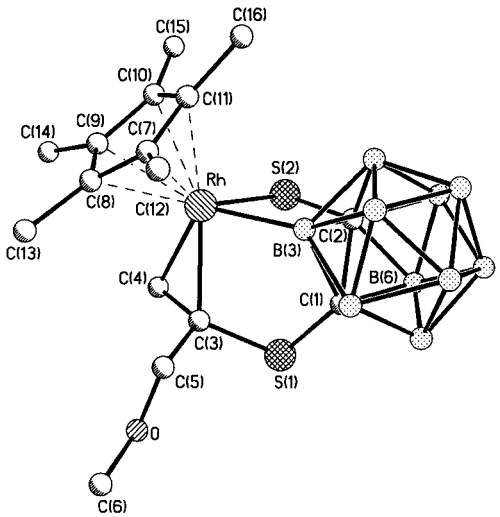


Figure 4. Molecular geometry of **9S**. Selected bond lengths [pm] and angles [°]: Rh–S(2) 239.12(7), S(1)–C(1) 175.7(3), Rh–B(3) 212.5(3), S(1)–C(3) 180.5(3), Rh–C(3) 217.5(2), C(3)–C(4) 140.9(4), Rh–C(4) 215.1(2), C(3)–C(5) 150.4(1), C(5)–O 140.9(3), Rh–C(7) 223.0(3), C(6)–O 141.2(4), Rh–C(8) 225.4(2), S(2)–C(2) 177.8(3), Rh–C(9) 228.7(3), C(2)–B(3) 171.7(4), Rh–C(10) 226.2(3), C(1)–C(2) 173.7(4), Rh–C(11) 221.9(3), C(1)–B(3) 174.6(4), Rh–Z 189.6; S(2)-Rh-B(3) 71.56(8), S(2)-Rh-C(3) 92.21(7), S(2)-Rh-C(4) 86.71(8), B(3)-Rh-C(3) 81.17(10), B(3)-Rh-C(4) 114.84(11), C(3)-Rh-C(4) 38.01(10), C(5)-O-C(6) 112.1(2), Rh-C(3)-S(1) 113.83(13), Rh-C(3)-C(4) 70.06(14), Rh-C(4)-C(3) 71.92(14), Rh-S(2)-C(2) 89.37(8), Rh-B(3)-C(1) 112.14(16), Rh-B(3)-C(2) 100.44(16); dihedral angles S(2)RhB(3)/S(2)C(2)B(3) 2.3, C(3)RhC(4)/C(3)RhB(3) 27.2, C(3)RhB(3)/B(3)C(1)S(1)C(3) 36.0, C(7)–C(11)/S(2)RhB(3) 133.8, C(7)–C(11)/C(1)C(2)B(3) 79.8.

The OsSCCS metallacycle in **4** (Figure 3) is planar within the experimental error. π Interactions, including metal-centered orbitals, are indicated by the comparatively short bond length C(1)–C(2) = 163.3(7) pm, which is typical of

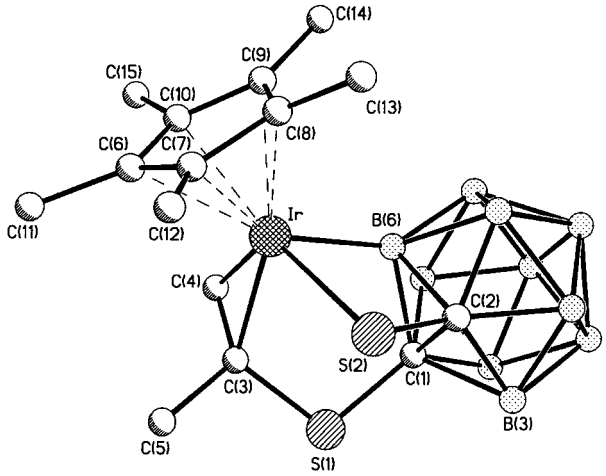


Figure 5. Molecular geometry of **12S**. Selected bond lengths [pm] and angles [°]: Ir–S(2) 239.99(15), S(1)–C(1) 176.2(6), Ir–B(6) 209.3(7), S(1)–C(3) 180.4(6), Ir–C(3) 214.6(5), C(3)–C(4) 140.9(10), Ir–C(4) 213.8(6), C(3)–C(5) 152.0(9), Ir–C(6) 232.1(6), S(2)–C(2) 177.3(6), Ir–C(7) 229.6(5), C(2)–B(6) 173.5(9), Ir–C(8) 223.6(5), C(1)–B(6) 175.3(8), Ir–C(9) 226.7(6), C(1)–C(2) 172.6(8), Ir–C(10) 225.2(6), Ir–Z 192.3; S(2)-Ir-B(6) 71.93(19), C(1)-B(6)-C(2) 59.3(3), S(2)-Ir-C(3) 84.41(17), C(4)-C(3)-C(5) 122.1(6), S(2)-Ir-C(4) 120.42(19), B(6)-Ir-C(3) 87.3(2), B(6)-Ir-C(4) 86.9(3), C(3)-Ir-C(4) 38.4(3), Ir-B(6)-C(1) 111.0(4), Ir-B(6)-C(2) 100.9(4), Ir-C(3)-S(1) 115.7(3), Ir-C(3)-C(4) 70.5(3), Ir-C(3)-C(5) 117.3(4), Ir-C(4)-C(3) 71.1(4), C(1)-S(1)-C(3) 101.9(3), C(2)-S(2)-Ir 89.04(19); dihedral angles S(2)IrB(6)/S(2)C(2)B(6) 2.0, C(3)IrC(4)/C(3)IrB(6) 88.4, C(3)IrB(6)/B(6)C(1)S(1)C(3) 23.8, C(6)–C(10)/S_2IrB(6) 44.4, C(6)–C(10)/C(1)C(2)B(6) 107.5.

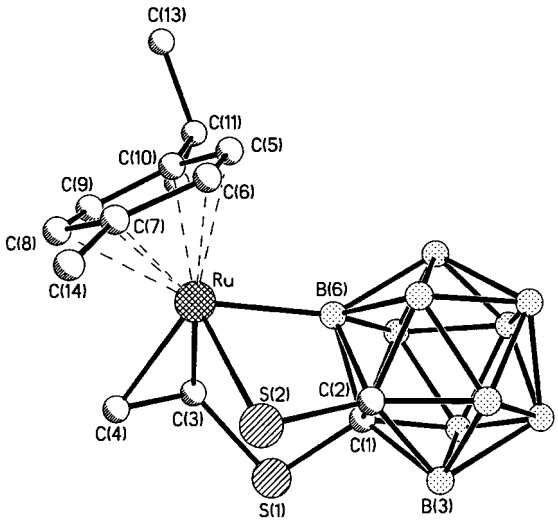


Figure 6. Molecular geometry of **14S**. Selected bond lengths [pm] and angles [°]: Ru–S(2) 241.9(2), S(1)–C(1) 176.3(8), Ru–B(6) 211.0(10), S(1)–C(3) 179.2(10), Ru–C(3) 215.5(8), C(3)–C(4) 140.7(13), Ru–C(4) 215.8(8), S(2)–C(2) 177.2(8), Ru–C(5) 226.1(8), C(2)–B(6) 171.4(12), Ru–C(6) 223.5(8), C(1)–B(6) 175.4(11), Ru–C(7) 230.1(8), C(1)–C(2) 176.4(11), Ru–C(8) 228.8(9), Ru–C(9) 222.8(9), Ru–C(10) 228.9(9), C(5)–C(6) 139.2(12), C(6)–C(7) 141.9(14), C(7)-C(8) 137.8(14), C(8)–C(9) 142.2(13), C(9)–C(10)-140.0(12), C(5)–C(10) 138.8(13), C(7)–C(14) 157.(5), C(10)–C(11) 151.7(12), C(11)–C(12) 142.2(2), C(11)–C(13) 153.5(16); S(2)-Ru-B(6) 70.6(3), S(2)-Ru-C(3) 90.1(3), S(2)-Ru-C(4) 85.5(3), B(6)-Ru-C(3) 79.1(3), B(6)-Ru-C(4) 113.0(3), C(3)-Ru-C(4) 38.1(3), Ru-B(6)-C(1) 114.9(5), Ru-B(6)-C(2) 102.0(5), Ru-C(3)-S(1), 117.1(5), 157(5), Ru-C(3)-C(4) 71.1(5), Ru-C(4)-C(3) 70.8(5), C(1)-S(1)-C(3) 98.3(4), C(2)-S(2)-Ru 89.4(3), C(1)-B(6)-C(2) 61.5(5).

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ortho-carborane dichalcogenolato derivatives in 16 e metal complexes, for example, in the carborane dithiolato complexes $[AuCl_2\{S_2C_2(B_{10}H_{10})\}]^-$ (162.2(8) pm),[21] $[AuCl(CH_2PPh_3)\{S_2C_2(B_{10}H_{10})\}]$ (164.3(5) pm),[21] $[PdI_2\{S_2C_2(B_{10}H_{10})\}]^{2-}$ (163.8(10) pm),[22] $[\{Re(O)[S_2C_2(B_{10}H_{10})]\}_2]^-$ (163.6(7) pm, 14 e complex),[22] and $[Ir(Cp^*)\{S_2C_2(B_{10}H_{10})\}]$ (**2S**, 165(2) and 166(3) pm)[13] and the carborane diselenolato complex $[Ir(Cp^*)\{S_2C_2(B_{10}H_{10})\}]$ (**2Se**, 161.2(9) pm)[2] (cf.[9] for B(3)/B(6)-substituted analogues of **2Se**).

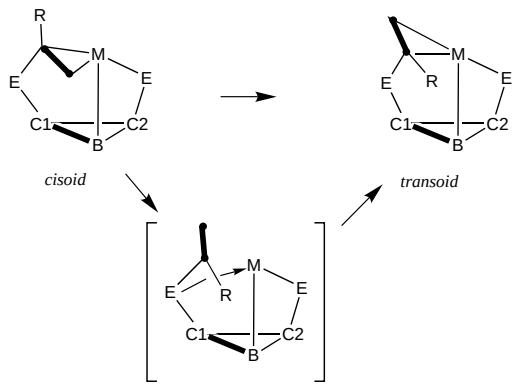
The *transoid* (**9S** in Figure 4, and **14S** in Figure 6) and *cisoid* (**12S** in Figure 5) arrangements can be easily recognized by inspection. The structural data given here, and a comparison with the data from previous studies of related half-sandwich complexes,[6–12] indicate some trends. The strongest distortion of the carborane cage is observed in the ruthenium complex **14S** (*transoid*) and in the related ruthenium complex with *cisoid* structure, obtained from the reaction of **3S** with phenylacetylene,[10] as indicated by the rather long C(1)–C(2) bonds in the carborane (176.4(11) and 178.4(5) pm; see the data for **9S** and **12S**, and compare with the general range 162–170 pm for *ortho*-carborane derivatives[14]). There is no general trend of changes in the M–B bond length which can be related to *cisoid* or *transoid* arrangement, and the same is true for M–S or M–Se bonds, and also for C(3)–C(4) and the chalcogen–C bond lengths. However, a fairly systematic variation is observed by comparison of the M–C(3) and M–C(4) bond lengths of *transoid* and *cisoid* complexes: in the *transoid* complexes, the M–C(3) bond is always shorter than in comparable *cisoid* complexes, whereas the M–C(4) bond is in the same order or even slightly longer. This fits to the observation that the ^{13}C NMR data are significantly affected, in particular the data of the η^2-bonded C(3)–C(4) olefinic fragment (vide supra).

Conclusion

The 16 e complexes **1**–**4** display a markedly different reactivity toward alkynes: **1S** > **2Se** > **3S** ≈ **4S** > **2S**. The reactivity of the alkynes decreases from acetylene over propyne to 3-methoxypropyne. The products with a metal–boron bond, formed after B–H activation and transfer of a carborane hydride through the metal to the alkyne, possess either a *cisoid* or a *transoid* structure, both of which have been characterized by structural analysis in the present study. It appears that the *cisoid* structure is formed first as a result of kinetic control, whereas the *transoid* structure is the thermodynamically controlled product, and in some cases it was possible to monitor the formation of the *transoid* isomer in solution by NMR spectroscopy. It is unlikely that the carborane cage itself is involved in the rearrangement. Scheme 4 shows a proposed mechanism for the rearrangement from the *cisoid* to the *transoid* arrangement.

Experimental Section

General: NMR measurements: Bruker ARX250 and DRX500 spectrometers (at 24 ± 1 °C in 5 mm tubes; see also Table 1); 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/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), and $\delta^{103}Rh = 0$ for $\Xi(^{103}Rh) = 3.16$ MHz; ^{103}Rh NMR data were obtained by heteronuclear $^1H\{^{103}Rh\}$ double-resonance experiments. Mass spectra: FINNIGAN MAT 8500 for EI-MS (70 eV), direct inlet; VARIAN MAT 311 A for FD-MS. IR spectra: Perkin–Elmer 983 G.



Scheme 4.

The 16 e parent complexes $Cp^*Rh[S_2(B_{10}H_{10})]$ (**1S**),[3] $Cp^*Ir[S_2(B_{10}H_{10})]$ (**2S**),[10, 13] $Cp^*Ir[Se_2C_2(B_{10}H_{10})]$ (**2Se**),[2] (*p*-cymene)$Ru[S_2C_2(B_{10}H_{10})]$ (**3S**),[4] and (*p*-cymene)$Os[S_2C_2(B_{10}H_{10})]$ (**4S**)[4] were synthesized according to our standard methods. The alkynes (ethyne, propyne, and 3-methoxypropyne) were obtained from commercial sources and used without further purification. The reactions were routinely carried out under argon atmosphere at room temperature.

Reactions of $Cp^*Rh[S_2C_2(B_{10}H_{10})]$ (1S)

Preparation of 5S (*transoid*): A slow stream of C_2H_2 was bubbled for 3 days through the green solution of **1S** (70 mg, 0.16 mmol) in CH_2Cl_2 (30 mL). The solution became red, and an orange crystalline solid of **5S** remained after the solvent had been removed. Yield 100 %; m.p. 190 °C (decomp); EI-MS (70 eV): *m*/*z* (%): 470 (100) $[M]^+$; ^1H NMR (250.1 MHz, CD_2Cl_2): $\delta = 1.78$ (s, 15 H; Cp*), 3.27 (dd, $^2J(H,H) < 0.2$ Hz, $^3J(H,H) = 6.6$ Hz, $^2J(Rh,H) = 1.3$ Hz; 1 H; Rh-CH_2), 4.01 (dd, $^2J(H,H) < 0.2$ Hz, $^3J(H,H) = 10.8$ Hz, $^2J(Rh-H) = 1.4$ Hz, 1 H; Rh-CH_2), 4.86 (ddd, $^3J(H,H) = 6.6$, 10.8 Hz, $^2J(Rh,H) = 3.0$ Hz; 1 H; Rh-CH); ^{11}B NMR (160.5 MHz, CD_2Cl_2): $\delta = -11.9$, −11.2, −9.1, −8.6, −7.3, 6.7, −6.1, −4.7, −3.9; ^{103}Rh NMR (15.8 MHz, CD_2Cl_2): $\delta = -233 \pm 1$; IR (Kbr): $\tilde{\nu} = 2571$ cm^{-1} (B-H).

Preparation of 6S and 7S: Propyne was slowly bubbled for 20 h through a green solution containing **1S** (70 mg, 0.16 mmol) in CH_2Cl_2 (30 mL). The color changed to orange, and an orange solid was obtained by evaporation of the solvent. The ^1H NMR spectrum indicated a 1:1 mixture of two isomers. Quantitative yield; EI-MS (70 eV): *m*/*z* (%): 485 (90) $[M]^+$, 444 (100) $[M - \text{propyne}]^+$ (= $\mathbf{1S}^+$) from the mixture.

Data for 6S (*cisoid*): ^1H NMR (250.1 MHz, CD_2Cl_2): $\delta = 1.77$ (s, 15 H; Cp*), 1.99 (s, 3 H; CH_3), 2.79 (dd, $^2J(H,H) \cong {}^2J(Rh,H) = 2.0$ Hz, 1 H; Rh-CH_2), 3.15 (dd, $^2J(H,H) \approx J(Rh,H) = 2.0$ Hz, 1 H; Rh-CH_2). ^{103}Rh NMR (15.8 MHz, CD_2Cl_2): $\delta = -243 \pm 2$.

Data for 7S (*transoid*): ^1H NMR (250.1 MHz, CD_2Cl_2): $\delta = 1.78$ (s, 15 H; Cp*), 1.92 (d, $^3J(Rh,H) = 1{,}3$ Hz, 3 H; CH_3), 3.22 (d, $^2J(Rh,H) = 1.4$ Hz, 1 H; Rh-CH_2), 4.06 (d, $^2J(Rh,H) = 1.4$ Hz, 1 H; Rh-CH_2); ^{103}Rh NMR (15.8 MHz, CD_2Cl_2): $\delta = 77 \pm 1$; ^{11}B NMR (160.5 MHz, CD_2Cl_2; mixture of the two isomers **6S** and **7S**): $\delta = -14.6$, −13.5, −13.0, −11.5, −9.4, −8.7, −7.1, −6.3, −6.0, −3.8; IR (KBr): $\tilde{\nu} = 2568$, 2607 cm^{-1} (B-H).

Preparation of 8S and 9S: Methyl propargyl ether (3-methoxypropyne, 0.17 mL, 0.2 mmol) was added to a solution of **1S** (90 mg, 0.2 mmol) in dichloromethane (20 mL). The solution was stirred at room temperature for 12 h to give a brown-red solution. The (1:1) product mixture was separated by column chromatography over silica; a yellow zone (**8S**) was eluted using hexane/CH_2Cl_2 (1:2), while **9S** was obtained as a second yellow zone upon elution with CH_2Cl_2.

Data for 8S (*cisoid*): Yield 40 mg (40 %); m.p. 172 °C (decomp); EI-MS (70 eV): *m*/*z* (%): 515 (65) $[M]^+$, 444 (100) $[M - \text{methoxypropyne}]$; ^1H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.80$ (s, 15 H; Cp*), 2.78 (dd,

$^2J(H,H) = {}^2J(Rh,H) = 1.9$ Hz, 1H; Rh-CH_2), 3.07 (d, $^2J(H,H)$ 10.2 Hz, 1H; OCH_2), 3.27 (br, 1H; Rh-CH_2), 3.35 (s, 3H; OCH_3), 4.30 (br d, $^2J(H,H) =$ 10.2 Hz, 1H; OCH_2); ^{11}B NMR (160.5 MHz, CD_2Cl_2): $\delta = -15.1, -12.7, -9.6, -6.7, -5.3$; ^{103}Rh NMR (15.8 MHz, CD_2Cl_2): $\delta = -361 \pm 1$; IR (KBr): $\tilde{\nu} = 2564, 2584$ cm^{-1} (B-H).

Data for 9S (*transoid*): Yield 42 mg (42%); m.p. 160 °C (decomp); FD-MS: *m/z* (%): 515 (100) $[M]^+$; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.81$ (s, 15H; Cp*), 2.76 (d, $^2J(H,H) = 10.6$ Hz, 1H; OCH_2), 3.22 (d, $^2J(Rh,H) = 1.4$ Hz, 1H; Rh-CH_2), 3.36 (s, 3H; OCH_3), 4.14 (br d, $^2J(H,H) = 10.6$ Hz, 1H; OCH_2), 4.16 (br, 1H; Rh-CH_2); ^{11}B NMR (160.5 MHz, $CDCl_3$): $\delta = -11.7, -9.9, -6.1, -4.3$; ^{103}Rh NMR (15.8 MHz, $CDCl_3$): $\delta = -176 \pm 1$; IR (KBr): $\tilde{\nu} = 2576$ cm^{-1} (B-H).

Reactions of Cp*Ir[$E_2C_2(B_{10}H_{10})$] (E = S (2S), Se (2Se))

Preparation of 10S and 11S: A solution of **2S** (134 mg, 0.25 mmol) in dichloromethane (20 mL) was stirred in a small autoclave (100 mL) under acetylene (1.5 bar) for one month at 30 °C. The solvent was then evaporated and the residue chromatographed on silica. Careful elution with hexane/CH_2Cl_2 (1:1) gave a broad zone, of which the first part contained **10S** (contaminated with unreacted **2S**), whereas the slower final part contained **11S**.

Data for 10S (*cisoid*): Yield 42 mg (30%); ^{1}H NMR ($CDCl_3$): $\delta = 1.85$ (s, 15H; Cp*), 2.58 (dd, $^2J(H,H) = 2.1$ Hz, $^3J(H,H) = 9.2$ Hz, 1H; Ir-CH_2), 2.69 (dd, $^2J(H,H) = 2.1$, $^3J(H,H) = 7.7$ Hz, 1H; Ir-CH_2), 4.61 (dd, $^3J(H,H) =$ 7.7 Hz, $^3J(H,H) = 9.2$ Hz, 1H; Ir-CH); ^{11}B NMR (160.5 MHz, $CDCl_3$): $\delta = -25.4$ (Ir-B)

Data for 11S (*transoid*): Yield 58 mg (42%); m.p. 265 °C (decomp); EI-MS (70 eV): *m/z* (%): 560 (100) $[M]^+$; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.85$ (s, 15H; Cp*), 2.87 (d, $^3J(H,H) = 6.4$ Hz, 1H; Ir-CH_2), 3.31 (d, $^3J(H,H) =$ 9.1 Hz, 1H; Ir-CH_2), 4.65 (dd, $^3J(H,H) = 6.4$ Hz, $^3J(H,H) = 9.1$ Hz, 1H; Ir-CH); ^{11}B NMR (160.5 MHz, $CDCl_3$): $\delta = -22.1$ (Ir-B), $-11.6, -8.9, -7.5, -6.8, -5.8, -4.6, -3.9$; IR (KBr): $\tilde{\nu} = 2574$ cm^{-1} (B-H).

Preparation of 12S: Gaseous propyne was slowly bubbled at ambient temperature through the purple solution of **2S** (100 mg, 0.19 mmol) in CH_2Cl_2 (30 mL). During one week a yellow solution was formed. Evaporation of the solvent gave a yellow solid of **12S** (108 mg) in quantitative yield. M.p. 235 °C (decomp); EI-MS (70 eV): *m/z* (%): 574 (44) $[M]^+$, 534 (100) $[M -$ propyne$]$ (= **2S**); ^{1}H NMR (250.1 MHz, CD_2Cl_2): $\delta =$ 1.82 (s, 15H; Cp*), 2.04 (s, 3H; Me), 2.66 (d, $^2J(H,H) = 2.1$ Hz, 1H; Ir-CH_2), 2.74 (d, $^2J(H,H) = 2.1$ Hz, 1H; Ir-CH_2); ^{11}B NMR (160.5 MHz, CD_2Cl_2): $\delta = -24.3$ (Ir-B), $-14.5, -13.4, -12.8, -10.6, -6.6, -5.4, -4.3$; IR (KBr): $\tilde{\nu} = 2547, 2572, 2605$ cm^{-1} (B-H).

Preparation of 10Se and 11Se: An autoclave containing a solution of **2Se** (150 mg, 0.24 mmol) in dichloromethane (30 mL) was pressurized with acetylene (1.5 bar). The reaction mixture was stirred at 30 °C for one month. Column chromatography over silica (elution by hexane/CH_2Cl_2 2:1) gave **10Se** as the front part of a green zone: Pure yellow **11Se** was obtained by crystallization from a mixture of **10Se** and **11Se**.

Data for 10Se (*cisoid*): Yield 40 mg (25%); EI-MS (70 eV): *m/z* (%): 654 (100) $[M]^+$; ^{1}H NMR ($CDCl_3$): $\delta = 1.89$ (s, 15H; Cp*), 2.60 (dd, $^2J(H,H) =$ 2.1 Hz, $^3J(H,H) = 9.5$ Hz, 1H; Ir-CH_2), 2.74 (dd, $^2J(H,H) = 2.1$ Hz, $^3J(H,H) = 7.7$ Hz, 1H; Ir-CH_2), 4.73 (dd, $^3J(H,H) = 9.5$ Hz, $^3J(H,H) =$ 7.7 Hz, 1H; Ir-CH); ^{11}B NMR (160.5 MHz, $CDCl_3$): $\delta = -23.7$ (Ir-B), $-13.9, -12.0, -11.4, -9.4, -8.3, -6.9, -5.3, -4.1$; ^{77}Se NMR (95.4 MHz, $CDCl_3$): $\delta = -305.8$ (Ir-Se), 531.3 (C^1-Se); IR (KBr): $\tilde{\nu} = 2580$ cm^{-1} (B-H).

Data for 11Se (*transoid*): Yield 63 mg (40%); m.p. 240 °C (decomp); EI-MS (70 eV): *m/z* (%): 654 (100) $[M]^+$; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta =$ 1.86 (s, 15H; Cp*), 2.96 (d, $^3J(H,H) = 6.4$ Hz, 1H; Ir-CH_2), 2.74 (d, $^3J(H,H) = 9.3$ Hz, 1H; Ir-CH_2), 4.71 (dd, $^3J(H,H) = 6.4$ Hz, $^3J(H,H) =$ 9.3 Hz, 1H; Ir-CH); ^{11}B NMR (160.5 MHz, $CDCl_3$): $\delta = -19.5$ (Ir-B), $-10.9, -9.5, -8.5, -7.6, -5.8, -3.7, -3.0$; ^{77}Se NMR (95.4 MHz, $CDCl_3$): $\delta = 370.4$ (Ir-Se), 603.4 (C^1-Se); IR (KBr): $\tilde{\nu} = 2577$ cm^{-1} (B-H).

Preparation of 12Se (*cisoid*): The green solution of **2Se** (100 mg, 0.16 mmol) in CH_2Cl_2 (30 mL) was repeatedly saturated with propyne while being stirred at ambient temperature for one week. The yellow solution was brought to dryness and the orange product **12Se** isolated in quantitative yield. M.p. 193 °C (decomp); EI-MS (70 eV): *m/z* (%): 670 (60) $[M]^+$, 628 (100), $[M -$ propyne$]^+$ (= **2Se**$^+$); ^{1}H NMR (250.1 MHz, CD_2Cl_2): $\delta = 1.87$ (s, 15H; Cp*), 2.17 (s, 3H; CH_3), 2.72 (d, $^2J(H,H) = 2.2$ Hz, 1H; Ir-CH_2), 2.77 (d, $^2J(H,H) = 2.2$ Hz, 1H; Ir-CH_2); ^{11}B NMR (160.5 MHz, CD_2Cl_2): $\delta = -22.6$ (Ir-B), $-13.9, -12.4, -11.3, -9.9, -6.7, -4.6$. ^{77}Se NMR (95.4 MHz, CD_2Cl_2): $\delta = 336.5$ (Ir-Se), 584.3 (C^1-Se); IR (KBr): $\tilde{\nu} =$ 2568, 2604 cm^{-1} (B-H).

Preparation of 13Se (*cisoid*): 3-Methoxypropyne (0.1 mL, 1.2 mmol) was added to the green solution of **2Se** (70 mg, 0.11 mmol) in CH_2Cl_2 (15 mL). The solution was stirred for 24 h at room temperature to give a brown-red solution. Chromatographic purification on silica with hexane/CH_2Cl_2 (1:3) for elution gave a yellow zone of **13Se**. Yield 50 mg (65%); m.p. 168 °C (decomp); EI-MS (70 eV): *m/z* (%): 698 (52) $[M]^+$, 628 (100) $[Cp^*Ir\{Se_2C_2(B_{10}H_{10})\}]^+$; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.90$ (s, 15H; Cp*), 2.76 (d, $^2J(H,H) = 2.2$ Hz, 1H; Ir-CH_2), 2.83 (d, $^2J(H,H)$, 1H; Ir-CH_2), 2.99 (d, $^2J(H,H) = 10.0$ Hz, 1H; OCH_2), 3.36 (s, 3H; OCH_3), 4.28 (d, $^2J(H,H)$, 10.0 Hz, 1H; OCH_2); ^{11}B NMR (160.5 MHz, $CDCl_3$): $\delta = -23.0$ (Ir-B), $-13.5, -11.8, -11.3, -9.7, -6.7, -4.5$; ^{77}Se NMR (95.4 MHz, $CDCl_3$): $\delta = 335.3$ (Ir-Se), 574.9 (C^1-Se); IR (KBr): $\tilde{\nu} = 2573$ cm^{-1} (B-H).

Reactions of (p-cymene)Ru[$S_2C_2(B_{10}H_{10})$] (3S)

Preparation of 14S (*transoid*): Acetylene was slowly bubbled through the blue solution of **3S** (180 mg, 0.4 mmol) in CH_2Cl_2 (40 mL). In the course of 2 days a brown-yellow solution was formed. Evaporation of the solvent gave a yellow solid of **14S** in quantitative yield. M.p. 175 °C (decomp); EI-MS (70 eV): *m/z* (%): 468 (100) $[M]^+$; ^{1}H NMR (250.1 MHz, CD_2Cl_2): $\delta =$ 1.22 (d, $^3J(H,H) = 7.0$ Hz, 3H; $CH(CH_3)_2$), 1.23 (d, $^3J(H,H) = 7.0$ Hz, 3H; $CH(CH_3)_2$), 2.23 (s, 3H; CH_3), 2.64 (sp, $^3J(H,H) = 7.0$ Hz, 1H; $CH(CH_3)_2$), 3.20 (d, $^3J(H,H)$, = 10.0 Hz, 1H; Ru-CH_2), 3.88 (d, $^3J(H,H) = 6.7$ Hz, 1H; Ru-CH_2), 4.85 (dd, $^3J(H,H) = 10.0$ Hz, $^3J(H,H)$, = 6.7 Hz, 1H; Ru-CH); 5.04, 5.42, 6.31, 6.37 (m, 4H; C_6H_4); ^{11}B NMR (160.5 MHz, CD_2Cl_2): $\delta =$ $-11.8, -9.7, -8.6, -6.1, -4.7, -2.9$; IR (KBr): $\tilde{\nu} = 2572$ cm^{-1} (B-H).

Preparation of 15S and 16S: A brown solution was formed when propyne was bubbled for 15 h through the (originally blue) solution of **3S** (50 mg, 0.11 mmol) in CH_2Cl_2 (30 mL). The brown product **15S** isolated in quantitative yield. M.p. 110 °C (decomp); EI-MS (70 eV): *m/z* (%): 484 (35) $[M]^+$, 442 (100) $[M -$ propyne$]^+$ (= **3S**$^+$). When the *cisoid* complex **15S** was kept in either $CDCl_3$ (for 1 day) or CD_2Cl_2 (for 2 months), partial isomerization to the *transoid* isomer **16S** took place. The isomers **16S** and **15S** were present in a ratio of 1:2.

Data for 15S (*cisoid*): ^{1}H NMR (250.1 MHz, CD_2Cl_2): $\delta = 1.22$ (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH(CH_3)_2$) and 1.25 (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH(CH_3)_2$), 2.20 (s, 3H; $CH_3C=$), 2.29 (s, 3H; CH_3), 2.40 (d, $^2J(H,H) =$ 1.4 Hz, 1H; Ru-CH_2), 2.74 (sept, $^3J(H,H) = 6.9$ Hz, 1H; $CH(CH_3)_2$), 3.22 (d, $^2J(H,H) = 1.4$ Hz, 1H; Ru-CH_2), 5.36, 6.06, 6.16 (m, 4H; C_6H_4); ^{11}B NMR (160.5 MHz, CD_2Cl_2): $\delta = -13.9, -10.7, -6.6, -5.6, -4.1$; IR (KBr): $\tilde{\nu} = 2580$ cm^{-1} (B-H).

Data for 16S (*transoid*): ^{1}H NMR (CD_2Cl_2): $\delta = 1.28$ (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH(CH_3)_2$), 1.31 (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH(CH_3)_2$), 1.92 (s, 3H; $CH_3C=$), 2.19 (s, 3H; CH_3), 2.77 (sept, $^3J(H,H) = 6.9$ Hz, 1H; $CH(CH_3)_2$), 3.22 (s, 1H; Ru-CH_2), 3.87 (s, 1H; Ru-CH_2), 4.63, 5.63, 6.32, 6.37 (m, 4H; C_6H_4).

Reactions of (p-cymene)Os[$S_2C_2(B_{10}H_{10})$] (4S)

Preparation of 17S (*transoid*): A solution of **4S** (70 mg, 0.132 mmol) in CH_2Cl_2 (20 mL) was stirred in a 100 mL autoclave under 1.5 bar of acetylene for 1 week at 40 °C. Workup by column chromatography (elution with hexane/CH_2Cl_2 (2:1)) gave the purple reactant **4S** and a yellow product **17S**. Yield 50 mg (68%); m.p. 202 °C (decomp); EI-MS (70 eV): *m/z* (%): 557 (100) $[M]^+$; ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.19$ (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH(CH_3)_2$), 1.25 (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH(CH_3)_2$), 2.39 (s, 3H; CH_3), 2.57 (sept, $^3J(H,H) = 6.9$ Hz, 1H; $CH(CH_3)_2$), 2.75 (dd, $^2J(H,H) = 1.3$ Hz, $^3J(H,H) = 9.1$ Hz, 1H; Os-CH_2), 3.65 (dd, $^2J(H,H) = 1.3$ Hz, $^3J(H,H)$, = 7.0 Hz, 1H; Os-CH_2), 4.87 (dd, $^3J(H,H) = 9.1$ Hz, $^3J(H,H) = 7.0$ Hz, 1H; Os-CH), 5.23, 5.38, 6.09, 6.15 (m, 4H; C_6H_4); ^{11}B NMR (160.5 MHz, $CDCl_3$): $\delta = -17.0$ (B-Os), $-11.8, -10.3, -8.2, -6.6, -5.5, -4.5, -2.8$; IR (KBr): $\tilde{\nu} = 2574$ cm^{-1} (B-H).

Preparation of 18S and 19S: The purple solution of **4S** (130 mg, 0.245 mmol) in CH_2Cl_2 (30 mL) was stirred under an atmosphere of propyne (in a balloon) for 5 days. Chromatography over silica was used for purification; a purple zone of unreacted **4S** was eluted with hexane/CH_2Cl_2 (2:1) and a yellow zone containing 84 mg (60%) of **18S** with hexane/CH_2Cl_2 (1:2). A solution of the *cisoid* complex **18S** in $CDCl_3$ isomerized slowly into the *transoid* isomer **19S**; after two weeks, the ratio of **18S**:**19S** was 4:1.

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Table 2. Crystal structure data (at 23 °C) for complexes **4S**, **9S**, **12S**, and **14S**.

	4S	**9S**	**12S**	**14S**
formula	$C_{12}H_{24}B_{10}S_2Os$	$C_{16}H_{31}B_{10}OS_2Rh$	$C_{15}H_{29}B_{10}S_2Ir$	$C_{14}H_{26}B_{10}S_2Ru$
crystal	dark red platelet	red prism	pale yellow prism	orange plate
size [mm]	0.16 × 0.12 × 0.06	0.15 × 0.12 × 0.10	0.18 × 0.14 × 0.08	0.30 × 0.20 × 0.08
crystal system	triclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	*Pbca*
a [pm]	697.64(5)	882.3(3)	1171.02(14)	1018.9(2)
b [pm]	1016.72(8)	999.58(8)	1281.79(11)	1394.07(17)
c [pm]	1452.92(7)	1448.55(8)	1471.57(17)	2977.1(5)
α [°]	83.358(6)	94.051(6)		
β [°]	83.176(6)	106.785(5)	95.599(10)	
γ [°]	82.160(7)	105.316(5)		
V [10^6 pm^3]	1008.50(12)	1164.66(12)	2198.3(4)	4288.6(13)
Z	2	2	4	8
ρ_{calcd} [g cm^{-3}]	1.748	1.467	1.734	1.469
μ [mm^{-1}]	6.521	0.920	6.263	0.936
θ range [°]	2–27.5	1.5–27.5	2–27.5	2–27.5
reflections collected	5428	6386	6257	6001
independent reflections	4361	5339	5031	4837
min./max. transmission	0.4462/0.8857	0.4986/0.5860	0.4034/0.9767	3580/00.5096
parameters	224	271	254	252
wR2/*R1* [$I >> 2\sigma(I)$]	0.079/0.032	0.0757/0.028	0.0844/0.036	0.193/0.080
max./min. residual electron density [e pm^{-3} × 10^{-6}]	1.23/ – 1.47	0.63/ – 0.60	2.81/ – 2.32	2.49/ – 1.63

Data for 18S (*cisoid*): Yellow crystals; m.p. 145 °C (decomp); EI-MS (70 eV): *m*/*z* (%): 572 (30) $[M]^+$, 530 (100) $[M-\text{propyne}]^+$ (= **4S**$^+$); ^{1}H NMR (250.1 MHz, CD_2Cl_2): $\delta = 1.21$ (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH(CH_3)_2$), 1.26 (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH(CH_3)_2$), 2.25 (d, $^2J(H,H) = 2.5$ Hz, 1H; Os-CH_2) and 3.48 (d, $^2J(H,H) = 2.5$ Hz, 1H; Os-CH_2), 2.30 (s, 3H; $CH_3C=$), 2.41 (s, 3H; CH_3), 2.71 (sep., $^3J(H,H) = 6.9$ Hz, 1H; $CH(CH_3)_2$), 5.33, 5.93, 5.99 (m, 4H; C_6H_4); ^{11}B NMR (160.5 MHz, CD_2Cl_2): $\delta = -18.1$ (B-Os), -14.7, -13.4, -10.7, -6.5, -5.7, -4.0; IR (KBr): $\tilde{\nu} = 2580$ cm^{-1} (B-H);

Data for 19S (*transoid*): ^{1}H NMR (250.1 MHz, $CDCl_3$): $\delta = 1.19$ (d, $^3J(H,H) = 6.9$ Hz, 3H; $CH(CH_3)_2$), 1.36 (d, $^3J(H,H)$, 3H; $CH(CH_3)_2$), 2.06 (s, 3H; $CH_3C=$), 2.32 (s, 3H; CH_3), 2.72 (sept, $^3J(H,H) = 6.9$ Hz, 1H; $CH(CH_3)_2$), 2.82 (d, $^2J(H,H) = 1.0$ Hz, 1H; Os-CH_2), 3.65 (d, $^2J(H,H) = 1.0$ Hz, 1H; Os-CH_2), 4.74, 5.69, 6.09, 6.16 (m, 4H; C_6H_4).

Crystal structures of 4S, 9S, 12S, and 14S: Single crystals were sealed in Lindemann capillaries. A Siemens P4 diffractometer was used for the measurements with $Mo_{K\alpha}$ (λ = 71.073 pm) radiation and a graphite monochromator. Empirical absorption corrections (Ψ-scans) were applied. Relevant experimental data for the determination of the crystal structures are given in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166814 (**4S**), CCDC-166812 (**9S**), CCDC-166813 (**12S**), and CCDC-166811 (**14S**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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