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Metal-induced B–H activation. Addition of phenylacetylene to Cp*Rh-, Cp*Ir-, (*p*-cymene)Ru- and (*p*-cymene)Os halfsandwich complexes containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolate ligand

Max Herberhold * [1], Hong Yan, Wolfgang Milius, Bernd Wrackmeyer * [2]

Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 10 12 51, D-95440 Bayreuth, Germany

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Dedicated to Professor Herbert W. Roesky on the occasion of his 65th birthday.

Abstract

The addition reactions of the 16e halfsandwich complexes Cp*M[$S_2C_2(B_{10}H_{10})$] (**1S** M = Rh, **2S** M = Ir) and η^6-(4-isopropyltoluene)M[$S_2C_2(B_{10}H_{10})$] (**3S** M = Ru and **4S** M = Os) with phenylacetylene lead selectively to the 18e complexes **5S**–**8S**, in which a metal–boron bond is present and the phenylacetylene is regio- and stereoselectively inserted into one of the M–S bonds, with one hydrogen atom transferred from the carborane cage to the terminal carbon of the alkyne, corresponding to *ortho*-metalation of the carborane cage. In all cases, the S-η^2-(Ph)CC and the C(1)B units are linked to the metal in *cisoid* positions. The analogous reaction of Cp*Ir[$Se_2C_2(B_{10}H_{10})$] **2Se** with phenylacetylene gives **6Se**. Complex **5S** undergoes an intramolecular rearrangement in solution to the isomer **9S**, where the Rh–B bond is cleaved, the B-atom now bearing the organic substituent, and a metal–carbon σ bond being formed together with a coordinative S → Rh bond. In contrast, the *p*-cymene complexes **7S** and **8S** rearrange into isomers **10S** and **11S**, in which the S-η^2-(Ph)C–C and the C(1)–B(M) moieties occupy *transoid* positions, preventing further intramolecular rearrangements. The proposed structures in solution were deduced from NMR data (^{1}H-, ^{11}B-, ^{13}C-, ^{77}Se-, and ^{103}Rh-NMR) and X-ray structural analyses were carried out for **5S**, **6Se**, **9S** and **10S**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carboranes; Iridium; Osmium; Rhodium; Ruthenium, Selenium; Sulfur; X-ray; NMR

1. Introduction

The conversion of 16e complexes into their 18e congeners by oxidative addition at the metal is a well-known systematic route to new products [1]. However, if additional reactive centres are available in the 16e complexes, the preferred mode of addition becomes less predictable. We have recently reported on the 16e half-sandwich complexes of rhodium (**1Se**) [2] and iridium (**2Se**) [3] which contain both the pentamethylcyclopentadienyl (Cp*) and the *ortho*-carborane diselenolato ligand $[Se_2C_2(B_{10}H_{10})]^{2-}$. In the present contribution we compare the sulphur analogues **1S** and **2S** with the corresponding *p*-cymene-ruthenium- and -osmium complexes (**3S** and **4S** [4]) in their reactivity towards phenylacetylene. We have already started to study the reactivity of **1S** towards acetylene carboxylic acid methyl esters and have found a remarkable activity not only for the Rh–S bonds but also for the carborane cage [5]. From the preliminary studies [5] it had become clear that in all these 16e complexes the metal itself, the metal–chalcogen bonds and also the carborane cage at the site of B(3) or B(6), being close to the metal, have to be considered as potentially reactive centres.

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[1] *Corresponding author. Tel.: +49-921-552540; fax: +49-921-552157; e-mail: max.herberhold@uni-bayreuth.de

[2] *Corresponding author. Tel.: +49-921-552542; fax: +49-921-552157.

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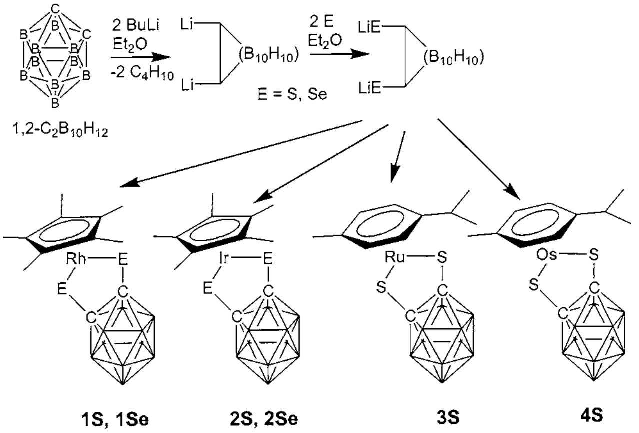
2. Results and discussion

2.1. Synthesis of the 16e complexes **1–4**

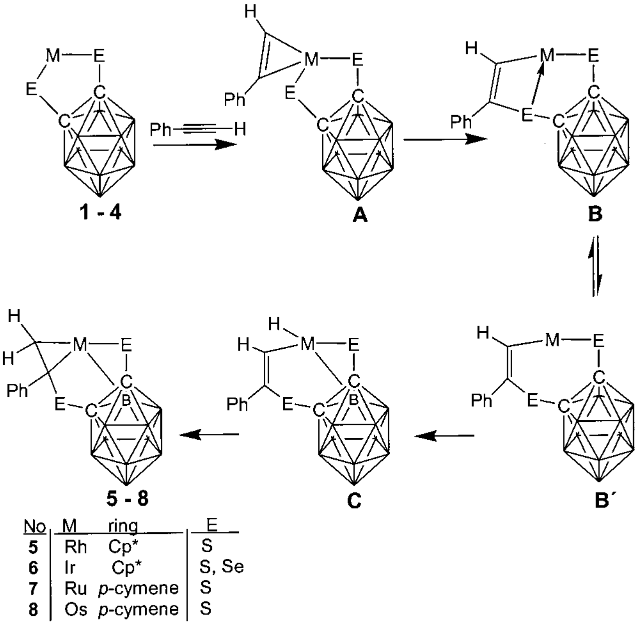
The starting complexes **1–4** were prepared following the published procedures [3,4] as shown in Scheme 1.

2.2. Reaction of the 16e complexes **1–4** with phenylacetylene

All complexes **1–4** react with phenylacetylene in 1:1 stoichiometry to give the 18e complexes **5–8** (Scheme 2). The intermediates **A**, **B** and **C** were not detected when the reactions were monitored by NMR. However, complexes analogous to **B** have been isolated from the reaction of **1S** with dimethyl acetylene dicarboxylate [5], and also from the reaction of the CpCo analogue of **1S** with terminal acetylenes [6]. If it is assumed that the coordinative E → M bond can be opened, the 18e complex **B** is in equilibrium with a 16e complex **B′**. The structure of **B′** is less rigid than that of **B**, thus the metal atom becomes able to approach the B(3,6) sites of the carborane cage and to induce B–H activation [7]. By this route the M–B and M–H bonds in **C** are formed and the final step is the transfer of hydrogen from the metal to the carbon atom to give **5–8**. In all complexes **5–8** the E-η^2-(Ph)C–C and the C(1)–B(M) bonds point into the same direction with respect to the metal centre (*cisoid* arrangement). A typical ^{13}C-NMR spectrum is shown for **7S** in Fig. 1. The presence of the M–B bond in **5–8** suggests that these complexes will be ready for further transformations.



Scheme 1.



No	M	ring	E
5	Rh	Cp*	S
6	Ir	Cp*	S, Se
7	Ru	*p*-cymene	S
8	Os	*p*-cymene	S

Scheme 2.

2.3. Rearrangement reactions of the complexes **5–8**

The iridium complexes **6S** and **6Se** appeared to be stable under the conditions which induced rearrangements in the other complexes **5S**, **7S** and **8S**.

2.3.1. Rearrangement of **5S** to its isomer **9S**

In boiling chloroform the Cp*Rh complex **5S** rearranges slowly as shown in Scheme 3. All NMR data (Table 1; see Fig. 2 for the ^{13}C-NMR spectrum) were in support of the structure **9S** in which the Rh–B bond has been cleaved, while new B–C and Rh–C σ bonds have been formed, together with a coordinative S → Rh interaction. The latter is proposed to be present in solution, since δ^{103}Rh = + 329 ± 1 is more typical [3,8] of an 18e complex. This structure was then confirmed for the solid state by an X-ray structural analysis of **9S** (see below).

2.3.2. Rearrangement of **7S** and **8S** to their isomers **10S** and **11S**

Heating of **7S** or **8S** in CDCl$_3$ or carrying out the reaction of **3S** or **4S** with phenylacetylene in boiling chloroform affords products which contain the same structural units as **7S** or **8S** but possess apparently a different structure (Scheme 4). The NMR data (Table 1) suggest striking structural differences between these isomers and this was confirmed by the X-ray structural analysis of **10S** (Fig. 6) which shows that the S-η^2-(Ph)C–C and the C(1)–B(M) bonds now point into opposite directions (*transoid* arrangement) in the coordination sphere of the ruthenium atom. The analogous NMR data sets of **10S** and **11S** suggest that the osmium derivative **11S** possesses the same structural features as **10S**. In contrast to the situation for **5S** (Fig. 3) and **9S** (Fig. 5), the *transoid* structure of **10S** and **11S** prevents further intramolecular rearrangements involving the M–B bond.

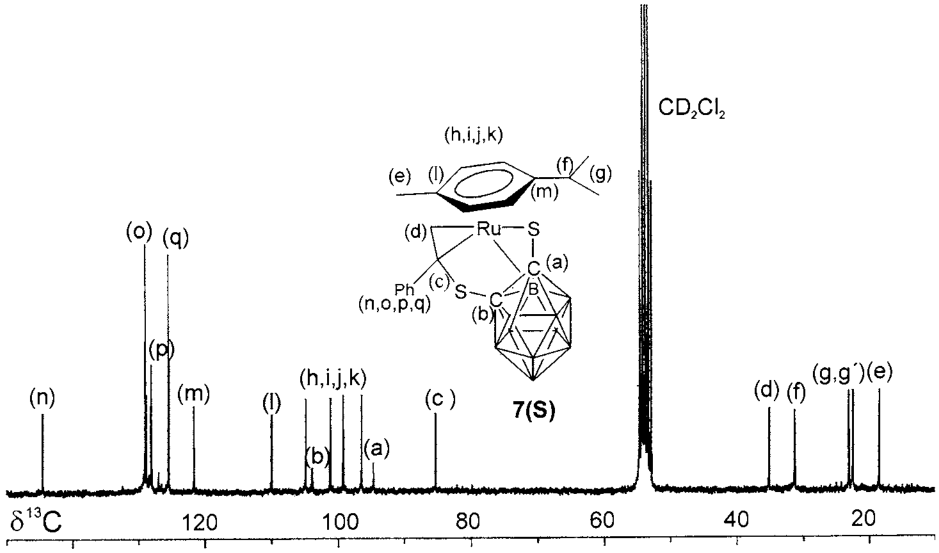


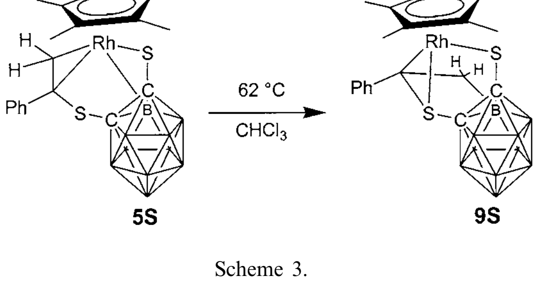
Fig. 1. 62.9 MHz ^{13}C{^{1}H}-NMR spectrum of **7S** in CD$_2$Cl$_2$, measured at 22°C. All 18 ^{13}C resonances are visible. The ^{13}C(1,2) carborane signals, marked (a) and (b), are somewhat broader and less intense than the other signals.

2.4. NMR spectroscopic results

The ^{13}C-NMR data (Table 1) and all other NMR data (see Section 4) of the complexes **5**–**11** are in agreement with the proposed structures and confirm that the relevant features of the solid state structures of **5S**, **6Se**, **9S** and **10S** are retained in solution. The Figs. 1 and 2 show typical ^{13}C-NMR spectra. Straightforward assignments were made by using both 2D ^{1}H/^{1}H COSY experiments and 2D ^{13}C/^{1}H HETCOR spectra, based on coupling constants $^1J(^{13}C,^1H)$ and long range coupling constants $^nJ(^{13}C,^1H)$ ($n = 2$, 3). The small values (< 3 Hz) of the geminal coupling constants $|^2J(^1H,^1H)|$ in **5**–**8**, **10** and **11** are typical of terminal alkenes coordinated to metal centres. In contrast, in **9S** the magnitude of $|^2J(^1H,^1H)|$ for the BCH$_2$ group is large (14.7 Hz) and characteristic of diastereotopic ^{1}H nuclei in geminal positions of an alkyl group. The ^{103}Rh chemical shifts were determined by selective heteronuclear ^{1}H{^{103}Rh} double resonance experiments which also served to distinguish between coupling constants $J(^1H,^1H)$ and $J(^{103}Rh,^1H)$. ^{11}B-NMR spectra of **5**–**11** showed the pattern of overlapping signals (see Section 4) expected for unsymmetrically substituted *ortho*-carborane derivatives [9]; the ^{11}B-NMR signal of the boron atom linked to the respective metal centre (**5**–**8**, **10** and **11**) or to the CH$_2$ group in **9S** is readily assigned in each case by comparison of ^{1}H coupled and ^{1}H decoupled ^{11}B-NMR spectra.

*2.5. X-ray structural analyses of the complexes **5S**, **6Se**, **9S** and **10S***

The molecular structures of the complexes **5S**, **6Se**, **9S** and **10S** are shown in the Figs. 3–6 together with selected bond lengths and bond angles. The *cisoid* arrangement of the E-η^2-(Ph)C–C and the C(1)–B(M) units in **5S** (Fig. 3) is also present in **6Se** (Fig. 4), in contrast to the situation in **10S** (Fig. 6). There are two independent molecules of **5S** in the unit cell and this was also found in the case of the rearranged product **9S** (Fig. 5). Most bond lengths and bond angles are in the usual ranges. However, the bond length C(1)–C(2) = 178.4(5) pm in **10S** is exceptionally long (as compared with the typical range of *o*-carborane derivatives of 162–170 pm [10]) whereas some of the bond lengths B–C are shorter than expected (cf. the typical range of 170–175 pm [10]). This indicates a considerable distortion of the carborane cage in **10S**, in agreement with changes of the δ^{13}C(1,2) values when compared with those of **7S** (see Table 1). The five-membered rings containing the metal centre are non-planar, as expected for 18e compounds (in contrast to the 16e starting complexes [2]). All four-membered metallacycles MS(2)CB are planar within experimental error.



Scheme 3.

Table 1
^{13}C-NMR data [a] of the complexes **5**–**11**

	($E_2C_2B_{10}H_{10}$)	*Cp** or *p-cymene*	E–*C*–(*Ph*)	*C*H$_2$	*Ph*
5S	95.5, 103.0 (3.6)	9.1, 105.5 (3.5)	94.9 (9.1)	46.2 (9.7)	128.1, 129.3, 129.4, 139.8
6S	97.5, 101.9	8.5, 101.6	73.9	28.6	128.2, 128.7, 129.4, 141.0
6Se	78.8, 91.6	8.9, 101.5	66.3	30.8	128.4, 128.6, 129.9, 142.2
7S	94.7, 103.9	18.5, 22.5, 23.1, 31.3, 96.4, 99.2, 101.1, 104.8, 110.0, 121.6	85.4	35.2	125.4, 128.0, 128.9, 144.5
8S	96.1, 103.0	17.5, 21.8, 23.6, 30.2, 88.8, 91.2, 93.1, 95.9, 107.4, 116.0	69.4	22.6	125.7, 127.2, 128.5, 145.3
9S	92.7, 96.5	9.1, 99.4 (6.2)	94.7 (21.8)	35.1 (br)	124.2, 125.5, 128.9, 150.6
10S	110.8, 111.0	17.0, 21.1, 24.9, 31.4, 97.4, 98.8, 100.8, 105.0, 105.8, 118.4	81.3	50.5	126.9, 128.3, 145.2
11S	109.1, 109.6	17.1, 21.1, 24.8, 31.1, 90.5, 90.8, 94.9, 98.7, 100.6, 112.2	67.0	37.1	126.7, 127.4, 128.3, 147.1

[a] All complexes were measured in CD_2Cl_2 (except **8S** in $CDCl_3$) at 22°C; $J(^{103}Rh,^{13}C)$ (± 0.5 Hz) in parentheses; (br) denotes the signal of a ^{13}C nucleus linked to boron by a 2c/2e bond.

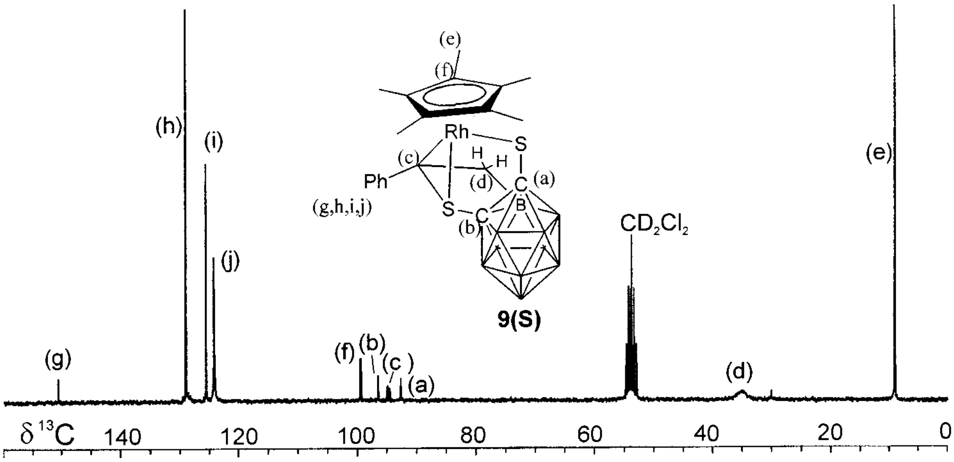


Fig. 2. 62.9 MHz $^{13}C\{^1H\}$-NMR spectrum of **9S** in CD_2Cl_2 at 22°C. The broad signal of a CH_2 group at high field, marked (d), indicates the presence of a carbon atom linked to boron by a 2c/2e bond. The signal marked (c) is a doublet with $^1J(^{103}Rh,^{13}C) = 21.8$ Hz, typical of a 2c/2e Rh–C bond.

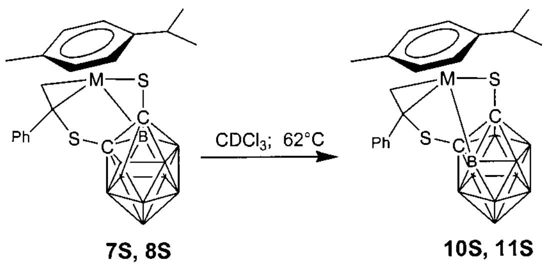
3. Conclusions

The 16e complexes **1**–**4** proved to be versatile reagents in their reactions with phenylacetylene and this is promising for future studies using other alkynes and comparable unsaturated substrates. The activation of B–H bonds and the formation of M–B bonds (*ortho*-metalation), followed by selective substitution of the carborane cage in the case of **9**(S), is an interesting aspect in carborane chemistry.

4. Experimental

4.1. General and starting materials

The starting complexes $[Cp^*MCl_2]_2$ (M = Rh [11], Ir [11]) and $[(p\text{-cymene})MCl_2]_2$ (M = Ru [12], Os [13]) were prepared according to established procedures; *n*-butyllithium (1.6 M in hexane), *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, and phenylacetylene were used as commercial products. The 16e complexes $Cp^*M[E_2C_2$-



7S, 8S
M = Ru, Os

10S, 11S
M = Ru, Os

Scheme 4.

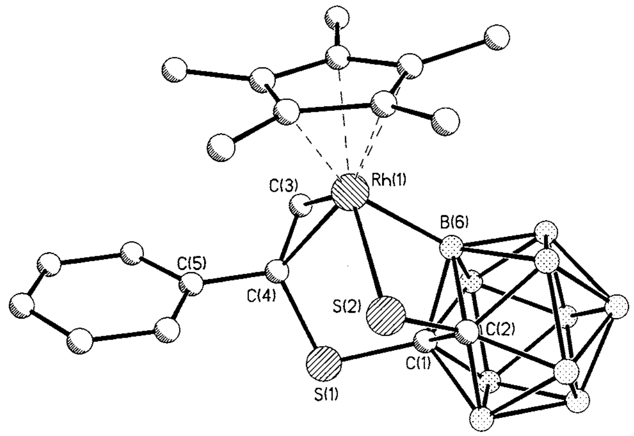


Fig. 3. Molecular geometry of **5S**. Selected bond lengths (pm) and angles (°): Rh(1)–B(6) 209.8(8), Rh(1)–C(3) 214.8(7), Rh(1)–C(4) 218.1(7), Rh(1)–S(2) 240.94(16), Rh(1)–ring centre 190.9, C(1)–S(1) 176.7(7), C(4)–S(1) 181.5(7), C(2)–S(2) 178.0(7), C(1)–C(2) 171.0(10), C(3)–C(4) 139.5(11); C(3)Rh(1)C(4) 37.6(3), C(3)Rh(1)S(2) 87.6(2), B(6)Rh(1)S(2) 72.4(2), B(6)Rh(1)C(3) 84.5(3), C(1)S(1)C(4) 102.5(3), C(2)C(1)S(1) 116.1(5), C(1)C(2)S(2) 112.1(4), C(2)S(2)Rh(1) 87.6(2); C(4)Rh(1)B(6)/C(4)S(1)C(1)B(6) 157.8; plane Rh(1)B(6)C(2)S(2), average deviation 1.5 pm.

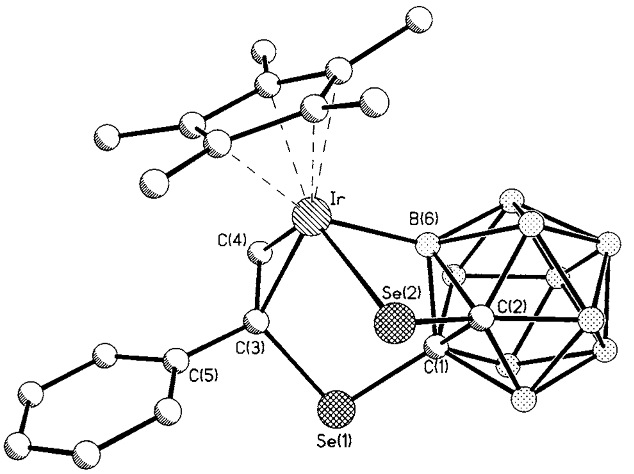


Fig. 4. Molecular geometry of **6Se**. Selected bond lengths (pm) and angles (°): Ir–B(6) 210.4(10), Ir–C(3) 214.7(9), Ir–C(4) 212.1(9), Ir–Se(2) 251.34(9), Ir–ring centre 192.4, C(1)–Se(1) 190.4(10), C(3)–Se(1) 197.8(9), C(2)–Se(2) 193.4(9), C(1)–C(2) 170.1(13), C(3)–C(4) 142.4(13); C(3)IrC(4) 39.0(4), C(3)IrSe(2) 87.8(3), B(6)IrC(3) 89.7(4), B(6)IrC(4) 85.5(4), C(1)Se(1)C(3) 99.1(4), C(2)C(1)Se(1) 117.9(6), C(1)C(2)Se(2) 111.7(6), C(2)Se(2)Ir 85.8, C(3)IrB(6)/C(3)Se(1)C(1)B(6) 155.0; plane IrB(6)C(2)Se(2), average deviation 1.6 pm.

$(B_{10}H_{10})]$ (M = Rh [3], Ir [2]; the syntheses for E = S is described below [14]) and (*p*-cymene)M$[S_2C_2(B_{10}H_{10})]$ (M = Ru, Os [4]) were obtained as described. NMR measurements: Bruker ARX 250 and DRX 500 spectrometers (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

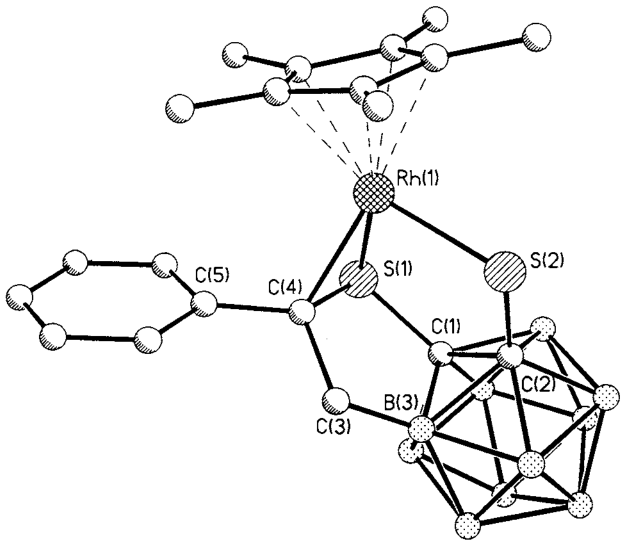


Fig. 5. Molecular geometry of **9S**. Selected bond lengths (pm) and angles (°): Rh(1)–C(4) 212.8(3), Rh(1)–S(1) 231.16(10), Rh(1)S(2) 235.38(10), Rh(1)–ring centre 185.8, C(1)–S(1) 178.2(3), C(2)–S(2) 176.6(3), C(4)–S(1) 182.4(4), C(1)–C(2) 168.8(5), C(3)–C(4) 153.5(4), B(3)–C(3) 157.2(5); C(4)Rh(1)S(1) 48.3(1), C(4)Rh(1)S(2) 91.22(9), S(1)Rh(1)S(1) 91.85(3), C(1)S(1)C(4) 97.20(16), C(2)C(1)S(1) 116.2(2); C(1)C(2)S(2) 119.6(2), C(1)S(1)Rh(1) 107.15(12), C(2)S(2)Rh(1) 104.81(12), B(3)C(3)C(4) 111.4(3), C(3)C(4)Rh(1)S(2)/C(3)B(3)C(2)S(2) 122.3; plane Rh(1)S(1)C(1)C(2)S(2), average deviation 2.9 pm.

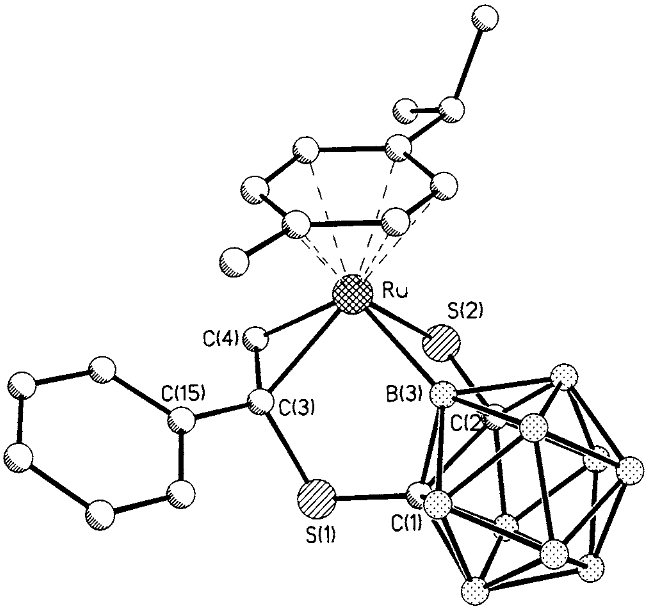


Fig. 6. Molecular geometry of **10S**. Selected bond lengths (pm) and angles (°): Ru–B(3) 214.3(4), Ru–C(3) 218.5(4), Ru–C(4) 213.4(4), Ru–S(2) 241.28(10), Ru–ring centre 179.8, C(1)S(1) 175.8(4), C(2)S(2) 176.2(4), C(3)S(1) 182.1(4), C(1)–C(2) 178.4(5), C(3)–C(4) 141.7(5); C(3)RuB(3) 84.34(17), C(4)RuC(3) 38.29(14), C(4)RuS(2) 81.26(11), B(3)RuS(2) 70.19(12), C(1)S(1)C(3) 102.52(18), C(2)C(1)S(1) 115.6(2), C(1)C(2)S(2) 112.5(2), C(2)S(2)Ru 90.30(12), C(3)RuB(3)/C(3)S(1)C(1)B(3) 149.1; plane RuS(2)C(2)B(3), average deviation 1.2 pm.

δ^{103}Rh = 0 for $\Xi(^{103}$Rh) = 3.16 MHz. Mass spectra: Finnigan MAT 8500 for EI-MS (70 eV), direct inlet; Varian MAT 311A for FD-MS. IR spectra: Perkin–Elmer 985.

4.2. Dilithio 1,2-dicarba-closo-dodecaborane-1,2-dithiolate and -diselenolate

A solution of 1,2-$C_2B_{10}H_{12}$ (0.29 g; 2 mmol) in Et_2O (40 ml) was treated with 2.75 ml of a solution of *n*-butyllithium (1.6 M in hexane; 4.4 mmol) at room temperature (r.t.). Addition of sulphur (0.14 g; 4 mmol) or selenium (0.35 g; 4 mmol) and stirring of the reaction mixture for 1–3 h at r.t. gave a yellow solution of $Li_2E_2C_2(B_{10}H_{10})$ in quantitative yield.

*4.3. Pentamethylcyclopentadienyl-(1,2-dicarba-closo-dodecaborane-1,2-dithiolato)-iridium, Cp*Ir[$S_2C_2(B_{10}H_{10})$]* **(2S)**

A solution of dilithium 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate (1 mmol) in Et_2O (60 ml) was added to a solution of [Cp*$IrCl_2$]$_2$ (0.5 mmol) in THF (60 ml). The colour of the Et_2O/THF solution changed immediately from yellow to purple. The solvents were evaporated under reduced pressure and the residue chromatographed on silica (Merck, Kieselgel 60). Elution with CH_2Cl_2/hexane (5/1) gave a purple zone which contained 0.49 g (92%) of **2S**. IR (CsI): ν(B–H) = 2566, 2590 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 1.87 (s, Cp*). ^{13}C-NMR ($CDCl_3$): δ = 10.1, 91.8 (Cp*), 92.8 (S_2C_2). ^{11}B-NMR: δ = −6.3, −7.8, −8.7, −10.1. EI-MS (70 eV): *m*/*z* (%) = 534 (100) [M$^+$].

4.4. Preparation of **5S**

A mixture of Cp*Rh[$S_2C_2(B_{10}H_{10})$] **1S** (0.3 mmol; 133.5 mg) and phenylacetylene (3 mmol; 0.3 ml) in CH_2Cl_2 (30 ml) was stirred at r.t. for 3 days; the colour gradually turned red. The solvent was then removed under reduced pressure, the residue was washed with hexane and finally recrystallised from a CH_2Cl_2 solution at −18°C. Yield, 140 mg, 85%, red crystals, m.p. = 145°C (dec.). ^{1}H-NMR (CD_2Cl_2): δ = 1.49 (s, 15H, Cp*), 3.11 (dd, $J_{H–H} = J_{Rh–H}$ = 2.3 Hz, 1H, PhC–CH_2), 3.18 (dd, $J_{H–H} = J_{Rh–H}$ = 2.3 Hz, 1H, PhC–CH_2), 7.24 (m, 3H, Ph) and 7.80 (m, 2H, Ph). ^{11}B-NMR (CD_2Cl_2): δ = −4.2, −5.0, −6.6, −9.8, −12.3, −13.4, −14.8 (Rh–B) (1:3:1:1:1:2:1). ^{103}Rh-NMR (CD_2Cl_2): δ = −174 ± 1. IR (KBr): 2567, 2583($\nu_{B–H}$). EI-MS (70 eV): 547 [M$^+$, 86%], 445 [M$^+$ − (PhC≡CH), 74%].

4.5. Preparation of **6S** *and* **6Se**

A solution of Cp*Ir[$S_2C_2(B_{10}H_{10})$] **2S** (0.2 mmol; 106.8 mg) or Cp*Ir[$Se_2C_2(B_{10}H_{10})$] **2Se** (0.2 mmol; 125.4 mg) and phenylacetylene (0.2 ml, 2 mmol) in $CHCl_3$ (30 ml) was stirred for 10 days at r.t. or 2 days at 62°C. The colours of the reaction mixtures changed gradually from blue–purple (**2S**) to light yellow for **6S** or from green (**2Se**) to yellow for **6Se**. The solvent was removed in vacuo and the respective residue was washed with hexane. Recrystallisation from CH_2Cl_2 solutions at −18°C gave light-yellow crystals of **6S** or yellow crystals of **6Se**.

6S: Yield, 101.8 mg, 80%, m.p. = 205°C (dec.). ^{1}H-NMR (CD_2Cl_2): δ = 1.55 (s, 15H, Cp*), 2.67 (d, $J_{H–H}$ = 2.5 Hz, 1H, PhC–CH_2), 3.22 (d, $J_{H–H}$ = 2.5 Hz, 1H, PhC–CH_2), 7.20 (m, 3H, Ph) and 7.69 (m, 2H, Ph). ^{11}B-NMR (CD_2Cl_2): δ = −5.4, −6.5, −10.6, −12.4, −13.4, −14.5, −25.0 (Ir–B) (5:1:1:1:1:1). IR (KBr): 2560, 2588($\nu_{B–H}$). EI-MS (70 ev): 636 [M$^+$, 30%], 534 [M$^+$ − (PhC≡CH), 100%].

6Se: Yield, 122.6 mg, 84%, m.p. = 192°C (dec.). ^{1}H-NMR (CD_2Cl_2): δ = 1.60 (s, 15H, Cp*), 2.70 (d, $J_{H–H}$ = 2.8 Hz, 1H, PhC–CH_2), 3.21 (d, $J_{H–H}$ = 2.8 Hz, 1H, PhC–CH_2), 7.19 (m, 3H, Ph) and 7.68 (m, 2H, Ph). ^{11}B-NMR (CD_2Cl_2): δ = −4.2, −5.2, −6.7, −10.0, −10.9, −12.3, −13.9, −23.2 (Ir–B) (2:2:1:1:1:1:1:1). ^{77}Se-NMR (CD_2Cl_2): δ = 315.4 (Ir–Se), 630.0 (C(Ph)–Se). IR (KBr): 2562, 2584($\nu_{B–H}$). FD-MS: 730 [M$^+$, 100%].

4.6. Preparation of **7S** *and* **8S**

The solution of either (*p*-cymene)Ru[$S_2C_2(B_{10}H_{10})$] **3S** (88.4 mg, 0.2 mmol) or (*p*-cymene)Os[$S_2C_2(B_{10}H_{10})$] **4S** (106 mg, 0.2 mmol) and phenylacetylene (0.2 ml, 2 mmol) in CH_2Cl_2 (30 ml) was stirred at r.t. for 1 day (**7S**) or 3 days (**8S**). The colour changed from blue (**3S**) or from purple (**4S**) to brown–red. Evaporation of the solvent and removal of the excess of phenylacetylene by washing with hexane gave **7S** as a deep-yellow powder; **8S** was isolated by chromatography on silica gel (Merck, Kieselgel 60) with a 1:1 mixture of hexane–CH_2Cl_2 (v/v) for elution. Recrystallisation of **8S** from CH_2Cl_2 at −18°C afforded yellow crystals.

7S: yield, 87 mg, 80%; m.p. = 124°C (dec.). ^{1}H-NMR (CD_2Cl_2): δ = 0.95 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$), 1.09 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$), 2.05 (s, 3H, CH_3), 2.46 (sp, *J* = 6.9 Hz, 1H, CH(CH_3)$_2$), 2.55 (d, *J* = 2.9 Hz, 1H, PhC–CH_2), 3.96 (d, *J* = 2.9 Hz, 1H, PhC–CH_2), 5.38 (d, *J* = 6.0 Hz, 1H, C_6H_4), 5.40 (d, *J* = 6.0 Hz, 1H, C_6H_4), 5.48 (d, *J* = 6.0 Hz, 1H, C_6H_4), 5.58 (d, *J* = 6.0 Hz, 1H, C_6H_4), 7.22 (m, 3H, Ph) and 7.90 (m, 2H, Ph). ^{11}B-NMR (CD_2Cl_2): δ = −4.5, −5.2, −6.7, −11.0 (Ru–B), −13.5 (2:2:1:3:2). IR (KBr): $\nu_{B–H}$ = 2581 cm^{-1}. FD-MS: 544 [M$^+$, 100%], 442 [M$^+$ − (PhC≡CH), 90%].

8S: yield, 95 mg, 75%; m.p. = 155°C (dec.). ^{1}H-NMR ($CDCl_3$): δ = 1.02 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$), 1.03 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$), 2.03 (s, 3H, CH_3), 2.27

(sp, $J = 6.9$ Hz, 1H, $CH(CH_3)_2$), 2.37 (d, $J = 3.5$ Hz, 1H, PhC–CH_2), 4.25 (d, $J = 3.5$ Hz, 1H, PhC–CH_2), 5.29 (d, $J = 6.3$ Hz, 2H, C_6H_4), 5.37 (d, $J = 6.3$ Hz, 2H, C_6H_4), 7.20 (m, 3H, Ph) and 7.80 (m, 2H, Ph). ^{11}B-NMR ($CDCl_3$): $\delta = -5.3, -10.9, -13.0, -14.3, -19.0$ (Os–B) (5:2:1:1:1). IR (KBr): $\nu_{B-H} = 2580$ cm^{-1}. EI-MS (70 eV): 633 [M^+, 8%], 531 [$M^+ - (PhC{\equiv}CH)$, 100%].

*4.7. Preparation of **9S***

Phenylacetylene (4 mmol; 0.4 ml) was added to the green solution of $Cp^*Rh[S_2C_2(B_{10}H_{10})]$ **1S** (0.4 mmol; 178 mg) in $CHCl_3$ (40 ml) and the mixture was heated under reflux for 2 days. The colour changed to red within the first two hours and then gradually to brown–red. Evaporation of the solvent in vacuo and chromatography on silica gel (Merck, Kieselgel 60) with 2:1 hexane–CH_2Cl_2 as eluent gave a red zone of **5S** (yield, 76.6 mg, 35%) and a green zone of **9S** (1:3 hexane–CH_2Cl_2, yield, 65%). Alternatively, the red solution of **5S** (0.2 mmol; 109.4 mg) in $CHCl_3$ (20 ml) was heated under reflux for 7 h, during which time the colour changed gradually to green. The same work-up procedure as described above gave **5S** (yield, 35 mg, 32%) and **9S** (yield, 43.8 mg, 40%). Recrystallisation from CH_2Cl_2/hexane afforded violet crystals of **9S** (m.p. = 167°C). ^{1}H-NMR (CD_2Cl_2): $\delta = 1.38$ (s, 15H, Cp*), 2.41 (d, $J = 14.7$ Hz, 1H, PhC–CH_2), 2.56 (d, $J = 14.7$ Hz, 1H, PhC–CH_2), 7.00 (m, 2H, Ph), 7.12 (m, 1H, Ph) and 7.30 (m, 2H, Ph). ^{11}B-NMR (CD_2Cl_2): $\delta = 1.6$ (B–CH_2), $-7.1, -8.0, -9.5, -10.9, -14.2$ (1:1:1:5:1:1). ^{103}Rh-NMR (CD_2Cl_2): $\delta = 329 \pm 1$. IR (KBr): 2571, 2580, 2602(ν_{B-H}). EI-MS (70 eV): 547 [M^+, 100%].

*4.8. Preparation of **10S** and **11S***

The solution of either **3S** (88.4 mg, 0.2 mmol) or **4S** (106 mg, 0.2 mmol) and phenylacetylene (0.2 ml, 2 mmol) in $CHCl_3$ (30 ml) was stirred under reflux for 22 h (**10S**) or 36 h (**11S**). The colour changed gradually to brown–red. In the case of ruthenium, the NMR spectra showed the presence of ca. 90% of **10S** and 10% of **7S** in the reaction mixture. The more soluble **7S** was removed from **10S** by washing the solid carefully with CH_2Cl_2. In the case of osmium, a first separation of comparable amounts of **8S** and **11S** was carried out by chromatography on silica gel (Merck, Kieselgel 60). By elution with 1:1 hexane–CH_2Cl_2, an extended zone of **8S** was obtained first, followed by a mixture of **8S** (minor) and **11S** (major). A complete removal of **8S** from **11S** was then achieved in the same way as described above.

10S: Yield, 65.3 mg, 60%; m.p. = 168°C (dec.). ^{1}H-NMR (CD_2Cl_2): $\delta = 1.19$ (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.21 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.62 (s, 3H, CH_3), 2.42 (sept, $J = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.60 (d, $J = 1.65$ Hz, 1H, PhC–CH_2), 4.44 (dd, $J_1 = 1.2$, $J_2 = 6.3$ Hz, 1H, C_6H_4), 4.98 (d, $J = 1.65$ Hz, 1H, PhC–CH_2), 5.51 (dd, $J_1 = 1.5$, $J_2 = 6.3$ Hz, 1H, C_6H_4), 6.37 (dd, $J_1 = 1.5$, $J_2 = 6.3$ Hz, 1H, C_6H_4), 6.45 (dd, $J_1 = 1.2$, $J_2 = 6.3$ Hz, 1H, C_6H_4), 7.14 (m, 1H, Ph), 7.24 (m, 2H, Ph) and 7.59 (m, 2H, Ph). ^{11}B-NMR (CD_2Cl_2): $\delta = -2.8, -4.9, -6.2, -8.7$ (Ru–B), $-9.6, -11.6$ (1:1:3:2:1:2). IR (KBr): 2547, 2568, 2584, 2603(ν_{B-H}). EI-MS (70 ev): 544 [M^+, 20%], 442 [$M^+ - (PhC{\equiv}CH)$, 100%].

11S: yield, 44.3 mg, 35%; m.p. = 196°C (dec.). ^{1}H-NMR (CD_2Cl_2): $\delta = 1.12$ (d, $J = 6.9$ Hz, 3H, $CH(CH_3)_2$), 1.21 (d, $J = 6.9$ Hz, 3H, $CH(CH_3)_2$), 1.80 (s, 3H, CH_3), 2.32 (sp, $J = 6.9$ Hz, 1H, $CH(CH_3)_2$), 3.15 (d, $J = 2.5$ Hz, 1H, PhC–CH_2), 4.72 (dd, $J_1 = 1.1$ Hz, $J_2 = 6.0$ Hz, 1H, C_6H_4), 4.75 (d, $J = 2.5$ Hz, 1H, PhC–CH_2), 5.66 (dd, $J_1 = 1.4$, $J_2 = 6.0$ Hz, 1H, C_6H_4), 6.14 (dd, $J_1 = 1.36$, $J_2 = 6.0$ Hz, 1H, C_6H_4), 6.23 (dd, $J_1 = 1.1$, $J_2 = 6.0$ Hz, 1H, C_6H_4), 7.11 (m, 1H, Ph), 7.25 (m, 2H, Ph) and 7.56 (m, 2H, Ph). ^{11}B-NMR (CD_2Cl_2): $\delta = -2.6, -5.0, -6.0, -6.5, -8.2, -10.3, -11.5, -20.0$ (Os–B) (2:1:2:1:1:2:1). IR (KBr): 2546, 2568, 2585, 2602(ν_{B-H}). EI-MS (70 eV): 633 [M^+, 30%], 531 [$M^+ - (PhC{\equiv}CH)$, 100%].

*4.9. Crystal structures of **5S**, **6Se**, **9S** and **10S***

The reflection intensities were collected on a Siemens P4 diffractometer (Mo–K_α radiation, $\lambda = 71.073$ pm, graphite monochromated). Structure solution and refinement was carried out with the program package SHELXTL-PLUS V.5.1. Measuring 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 have been 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.

*4.9.1. Crystal structure of **5S***

$C_{20}H_{31}B_{10}S_2Rh \cdot 0.3CHCl_3$, red platelet with dimensions $0.30 \times 0.18 \times 0.06$ mm crystallises in the triclinic space group $P\bar{1}$ with the lattice parameters $a = 1112.35(12)$, $b = 1509.78(11)$, $c = 1746.62(12)$ pm, $\alpha = 90.910(6)$, $\beta = 102.405(7)$, $\gamma = 90.522(7)°$, $V = 2864.2(4)$ 10^6 pm^3, $Z = 4$, $\mu = 0.845$ mm^{-1}; 11 712 reflections collected in the range $3° \leq 2\theta \leq 50°$, 10 038 reflections independent, 8109 assigned to be observed [$I > 2\sigma(I)$], full-matrix least-squares refinement against F^2 with 621 parameters converged at R_1/wR_2 values of 0.077/0.207, empirical absorption correction (Ψ-scans) resulted in min./max. transmission factors of 0.3087/0.3747, the max./min. residual electron density was $4.680/-1.822$ 10^{-6} e pm^{-3}.

4.9.2. *Crystal structure of* ***6Se***

$C_{20}H_{31}B_{10}Se_2Ir\cdot 0.5CH_2Cl_2$, irregularly shaped, orange crystal with dimensions $0.25 \times 0.18 \times 0.12$ mm crystallises in the monoclinic space group $P2_1/n$ with the lattice parameters $a = 1510.18(11)$, $b = 1009.66(7)$, $c = 1952.18(19)$ pm, $\beta = 95.023(7)°$, $V = 2965.2(4)$ 10^6 pm^3, $Z = 4$, $\mu = 7.058$ mm^{-1}; 6501 reflections collected in the range $3° \leq 2\theta \leq 50°$, 5176 reflections independent, 4029 assigned to be observed $[I > 2\sigma(I)]$, full-matrix least-squares refinement against F^2 with 325 parameters converged at R_1/wR_2 values of 0.043/0.114; empirical absorption correction (Ψ-scans) resulted in min./max. transmission factors of 0.4095/0.9473, the max./min. residual electron density was $0.204/-1.01$ 10^{-6} e pm^{-3}.

4.9.3. *Crystal structure of* ***9S***

$C_{20}H_{31}B_{10}S_2Rh$, dark red prism of dimensions $0.30 \times 0.18 \times 0.15$ mm crystallises in the triclinic space group $P\bar{1}$ with the lattice parameters $a = 1182.0(3)$, $b = 1344.6(2)$, $c = 1733.5(3)$ pm, $\alpha = 93.154(8)$, $\beta = 105.267(9)$, $\gamma = 103.760(8)°$, $V = 2561.2(8)$ 10^6 pm^3, $Z = 4$, $\mu = 0.839$ mm^{-1}; 13 496 reflections collected in the range $3° \leq 2\theta \leq 55°$, 11 781 reflections independent, 8986 assigned to be observed $[I > 2\sigma(I)]$, full-matrix least-squares refinement against F^2 with 596 parameters converged at R_1/wR_2 values of 0.043/0.105, empirical absorption correction (Ψ-scans) yielded min./max. transmission factors of 0.3534/0.4000, the max./min. residual electron density was $0.669/-1.549$ 10^{-6} e pm^{-3}.

4.9.4. *Crystal structure of* ***10S***

$C_{20}H_{30}B_{10}S_2Ru$, yellow prism of dimensions $0.30 \times 0.15 \times 0.15$ mm crystallises in the orthorhombic space group *Pbca* with the lattice parameters $a = 11.5185(12)$, $b = 1598.38(16)$, $c = 2718.7(3)$ pm, $V = 5005.4(9)$ 10^6 pm^3, $Z = 8$, $\mu = 0.802$ mm^{-1}; 7022 reflections collected in the range $3° \leq 2\theta \leq 55°$, 5757 reflections independent, 3622 assigned to be observed $[I > 2\sigma(I)]$, full-matrix least-squares refinement against F^2 with 299 parameters converged at R_1/wR_2 values of 0.046/0.082; empirical absorption correction (Ψ-scans) yielded min./max. transmission factors of 0.4026/0.4417, the max./min. residual electron density was $0.502/-0.534$ 10^{-6} e pm^{-3}.

5. Supplementary material

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-138360 (**5S**), -138359 (**6Se**), -138362 (**9S**) and -138361 (**10S**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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