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Selective stepwise carborane substitution in B(3,6) positions in Cp*Ir half-sandwich complexes containing a chelating 1,2-dicarba-*closo*-dodecaborane-1,2-dichalcogenolato ligand

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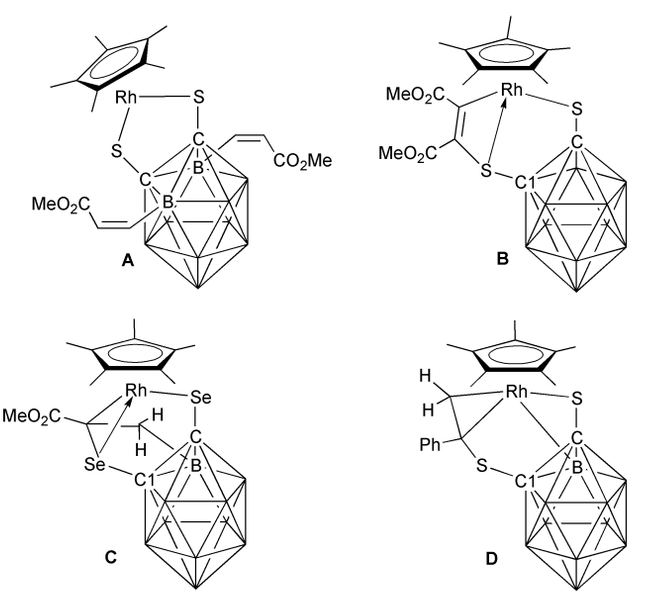
The 16e complexes IrCp*[$E_2C_2(B_{10}H_{10})$] (E = S **1S** or Se **1Se**) react with methyl acetylenecarboxylate, $MeO_2CC{\equiv}CH$, at room temperature to give the 18e complexes **2S**, **3S** and **2Se**, **3Se**, respectively, as mixtures of isomers, in which the alkyne has been inserted into one of the Ir–chalcogen bonds, Ir-induced B–H activation has taken place, and, after transfer of a carborane hydrogen *via* the iridium to the alkyne, an Ir–B bond has been formed. Heating of these mixtures at 110 °C in toluene gives again mixtures of isomers as the 16e complexes **4S**, **5S** and **4Se**, **5Se**, which differ in the configuration of the olefinic substituent at B(3) and could be separated by chromatography. Treatment of these 16e complexes with $MeO_2CC{\equiv}CH$ again produces 18e complexes **6S**–**9S** and **6Se**–**9Se**, respectively, analogous to **2** and **3**, but now with an olefinic substituent at one of the boron atoms (B(3) or B(6)). Heating of these complexes at 110 °C in toluene leads selectively to 16e complexes **10S**, **11S** and **10Se**, **11Se**, **12Se**, in which the carborane is now substituted both in the B(3) and B(6) positions. In the cases of **9S** and **9Se**, the major product upon heating in boiling toluene is another type of complex (**13S** and **13Se**), in which the two former alkyne units are linked by a C–C bond and only one Ir–C σ bond is left. The complexes **3Se**, **4Se**, **7S**, **11Se** and **13Se** were characterized by X-ray structural analysis.

Introduction

The 16e half-sandwich complexes of the type MCp*[E_2C_2-$(B_{10}H_{10})$] (M = Rh or Ir; E = S or Se) are stabilised as monomers by the voluminous pentamethylcyclopentadienyl (Cp*) and 1,2-dicarba-*closo*-dodecarborane-1,2-dichalcogenolato ligands.[1–3] The combination of electron deficiency at the (coordinatively unsaturated) metal centre and reactivity of metal–chalcogen bonds[4,5] renders these complexes interesting candidates for reactions with unsaturated substrates such as alkynes. The incorporation of the 1,2-dithiolato or 1,2-diselenolato structural unit into the bulky *closo*-dicarbadodecaborane ligand protects the inner coordination sphere and makes cycloadditions, which have occasionally been observed at dithiolene ligands,[4,6] impossible.

Furthermore, the B–H activation of the *ortho*-carborane[7] is conceivable if the electron deficient metal atom is located in close proximity to the B–H sites. Thus, selective substitution of the carborane cage may be accomplished in the positions B(3) and/or B(6) which is rather difficult to achieve by other methods.[8] We have already shown, mainly for M = Rh and E = S[9] or Se,[10] that it is possible to obtain such products (see Scheme 1 for selected examples) depending on the reaction conditions.

So far the rhodium complex **A** is the only example of B(3,6) disubstitution, and attempts to change the reaction conditions have led to completely different products.[9b,10] Previous work has indicated[9b] that the iridium complexes IrCp*[$E_2C_2(B_{10}H_{10})$] **1S** and **1Se** are less reactive than their rhodium analogues. This provides a chance to study the reactions of **1** with alkynes in more detail with respect to isolation and characterisation of intermediates. In this work we report on the reactivity of **1S** and **1Se** towards methyl acetylenecarboxylate, $MeO_2CC{\equiv}CH$. The goal was to characterise initial reaction products, to study their rearrangement in solution, and to find out about potential stepwise substitution of the carborane cage.



Scheme 1 Some examples of structurally characterised complexes from the reactions of RhCp*[$E_2C_2(B_{10}H_{10})$] with alkynes (**A**,[9a] **B**,[9a] **C**,[10] **D**[11]).

Results and discussion

Synthesis

As reported previously,[9,10] both **1S** and **1Se** react with MeO_2-$CC{\equiv}CH$ at room temperature to give mixtures of isomers **2S**, **3S**

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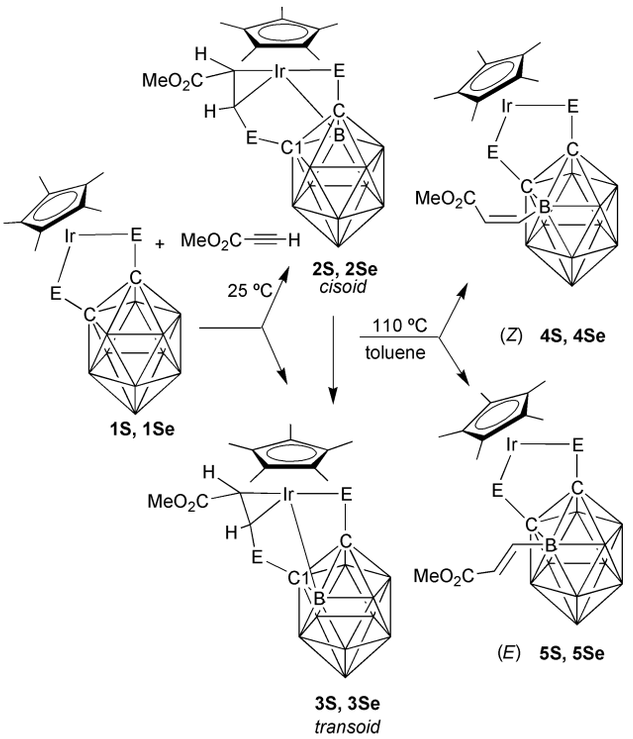
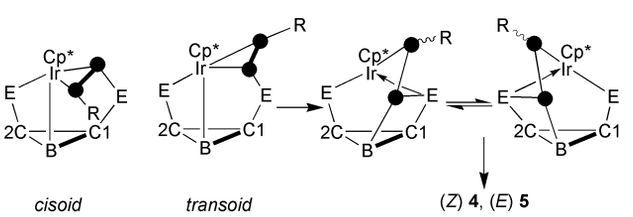


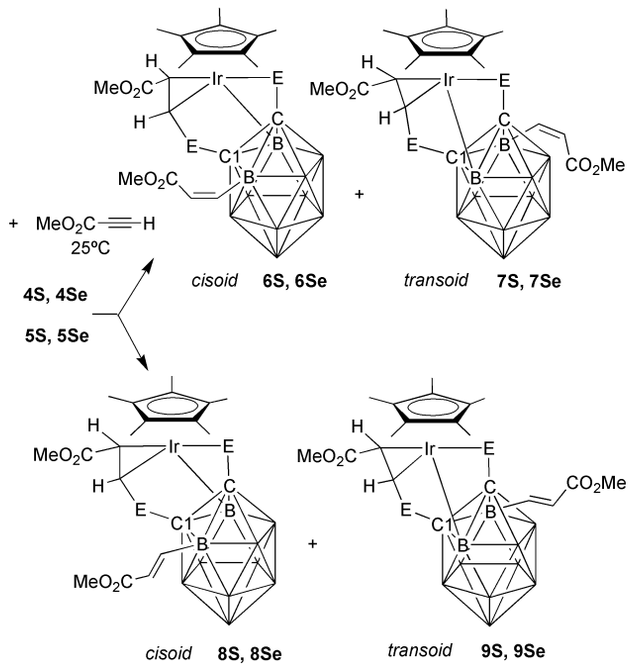
Scheme 2 Reactions of the 16e iridium complexes **1S** and **1Se** with methyl acetylenecarboxylate at room temperature, and their transformation upon heating in boiling toluene.



Scheme 3 Looking at the C(1)C(2)B triangular face of the carborane, the C(1)–B bond and the η^2-ECHCHR units (R = CO_2Me) are arranged either *cisoid* or *transoid*; the rearrangement of the *transoid* species *via* an 18e intermediate to the 16e complex **4** or **5** is proposed.

and **2Se**, **3Se** (Scheme 2). NMR spectra suggest that the complexes **2** and **3** differ in their respective orientation of the η^2-(E)CH=CH and the B–C(1) bonds in the coordination sphere of the metal, **2** possessing the *cisoid* and **3** the *transoid* orientations of these bonds (Scheme 3). We have now obtained single crystals of the *transoid* complex **3Se**, and the results of the X-ray structural analysis (*vide infra*) confirm that the structure in the solid state is in agreement with that in solution which had been proposed only on the basis of NMR data.[10] Apparently, the compounds **2** in solution slowly rearrange into **3**.

Heating mixtures of **2** and **3**, in the absence of the alkyne, gives mixtures of the 16e complexes **4S**, **5S** and **4Se**, **5Se**, in which the carborane cages are now substituted selectively in the B(3) position; however, the olefinic substituent possesses *Z* configuration in **4** and *E* configuration in **5**. Separation by column chromatography affords all four complexes as pure compounds, and the molecular structure of **4Se** could be established by an X-ray analysis. In the *cisoid* structures **2** the transfer of the CH=CHCO$_2$Me unit to give **4** or **5** cannot be favourable, and the formation of complexes of the type **C** or **D** (Scheme 1) would be more likely. In contrast, in the *transoid* arrangement **3**, the reactive centres (Ir–B bond and ECH= unit) are already in close neighbourhood. By transforming the Ir–B into the Ir–C bond, the chalcogen atom can coordinate to iridium and an Ir–C σ bond remains in the 18e complex (Scheme 3). This intermediate is not observed since it rearranges to the 16e complex **4** or **5**.



Scheme 4 Reactions of the 16e iridium complexes **4S**, **4Se**, **5S**, **5Se** with methyl acetylenecarboxylate at room temperature.

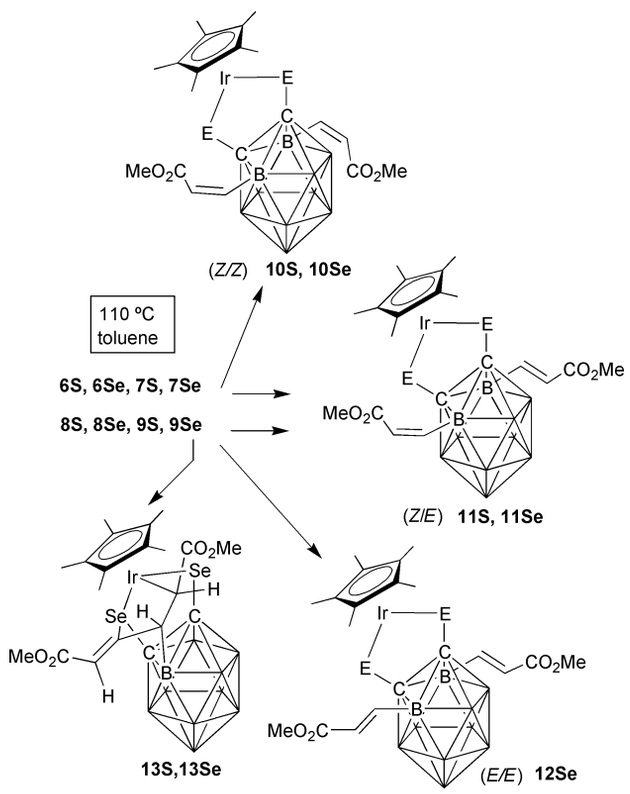
The 16e complexes **4** and **5** are able to react with a second equivalent of MeO$_2$CC≡CH (Scheme 4). As in the case of formation of **2** and **3**, these reactions proceed smoothly at room temperature and lead to eight complexes as mixtures owing to *cisoid* (**6S**, **6Se**, **8S**, **8Se**) and *transoid* (**7S**, **7Se**, **9S**, **9Se**) arrangements, starting from the *Z* (gives **6**, **7**) or from the *E* configuration (gives **8**, **9**). The isomer **7S** (X-ray analysis) was obtained in a pure state, as was **9Se**, and almost pure samples of **7Se** could be isolated.

The next step aims for the second boron substitution of the carborane cage by heating the complexes **6**, **7** or **8**, **9** at 110 °C in toluene (Scheme 5). In the cases of the sulfur complexes **6S**, **7S** a mixture is formed, where the two B(3) and B(6) substituents have *Z* configuration (**10S**) or *Z* and *E* configuration (**11S**). Starting from **8S**, **9S**, again the formation of **11S** is observed along with **13S**. The complex **12S** was neither isolated nor detected by NMR. The selenium derivatives **10Se**, **11Se**, **12Se** are formed, of which **11Se** and **12Se** could be obtained pure, and the proposed structure of **11Se** was confirmed by an X-ray structural analysis (*vide infra*). As in the case of the sulfur derivative **9S** (precursor of **13S**), heating of the selenium analogue **9Se** leads to the complex **13Se** as the main product. In both **13S** and **13Se**, only one of the boron atoms of the carborane cage is substituted, and two former alkyne units are linked by a C–C bond. Although several alternatives could be proposed for the molecular structures of **13** on the basis of the NMR spectra in solution, these data are consistent with the direct structural information for the solid state obtained by X-ray analysis of **13Se** (*vide infra*).

In comparison with previous studies of the rhodium analogues of **1**, the iridium complexes **1S** and **1Se** behave differently. In the case of the reaction of RhCp*[$S_2C_2(B_{10}H_{10})$] with MeO$_2$CC≡CH in boiling chloroform the complex **A** (Scheme 1), analogous to **10S**, was obtained selectively in high yield.[9] The selenium complex RhCp*[$Se_2C_2(B_{10}H_{10})$] reacted with MeO$_2$CC≡CH quite differently, and **C** (Scheme 1) was one of the final products.[10] When the reactions of the rhodium complexes with MeO$_2$CC≡CH were carried out in toluene, catalysed cyclo-trimerisation of the alkyne occurred at 70 °C.[12] Apparently there is a fine balance of bond strengths and kinetic effects which controls the interplay between 16e and 18e complexes. Catalytic effects appear to be almost absent (see

Table 1 ^{13}C and ^{77}Se NMR data

	δ ^{13}C								
	$C_2B_{10}H_{10}$	Cp*	C=	C–B(br)	C–E	C–Ir	C=O	MeO	δ ^{77}Se
4S	93.6	10.1, 91.9	132.8	137.6	—	—	166.8	51.0	—
4Se	75.2	10.6, 90.8	132.6	138.9	—	—	166.9	51.0	817.1
5S	93.6	10.0, 92.0	133.1	142.1	—	—	166.8	51.5	—
5Se	74.7	10.5, 90.9	133.1	142.5	—	—	166.7	51.5	810.8
6S	95.3, 98.0	8.7, 103.8	134.6	135.4	58.6	30.2	166.2, 174.0	51.0, 51.5	—
6Se	78.0, 89.6	9.1, 103.3	134.6	137.1	48.7	32.0	166.4, 174.6	51.3, 51.6	354.4, 504.4
7S	102.0, 106.6	8.9, 100.6	134.3	135.5	53.0	49.7	166.0, 174.1	51.1, 51.6	—
7Se	78.5, 97.1	9.0, 100.6	134.5	137.1	47.0	44.1	166.4, 172.3	51.2, 51.5	408.7, 599.7
8S	95.4, 98.8	8.8, 104.0	134.8	138.6	59.2	30.3	166.0, 174.1	51.5, 51.6	—
8Se	77.5, 89.5	9.1, 103.4	134.8	139.3	49.5	32.2	166.1, 174.4	51.6, 51.7	342.9, 505.6
9S	102.8, 106.9	8.9, 100.6	134.5	138.8	53.4	49.8	166.2, 171.6	51.3, 51.6	—
9Se	78.1, 97.1	9.0, 100.7	134.7	139.6	47.1	44.2	166.2, 172.3	51.6, 51.7	400.8, 598.4
10S	94.7	10.1, 92.0	132.2	137.4	—	—	166.9	51.0	—
10Se	78.0	10.5, 91.2	130.6	137.2	—	—	166.9	51.0	761.0
11S	94.5	10.1, 92.1	132.9, 133.0	137.4, 142.8	—	—	166.8, 166.9	51.0, 51.5	—
11Se	77.2	10.5, 91.0	132.7, 132.9	138.8, 144.5	—	—	166.7, 166.9	51.0, 51.5	765.0
13S	87.3, 94.7	8.2, 93.0	108.6	42.6	166.6	18.1	165.6, 181.5	50.2, 51.8	—
13Se	69.8, 77.4	8.8, 92.4	109.2	45.7	173.7	16.5	165.7, 178.6	50.4, 52.3	375.4, 641.6



Scheme 5 Rearrangement of the 18e iridium complexes into 16e complexes bearing substituents in 3,6 positions (**10**, **11**, **12**), and into the novel type of complex **13**.

Experimental section) in the case of the iridium complexes **1S** and **1Se**, whereas they become dominant in the rhodium analogues.

NMR spectroscopic results

All NMR spectroscopic data support the proposed molecular structures, and relevant ^{13}C and ^{77}Se NMR data of the complexes **4**–**13** are given in Table 1.

The ^1H NMR spectra are simple, showing singlets (Cp* and OMe groups) or doublets owing to $^3J(^1H,^1H)$ across the C=C bond, where the *trans* coupling (*E* configuration) is typically larger than the *cis* coupling (*Z* configuration). The fairly small value of $^3J(H,H) = 4.3$ Hz in **13Se** can be explained by considering the calculated value of the respective dihedral angle HCCH (69°; from results of the X-ray analysis). The corresponding value $^3J(H,H) = 0.8$ Hz observed for **13S** is even smaller, pointing to a dihedral angle close to 90°. In the case of **13Se** a rather large value $^3J(^{77}Se,^1H) = 15.3$ Hz was found for the coupling across the C=C bond. This value was then used in polarisation transfer experiments in order to assign the ^{77}Se resonances of **13Se**. The carborane cage gives broad, overlapping ^1H resonances which were not assigned. ^1H-{^{11}B} broad band decoupling confirms that the number of ^1H(carborane) resonances is in agreement with the number of ^{11}B(H) nuclei.

The ^{11}B NMR spectra show broad, overlapping resonances in the region typical of C-substituted carboranes.[13] The presence of the Ir–B bond is indicated in each case by a signal shifted to high field which is readily identified in the ^1H coupled ^{11}B NMR spectrum as a singlet.[14] Similarly, the ^{11}B(3,6) NMR signals of the 16e complexes **4**, **5**, **10**–**12**, and of the 18e complex **13Se** appear as broad singlets at low field, not well resolved from the other ^{11}B(carborane) signals.

Together with the ^1H NMR spectra, the ^{13}C NMR spectra provide convincing structural evidence, confirmed in ambiguous cases by 2-D $^{13}C/^1H$ HETCOR experiments. In the cases of **4**, **5**, **10**–**12** and **13Se**, the broad ^{13}C resonances[15] of the substituted ^{13}C nuclei linked directly to B(3) or B(6) are indicative, and the appearance of the slightly broadened ^{13}C(1,2) NMR signals of the carborane confirms the assignment. An inspection of the data in Table 1 reveals that *cisoid* and *transoid* complexes are readily distinguished on the basis of their ^{13}C NMR data. The ^{13}C NMR spectrum of **13Se** (Fig. 1) was recorded to obtain a signal to noise ratio which would allow detection of ^{77}Se satellites for most of the ^{13}C resonances. This showed that only one ^{13}C nucleus of the former alkyne units had ^{77}Se satellites, $^1J(^{77}Se,^{13}C) = 78.0$ Hz, consistent with the solid state structure.

The ^{77}Se NMR spectra[16] were recorded for all examples studied (Fig. 2). For the 16e complexes, similar to the starting complex **1Se** (δ ^{77}Se 855.5), the ^{77}Se NMR signal appeared at rather low field in each case. For the 18e complexes, always two ^{77}Se NMR signals were observed, one of which, that for Se(2), appeared in the vicinity of the signal for $IrCp^*(PMe_3)$-$[Se_2C_2(B_{10}H_{10})]$ (δ ^{77}Se 363.4), with the other one for Se(1) at lower field. The deshielding in the *transoid* complexes is always greater than in the *cisoid* complexes; the same trend is apparent in the ^{13}C NMR data (Table 1).

Dynamic broadening of ^1H, ^{13}C and ^{77}Se resonance signals was observed in the cases of **10Se** and **11Se**. Apparently, there is hindered rotation about the B–C bond to the olefinic substituent with *Z* configuration. In solution at low temperature, the

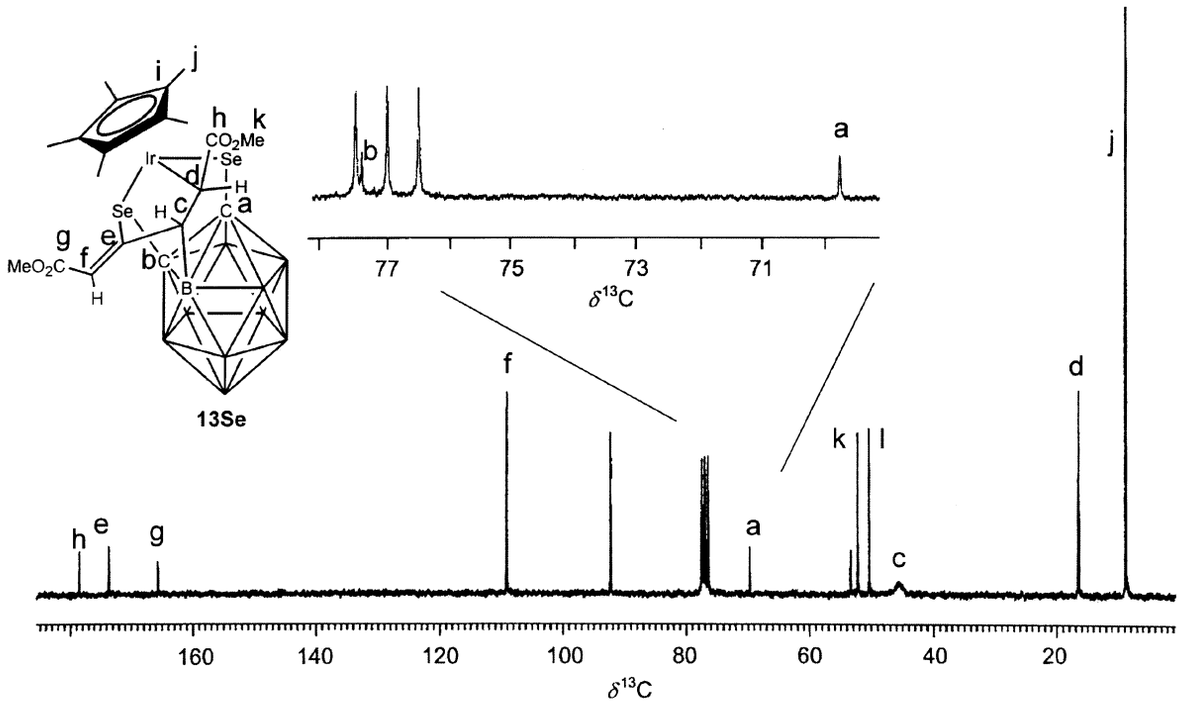


Fig. 1 62.9 MHz ^{13}C-{^{1}H} NMR spectrum of the iridium complex **13Se**. Note the broad ^{13}C(c) resonance signal typical of a carbon atom linked to a three-coordinate boron atom; the carborane ^{13}C signals are less broadened since the scalar ^{11}B–^{13}C couplings in 2e/3c (2 electron/3 centre) bonds are significantly reduced when compared with scalar ^{13}C(*exo*)–^{11}B coupling in a 2e/2c bond.

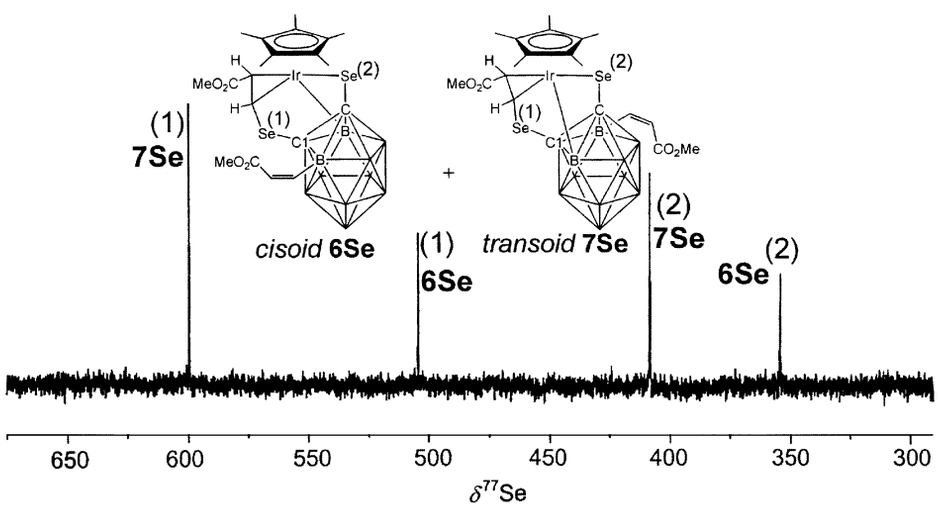


Fig. 2 95.4 MHz ^{77}Se-{^{1}H} NMR spectrum of a reaction solution containing a mixture of the *cisoid* complex **6Se** and the *transoid* complex **7Se**.

conformation of the *Z*-CH=C(H)CO_2Me unit with respect to the planar C(1)C(2)Se(2)IrSe(1) ring is fixed with respect to the NMR timescale, and it is assumed to be comparable to the conformation shown in the molecular structure of **11Se** (Fig. 5). At room temperature or above faster rotation takes place, leading to extensive broadening of the ^{77}Se NMR signals (**11Se**: $h_{1/2} = 1700 \pm 50$ Hz at 25 °C and 90 ± 5 Hz at −30 °C), and also to broadening of all NMR signals of the *Z*-CH=C(H)CO_2Me unit. This behaviour was not found for the *E*-CH=C(H)CO_2Me units in **11Se** or in **12Se**, which can be attributed to less steric hindrance for rotation about the B–C= bond. Interestingly, it was also not observed in the cases of the sulfur complexes **10S** or **11S** or the rhodium analogue of **10S**.[9a]

Crystal structure analyses

The molecular structures of the four selenium complexes **3Se**, **4Se**, **11Se** and **13Se** are shown in Figs. 3, 4, 5, 6 and that of the sulfur complex **7S** in Fig. 7. Selected bond lengths and angles are given in the legends. The *transoid* structure of **3Se** (Fig. 3) is related to that of the product of the reaction of PhC≡CH with Ru(η^6-*p*-$MeC_6H_4Pr^i$)[$S_2C_2(B_{10}H_{10})$],[11] except for the arrangement of the substituents at the C=C double bond coordinated to ruthenium or iridium (in **3Se**, SeCH=C(H)-CO_2Me; in the previous work,[11] SCPh=CH_2). Apparently, these differences cause marked distortions (*e.g.* C(1)–C(2) 178.4 pm) in the geometry of the carborane cage of the ruthenium complex[11] which are not present in the iridium compound **3Se**. Thus, C(1)–C(2) 171.5(10) pm in **3Se** is at the long end of the range reported for numerous *ortho*-carboranes.[8] The C(3)–C(4) bond (141.3(9) pm) in **3Se** is elongated when compared with the C=C bond in normal olefins (134 pm). The molecular structure of the 16e complex **4Se** (Fig. 4) is similar to that of **1Se**.[1] There are three independent molecules of **4Se** with almost identical structural parameters in the unit cell (only the data of the molecule containing Ir(1) will be discussed here). The five-membered ring Ir(1)Se(11)C(11)C(12)Se(12) is planar within experimental error (mean deviation from the plane 4.3 pm). The

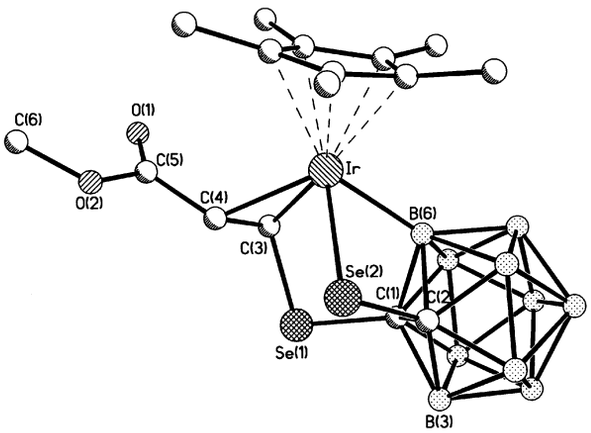


Fig. 3 Molecular structure of **3Se**. Selected bond lengths [pm] and angles [°]: Ir–ring centroid 190.2, Ir–C(3) 211.0(7), Ir–C(4) 217.2(7), Ir–B(6) 216.3(7), Ir–Se(2) 252.68(8), Se(1)–C(1) 189.6(7), Se(1)–C(3) 194.5(8), Se(2)–C(2) 193.4(6), C(1)–C(2) 171.5(10), C(3)–C(4) 141.3(9), C(1)–B(3) 171.3(12), C(1)–B(6) 174.9(11), C(2)–B(3) 173.4(11), C(2)–B(6) 171.5(10); C(3)IrB(6) 84.0(3), C(3)IrC(4) 38.5(3), B(6)IrC(4) 115.5(3), C(3)IrSe(2) 93.3(2), B(6)IrSe(2) 70.7(2), C(4)IrSe(2) 93.8(2), C(1)Se(1)C(3) 95.8(3), C(2)Se(2)Ir 86.9(2), C(1)C(2)Se(2) 114.2(4), C(2)C(1)Se(1) 119.8(5), C(3)C(4)C(5) 120.0(7).

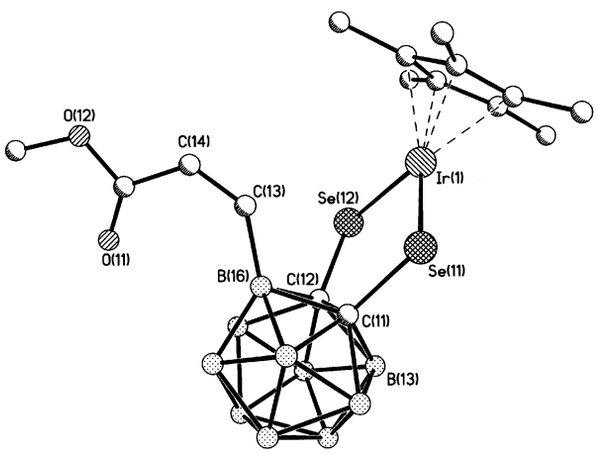


Fig. 4 Molecular structure of **4Se**. Selected bond lengths [pm] and angles [°]: Ir–ring centroid 179.3, 179.7, 179.9, Ir(1)–Se(11) 237.91(18), Ir(1)–Se(12) 236.94(17), Se(11)–C(11) 199.0(14), Se(12)–C(12) 195.7(16), C(11)–C(12) 158(2), C(11)–B(13) 171(3), C(11)–B(16) 174(2), C(12)–B(13) 173(2), C(12)–B(16) 175(2), BN(16)–C(13) 172(2), C(13)–C(14) 134(2); Se(11)Ir(1)Se(12) 94.09(6), C(11)Se(11)Ir(21) 103.6(4), C(12)Se(12)Ir(1), 104.3(4), C(12)C(11)Se(211) 118.1(10), C(11)C(12)Se(12) 119.3(10), C(14)C(13)B(16) 131.6(16).

distance C(11)–C(12) (158.0(20) pm) is short when compared with other data for *ortho*-carboranes.[8] We find similar structural parameters for **11Se** (Fig. 5), as expected for a 16e complex which is also related to the rhodium analogue of **11S**.[9a] The *E* and *Z* configurations of the substituents in B(3)and B(6) positions are obvious. In **11Se** there is again a planar, within the experimental error, IrSe(1)C(1)C(2)Se(2) ring with a fairly short C(1)–C(2) bond length (162.0(7) pm) as well as short bond lengths Ir–Se (236.5 to 238 pm), all characteristic for 16e iridium complexes when compared with 18e complexes (*e.g.*, Ir–Se 246–253 pm). There are only small differences in comparable structural features of **11Se**, when related to **4Se** and **1Se**. Thus, the bond angles Se(1)–Ir–Se(2) 93.6° are almost identical in the three complexes, and this also holds within the experimental error for the bond lengths Ir–Se and Se–C. The different steric repulsion in the *E* and *Z* configurations of the olefinic substituents in **11Se** is reflected by the markedly smaller angle C(4)–C(3)–B(3) (125.6)°) when compared to C(8)–C(7)–B(6) (133.5(6)°; *cf*. 131.6(16)° in **4Se**).

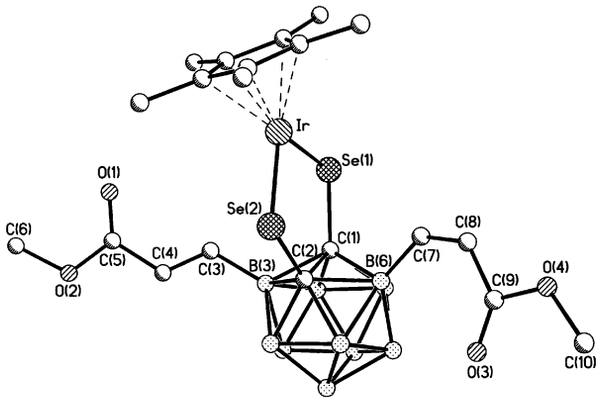


Fig. 5 Molecular structure of **11Se**. Selected bond lengths [pm] and angles [°]: Ir–ring centroid 184.1, Ir–Se(1) 238.97(7), Ir–Se(2) 237.12(9), Se(1)–C(1) 194.6(6), Se(2)–C(2) 194.9(6), C(1)–C(2) 162.0(7), C(1)–B(3) 176.1(8), C(1)–B(6) 179.0(8), C(2)–B(3) 175.6(9), C(2)–B(6) 176.8(8), B(3)–C(3) 155.3(9), B(6)–C(7) 156.0(9), C(3)–C(4) 131.3(8), C(7)–C(8) 133.5(8); Se(1)IrSe(2) 93.63(3), C(1)Se(1)Ir 104.32(16), C(2)Se(2)Ir 104.96(15), C(2)C(1)Se(1) 118.7(4), C(21)C(2)Se(2) 118.0(4), C(4)C(3)B(3) 125.6(6), C(8)C(7)(6) 133.5(6).

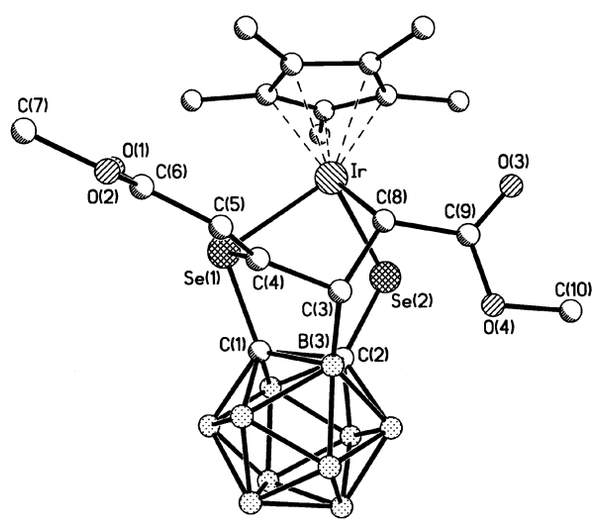


Fig. 6 Molecular structure of **13Se**. Selected bond lengths [pm] and angles [°]: Ir–ring centroid 183.6, Ir–C(8) 214.5(9), Ir–Se(1) 246.17(9), Ir–Se(2) 245.08(11), Se(1)–C(4) 195.2(9), Se(1)–C(1) 196.2(9), Se(2)–C(2) 192.8(9), C(1)–C(2) 167.4(13), C(1)–B(6) 169.5(14), C(1)–B(3) 172.9(13), C(2)–B(3) 174.4(14), C(2)–B(6) 173.7(14), C(3)–C(4) 152.0(13), C(3)–C(8) 155.8(14), C(4)–C(5) 131.0(14), C(5)–C(6) 148.3(15), C(8)–C(9) 151.6(15); C(8)IrSe(1) 85.7(2), C(8)IrSe(2) 85.2(3), Se(1)IrSe(2) 92.16(3), C(4)Se(1)Ir 89.3(3), C(1)Se(1)Ir 103.1(3), C(2)Se(2)Ir 100.9(3), C(4)C(3)C(8) 101.9(7), C(3)C(8)Ir 112.1(6), C(9)C(8)Ir 114.2(7), C(2)C(1)Se(1) 116.5(6), C(1)C(2)Se(2) 119.5(6).

The structure of **13Se** (Fig. 6) is unique so far. The two former alkynes are now linked by the C(3)–C(4) bond, and their origin as alkynes is well disguised. If the triangular CCB face of the carborane is included, a formally pentacyclic framework has been built up opposite to the Cp* ligand at the iridium centre. In agreement with electron counting, the bond distances correspond to those usually found in 18e iridium complexes. None of the 4 five-membered rings in the pentacyclic system is planar. The Se(1) and the CO_2Me group are found in *cis* positions at the C=C bond, consistent with the large value of $^3J(^{77}Se, ^1H)$ (15.3 Hz) found in the ^1H NMR spectra in solution. Although the hydrogen atoms at C(3) and C(8) were not located, the calculated dihedral angle (69°) is in the expected range for a small value of $^3J(^1H,^1H)$ (4.3 Hz).

Complex **7S** (Fig. 7) has the *transoid* arrangement and *Z* configuration of the carborane substituent (typical is the wide bond angle C(8)C(7)B(6) 132.6(8)°). Thus, except for the carborane substitution, the basic structural properties of **7S** are

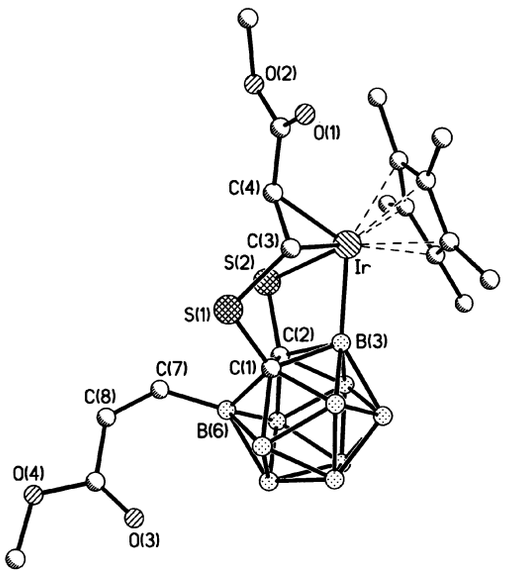


Fig. 7 Molecular structure of **7S**. Selected bond lengths [pm] and angles [°]: Ir–ring centroid 191.1, Ir–S(2) 241.47(19), Ir–B(3) 214.9(8), Ir–C(3) 210.2(7), Ir–C(4) 217.4(7), S(1)–C(1) 176.1(7), S(2)–C(2) 177.7(7), S(1)–C(3) 181.3(7), C(3)–C(4) 143.0(10), C(1)–C(2) 170.8(9), C(1)–B(3) 174.5(10), C(1)–B(6) 175.6(10), C(2)–B(3) 170.2(10), C(2)–B(6) 175.8(11), B(6)–C(7) 156.4(11), C(7)–C(8) 133.8(11); B(3)IrS(2) 70.2(2), C(3)IrC(4) 39.0(3), S(1)C(3)C(4) 113.9(5), C(3)C(4)C(5) 118.3(7), C(1)S(1)C(3) 98.6(3), C(2)S(2)Ir 89.8(2), C(2)C(1)S(1) 117.1, C(1)C(2)S(2) 114.2(4), C(8)C(7)B(6) 132.6(8).

very similar to those already discussed for **3Se**. Even the structural data of both the S(1)–C(3)–C(4) and Se(1)–C(3)–C(4) units coordinated to iridium in **7S** and in **3Se** are almost the same.

Conclusion

The selective stepwise substitution of the *ortho*-carborane cage in B(3,6) positions could be achieved by taking advantage of the slightly reduced reactivity of the iridium complexes **1S** and **1Se** when compared with their rhodium analogues. The formation of isomers with *cisoid* and *transoid* arrangement and Ir–B bonds as intermediates prior to carborane substitution in both steps could be proved unambiguously. All evidence points towards an important role of the *transoid* isomers as the precursors of the B(3,6) substituted 16e complexes. Although the question of the mechanism of the *cisoid*-to-*transoid* rearrangement is not completely settled as yet, a rearrangement of the carborane skeleton appears to be unlikely considering the relatively mild reaction conditions. Instead, we propose that opening of the η^2-C=C coordination to the iridium in the *cisoid* structure (Scheme 3) is followed by E→Ir coordination; opening of this E→Ir bond and restoring the η^2-C=C coordination in the *transoid* isomer (Scheme 3) finishes the isomerisation process. The novel structure of the complex **13Se** indicates that the system responds in an unpredictable manner to apparently minor changes. In contrast with the rhodium analogues where major differences in the reactivity of sulfur and selenium complexes were found, most reactions of the iridium complexes **1S** and **1Se** seem to follow the same pathways.

Experimental

The starting complexes $[IrCp^*Cl_2]_2$[17] and $IrCp^*[E_2C_2(B_{10}H_{10})]$[1–3] **1S** and **1Se** were prepared according to established procedures; *ortho*-carborane, 1,2-$C_2B_{10}H_{12}$, sulfur, selenium and methyl acetylenecarboxylate were used as commercial products. NMR measurements (at ambient temperatures): Bruker ARX 250 and DRX 500 spectrometers (chemical shifts are given with respect to $CHCl_3$–$CDCl_3$ (δ ^{1}H 7.24; δ ^{13}C 77.0), external $Et_2O{\cdot}BF_3$ (δ ^{11}B = 0 for $\Xi(^{11}B)$ = 32.083971 MHz), external Me_2Se (δ ^{77}Se = 0 for $\Xi(^{77}Se)$ = 19.071523 MHz). Mass spectra: Varian MAT CH7, EI-MS (70 eV), direct inlet. IR spectra: Perkin-Elmer 983 G.

Syntheses

4S, 5S and 4Se, 5Se. A yellow solution containing **2S** and **3S** (0.62 g, 1 mmol) or **2Se** and **3Se** (0.71 g, 1 mmol) was kept in boiling toluene (40 ml) for 7 days (S, sulfur complexes) or 3 days (Se, selenium complexes) to give a violet (S) or a green solution (Se). The solvent was removed *in vacuo*, then chromatography on silica gel (Merck, Kieselgel 60) and elution with CH_2Cl_2 gave either **1S** (violet, 53 mg, 10%), **4S**, **5S** and a mixture of carborane-disubstituted products (violet, 35 mg, 5%), or **1Se** (green, 94 mg, 15%), **4Se**, **5Se** and a mixture or carborane-disubstituted products (green, 40 mg, 5%).

4S: violet, 463 mg (75%), mp *ca.* 200 °C. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.87 (s, 15H, Cp*), 3.71 (s, 3H, OMe), 5.57 (d, ^3J(H,H) = 15.2, 1H, =C(B)H), 6.25 (d, ^3J(H,H) = 15.2 Hz, br, 1H, HC=). ^{11}B NMR (160.5 MHz: $CDCl_3$): δ −10.5, −9.2, −8.2, −5.2. EI-MS (70 eV): *m*/*z* 618 (100%, M^+). IR (CsI): 2586 ($\nu_{B–H}$).

4Se: green, 320 mg (45%), mp = 198 °C. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.84 (s, 15H, Cp*), 3.71 (s, 3H, OMe), 5.55 (d, ^3J(H,H) = 15.2, 1H, =C(B)H), 6.20 (d, ^3J(H,H) = 15.2 Hz, br, 1H, HC=). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −8.6, −8.0, −7.0, −5.4. EI-MS (70 eV): *m*/*z* 712 (100%, M^+). IR (CsI): 2584 ($\nu_{B–H}$).

5S: violet, 31 mg (5%), mp = 188 °C. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.88 (s, 15H, Cp*), 3.71 (s, 3H, OMe), 6.35 (d, ^3J(H,H) = 17.8, br, 1H, HC=), 6.47 (d, ^3J(H,H) = 17.8 Hz, 1H, =C(B)H). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −10.6, −8.8, −5.3. EI-MS (70 eV): *m*/*z* 618 (100%, M^+). IR (CsI): 2586 ($\nu_{B–H}$).

5Se: green, 249 mg (35%), mp = 212 °C. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.85 (s, 15H, Cp*), 3.70 (s, 3H, OMe), 6.34 (d, ^3J(H,H) = 17.8, br, 1H, HC=), 6.45 (d, ^3J(H,H) = 17.8 Hz, 1H, =C(B)H). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −9.0, −7.8. EI-MS (70 eV): *m*/*z* 712 (100%, M^+). IR (CsI): 2583 ($\nu_{B–H}$).

6S/7S and 8S/9S. Methyl acetylenecarboxylate (0.85 mL; 10 mmol) was added to a violet solution of **4S** or **5S** (0.62 g, 1 mmol) in CH_2Cl_2 (30 ml) and the mixture was stirred at r.t. for 7 d. After removal of the solvent, chromatography with elution by CH_2Cl_2 gave unchanged **4S** (111 mg, 18%) and a 1 : 1 mixture of **6S/7S** (491 mg, 70%) or unchanged **5S** (197 mg, 32%) and a 1 : 2.5 mixture of **8S/9S** (407 mg, 58%). Elution with CH_2Cl_2–THF (10 : 1) produced a red zone which contained trimethyl 1,3,5-benzenetricarboxylate (0.25–0.34 g), the cyclotrimerisation product from catalysis.

When the reaction mixtures were prepared in $CHCl_3$ and heated for 2 days at 62 °C, a complete transformation of *cisoid* (**6S**, **8S**) to *transoid* (**7S**, **9S**) was achieved, and the pure *transoid* isomers could be isolated; however, under these conditions the reaction mixtures also contained 3–20% of the final carborane-disubstituted complexes.

6S: yellow. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.78 (s, 15H, Cp*), 3.66 (s, 3H, OMe), 3.70 (s, 3H, OMe), 5.32 (d, ^3J(H,H) = 8.3, 1H, CH; another doublet is hidden by the OMe signals), 5.91 (d, ^3J(H,H) = 14.8, 1H, =C(B)H), 6.41 (d, ^3J(H,H) = 14.8 Hz, br, 1H, HC=). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −26.9 (B–Ir) (all other signals overlap with those of the *transoid* isomer). EI-MS (70 eV): *m*/*z* 702 (100%, M^+).

7S: yellow, mp = 189 °C. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.80 (s, 15H, Cp*), 3.66 (s, 3H, OMe), 3.71 (s, 3H, OMe), 4.26 (d, ^3J(H,H) = 8.6, 1H, CH), 5.21 (d, ^3J(H,H) = 8.6, 1H, CH), 5.64 (d, ^3J(H,H) = 14.7, 1H, =C(B)H), 6.32 (d, ^3J(H,H) = 14.7 Hz, br, 1H, HC=). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −23.5 (B–Ir), −12.2, −11.0, −9.8, −7.7, −4.6. EI-MS (70 eV): *m*/*z* 702 (100%, M^+). IR (CsI): 2580 ($\nu_{B–H}$).

8S: yellow. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.80 (s, 15H, Cp*), 3.71 (s, 3H, OMe), 3.72 (s, 3H, OMe), 5.37 (d,

Table 2 Crystal structure data (at 23 °C) for complexes **3Se, 4Se, 11Se, 13Se** and **7S**

	3Se	**4Se**	**11Se**	**13Se**	**7S**
Formula	$C_{16}H_{29}B_{10}IrO_2Se_2$	$C_{16}H_{29}B_{10}IrO_2Se_2$	$C_{20}H_{33}B_{10}IrO_4Se_2$	$C_{20}H_{33}B_{10}IrO_4Se_2$	$C_{20}H_{33}B_{10}IrO_4S_2$
Crystal	Orange prism	Black prism	Dark red platelet	Orange platelet	Orange prism
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a/pm	2222.2(4)	2710.4(5)	1153.9(2)	1103.20(9)	1166.95(16)
b/pm	1591.3(3)	1557.2(3)	1851.6(4)	1189.63(11)	1638.27(14)
c/pm	1462.8(3)	1939.3(4)	1498.9(3)	1270.22(11)	1465.31(15)
α/°				67.680(5)	
β/°	108.50(3)	100.74(3)	108.81(3)	70.311(6)	93.620(8)
γ/°				71.103(8)	
V/10^6 Å^3	4905.4(17)	8042(3)	3031.3(10)	1414.8(2)	2795.8(5)
Z	8	12	4	2	4
μ/mm^{-1}	8.424	7.708	6.831	7.318	4.952
Reflections collected	18349	53599	22019	5439	13245
Independent reflections	4399	15369	5573	4661	6396
Absorption correction	Numerical	Numerical	Numerical	Empirical (Ψ scans)	Empirical (Ψ scans)
Refined parameters	280	839	334	335	335
$wR2/R1$ values ($I > 2\sigma(I)$)	0.088/0.035	0.151/0.058	0.074/0.031	0.109/0.043	0.111/0.044

^3J(H,H) = 8.4, 1H, CH; another doublet is hidden by the OMe signals), 6.37 (d, ^3J(H,H) = 17.9, br, H, HC=), 6.82 (d, ^3J(H,H) = 17.9 Hz, 1H, =C(B)H). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −26.6 (B–Ir) (all other signals overlap with those of the *transoid* complex). EI-MS (70 eV): *m*/*z* 702 (100%, M^+).

9S: yellow, mp = 176 °C (decomp.). ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.83 (s, 15H, Cp*), 3.70 (s, 3H, OMe), 3.74 (s, 3H, OMe), 4.34 (d, ^3J(H,H) = 8.6, 1H, CH), 5.25 (d, ^3J(H,H) = 8.6, 1H, CH), 6.33 (d, ^3J(H,H) = 17.8, br, 1H, HC=), 6.64 (d, ^3J(H,H) = 17.8 Hz, 1H, =C(B)H). ^{11}B NMR (160.5 MHz: $CDCl_3$): δ −23.3 (Ir–B), −12.4, −11.0, −10.2, −7.3, −4.7. EI-MS (70 eV): *m*/*z* 702 (100%, M^+). IR (CsI): 2581 (ν_{B-H}).

6Se/7Se and 8Se/9Se. Methyl acetylenecarboxylate (0.85 mL; 10 mmol) was added to a green solution of **4Se** and **5Se** (0.71 g; 1 mmol) in CH_2Cl_2 (30 ml), and the mixture was stirred at room temperature for 24 hours during which time it changed from green to red. After removing the solvent *in vacuo*, chromatography on silica gel including elution with CH_2Cl_2 gave a mixture of 1 : 1 **6Se/7Se** (0.73 g, 91%) or of 1 : 2.5 **8Se/9Se** (0.68 g, 86%); elution with CH_2Cl_2–THF (10 : 1) gave a red zone which contained trimethyl 1,3,5-benzenetricarboxylate (0.4–0.6 g) as a result of catalysed cyclo-trimerisation. When the reaction mixtures were prepared in $CHCl_3$, heating at 62 °C for 1 or 2 days induced complete transformation of the *cisoid* **6Se**, **8Se** into the *transoid* complexes **7Se**, **9Se**, respectively

6Se: yellow. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.85 (s, 15H, Cp*), 3.72 (s, 3H, OMe), 3.74 (d, ^3J(H,H) = 8.7, 1H, CH), 3.75 (s, 3H, OMe), 5.43 (d, ^3J(H,H) = 8.7, 1H, CH), 5.91 (d, ^3J(H,H) = 14.7, 1H, =C(B)H), 6.43 (d, ^3J(H,H) = 14.7 Hz, br, 1H, HC=). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −24.6 (B–Ir) (all other signals overlap with those of the *transoid* isomer). EI-MS (70 eV): *m*/*z* 796 (100%, M^+).

7Se, yellow, mp = 145 °C (decomp.). ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.87 (s, 15H, Cp*), 3.71 (s, 3H, OMe), 3.74 (s, 3H, OMe), 4.69 (d, ^3J(H,H) = 9.0, 1H, CH), 5.18 (d, ^3J(H,H) = 9.0, 1H, C(Se)H), 5.70 (d, ^3J(H,H) = 14.7, 1H, =C(B)H), 6.36 (d, ^3J(H,H) = 14.7 Hz, br, 1H, HC=). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −21.2 (B–Ir), −10.4, −9.0, −6.3, −3.3. EI-MS (70 eV): *m*/*z* 796 (100%, M^+). IR (CsI): 2580 (ν_{B-H}).

8Se: yellow. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.85 (s, 15H, Cp*), 3.73 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.75 (d, ^3J(H,H) = 8.7, 1H, CH), 5.45 (d, ^3J(H,H) = 8.7, 1H, CH), 6.39 (d, ^3J(H,H) = 17.8, br, 1H, HC=), 6.81 (d, ^3J(H,H) = 17.8 Hz, 1H, =C(B)H). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −24.7 (B–Ir) (all other signals overlap with those of the *transoid* isomer). EI-MS (70 eV): *m*/*z* 796 (100%, M^+).

9Se: yellow, mp = 140 °C (decomp.). ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.87 (s, 15H, Cp*), 3.72 (s, 3H, OMe), 3.74 (s, 3H, OMe), 4.73 (d, ^3J(H,H) = 9.0, 1H, CH), 5.18 (d, ^3J(H,H) = 8.6, 1H, CH), 6.37 (d, ^3J(H,H) = 17.8, br, 1H, HC=), 6.65 (d, ^3J(H,H) = 17.8 Hz, 1H, =C(B)H). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −21.0 (B–Ir), −10.8, −9.2, −6.0, −3.5. EI-MS (70 eV): *m*/*z* 796 (100%, M^+). IR (CsI): 2580 (ν_{B-H}).

10S, 11S and 10Se, 11Se. Yellow solutions of either **6S/7S** (351 mg; 0.5 mmol) or **6Se/7Se** (398 mg; 0.5 mmol) in toluene (30 ml) were heated for 3 days at 110 °C, by which time they had changed to violet (S) or green (Se). After the solvent had been removed *in vacuo*, chromatography on silica gel and elution with CH_2Cl_2 afforded either **10S** and **11S** or **4Se** (71 mg, 20%), **10Se** and **11Se**.

10S: violet, yield 297 mg, 84%, mp = 220 °C. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.88 (s, 15H, Cp*), 3.71 (s, 6H, OMe), 5.57 (d, ^3J(H,H) = 15.2, 2H, =C(B)H), 6.22 (d, ^3J(H,H) = 15.2 Hz, br, 2H, HC=). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −10.7, −8.6 (strong overlap of ^{11}B NMR signals). EI-MS (70 eV): *m*/*z* 702 (100%, M^+). IR (CsI): 2583 (ν_{B-H}).

10Se: green, yield 179 mg, 45%, mp = 203 °C. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.85 (s, 15H, Cp*), 3.72 (s, 6H, OMe), 5.55 (d, ^3J(H,H) = 15.1, 2H, =C(B)H), 6.14 (d, ^3J(H,H) = 15.1 Hz, br, 2H, HC=). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −8.1 (strong overlap of ^{11}B NMR signals). EI-MS (70 eV): *m*/*z* 796 (100%, M^+). IR (CsI): 2583 (ν_{B-H}).

11S: violet, yield 10.8 mg, 3%, mp = 214 °C. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.89 (s, 15H, Cp*), 3.70 (s, 3H, OMe), 3.72 (s, 3H, OMe), 5.57 (d, ^3J(H,H) = 15.2, 1H, =C(B)H), 6.25 (d, ^3J(H,H) = 15.2, br, 1H, HC=), 6.34 (d, ^3J(H,H)) = 17.9, br, 1H, HC=), 6.44 (d, ^3J(H,H) = 17.9 Hz, 1H, =C(B)H). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −10.8, −8.6 (strong overlap of ^{11}B NMR signals). EI-MS (70 eV): *m*/*z* 702 (100%, M^+). IR (CsI): 2584 (ν_{B-H}).

11Se: green, yield 119 mg, 30%, mp = 196 °C. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.85 (s, 15H, Cp*), 3.70 (s, 3H, OMe), 3.72 (s, 3H, OMe), 5.56 (d, ^3J(H,H) = 15.2, 1H, =C(B)H), 6.20 (d, ^3J(H,H) = 15.2, br, 1H, HC=), 6.33 (d, ^3J(H,H) = 17.8, br, 1H, HC=), 6.44 (d, ^3J(H,H) = 17.8 Hz, 1H, =C(B)H).^{11}B NMR (160.5 MHz; $CDCl_3$): δ −8.9, −8.3, −7.8 (strong overlap of ^{11}B NMR signals). EI-MS (70 eV): *m*/*z* 796 (100%, M^+). IR (CsI): 2582 (ν_{B-H}).

13S and 12Se, 13Se. Yellow solutions of **8S/9S** (100 mg, 0.143 mmol) or **8Se/9Se** (398 mg, 0.5 mmol) in toluene (25–30 ml) were heated for 3 days at 110 °C. The solvent was evaporated, and chromatography on silica gel followed by elution with

CH_2Cl_2 afforded in turn **13S** (62 mg, 62%) and **11S** (23.8 mg, 23.8%) or **5Se** (53 mg, 15%), **13Se** (199 mg, 50%), **12Se** (2–3%) and **11Se** (100 mg, 25%). The complex **12S** was not observed.

12Se: violet; it could not be isolated free of **13Se**; therefore, only ^{1}H NMR data are available. ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.85 (s, 15H, Cp*), 3.69 (s, 6H, OMe), 6.33 (d, ^3J(H,H) = 17.9, br, 2H, =CH), 6.42 (d, ^3J(H,H) = 17.9 Hz, 2H, =C(B)H).

13S: orange, mp = 229 °C (decomp.). ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.63 (s, 15H, Cp*), 3.32 (s, br, 1H, HC(B)), 3.36 (d, ^3J(H,H) = 0.8 Hz, 1H, CH), 3.61 (s, 3H, OMe), 3.72 (s, 3H, OMe), 6.02 (s, 1H, HC=). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −10.5, −9.5, −8.0, −5.1. EI-MS (70 eV): *m*/*z* 702 (100%, M^+). IR (CsI): 2580, 2590 ($\nu_{B–H}$).

13Se: orange, mp = 215 °C (decomp.). ^{1}H NMR (250.13 MHz; $CDCl_3$): δ 1.76 (s, 15H, Cp*), 3.23 (d, ^3J(H,H) = 4.3, br, 1H, HC(B)), 3.48 (d, ^3J(H,H) = 4.3 Hz, 1H, CH), 3.59 (s, 3H, OMe), 3.75 (s, 3H, OMe), 5.69 (s, 1H, HC=). ^{11}B NMR (160.5 MHz; $CDCl_3$): δ −11.2, −9.6, −7.8, −6.4, −4.5. EI-MS (70 eV): *m*/*z* 796 (100%, M^+). IR (CsI): 2570, 2585 ($\nu_{B–H}$).

Crystal structure determinations

Experimental data for the X-ray structural analyses are given in Table 2. Those for **3Se**, **4Se**, **11Se** were obtained on a STOE IPDS diffractometer, for **13Se** and **7S** on a Siemens P4, all with graphite monochromated Mo-Kα radiation (λ = 71.073 pm).

CCDC reference numbers 156008–156012.

See http://www.rsc.org/suppdata/dt/b1/b100120p/ for crystallographic data in CIF or other electronic format.

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