The NMR-Spectroscopic and X-ray Crystal-Structural Characterization of Two Cp*Ir Halfsandwich Complexes Containing the 1,2-Dicarba-*closo*-dodecaborane-1,2-diselenolato Ligand

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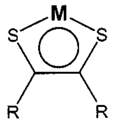
The reaction of $[Cp^*IrCl_2]_2$ with dilithium 1,2-*ortho*-carborane-1,2-diselenolate **3** leads to the green 16-electron diselenolene complex $[Cp^*Ir\{Se_2C_2(B_{10}H_{10})\}]$ (**4**) which takes up two-electron ligands such as trimethylphosphane to give the 18-electron diselenolate derivative $[Cp^*Ir(PMe_3)\{Se_2C_2(B_{10}H_{10})\}]$ (**5**). The molecular structures of **4** and **5** were determined by X-ray crystal structure analysis. The ^{77}Se-nuclear shielding in **4** is lower by almost 500 ppm relative to that in **5**.

The bonding in metallacyclic 16-electron dithiolene complexes of type **1** is a matter of debate.[1] In this context, we have recently reported[2] the X-ray crystal structure analysis of the 1,2-bis(methoxycarbonyl)dithiolene complex **2** in which **M** is the (pentamethylcyclopentadienyl)iridium moiety (Cp*Ir). In order to obtain further structural and spectroscopic information, we have now combined the Cp*Ir half-sandwich fragment with the *ortho*-carboranediselenolate ligand $[H_{10}B_{10}C_2Se_2]^{2-}$ (**3**). Direct structural evidence is expected to correlate in particular with the ^{77}Se-NMR data.



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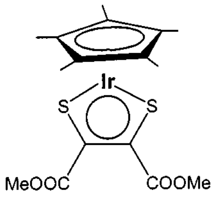

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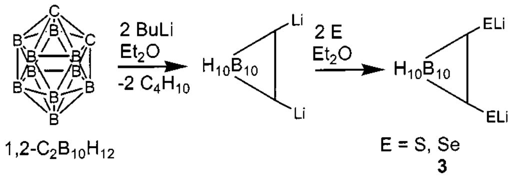
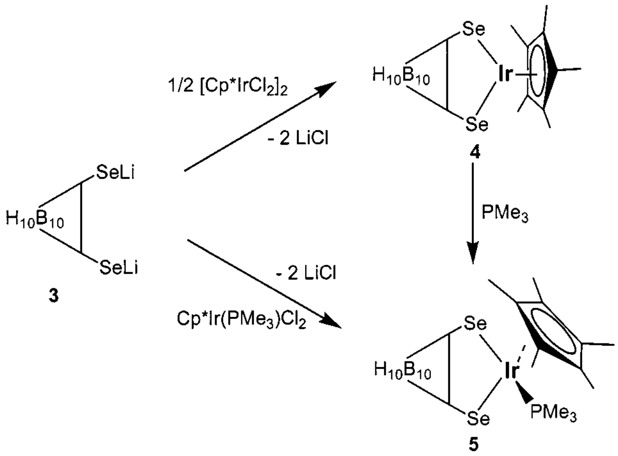
Although complexes containing the *ortho*-carboranedithiolate ligand chelated to Mo,[3] Re,[3] Co,[4] Ni,[4] Pd,[3] Pt,[5] and Au[6] have been prepared starting from the dithiol $H_{10}B_{10}C_2(SH)_2$, the analogous or related diselenolate compounds have not been described. We prepared both *ortho*-carboranedithiolate and -diselenolate complexes from the dilithium dichalcogenates $H_{10}B_{10}C_2(ELi)_2$ [E = S, Se (**3**)] which were obtained in situ by insertion of either sulfur or selenium (1:2) into the dilithiated *ortho*-carborane intermediate (Equation 1).



(1)

As shown in Scheme 1, the dilithium *o*-carboranediselenolate **3** reacts with $[(Cp^*IrCl_2)_2]$ to give the green diselenolene complex **4**, and with $[Cp^*IrCl_2(PMe_3)]$ the yellow diselenolate complex **5**. Compound **4** takes up two-electron ligands L such as L = CO, CN*t*Bu, phosphanes and pyridines. However, attempts to remove PMe_3 from **5** using sulfur were not successful.



Scheme 1

The molecular structures of both **4** and **5** in the crystal were determined by X-ray crystal structure analyses (Figures 1 and 2). The molecule of **4** corresponds to point group symmetry C_{2v} with two perpendicular mirror planes. Addition of PMe_3 to form the 18-electron complex **5** leads to

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C_s symmetry with only one mirror plane left. The iridadiselenolene heterocycle in **4** (which is coplanar with the centers of both the Cp* ring and the *ortho*-dicarbadodecaborane cluster) is bent in **5** with a dihedral angle at the Se····Se vector of 156.1°. Apparently, the ligand L = PMe_3 destroys the pseudoaromatic $IrSe_2C_2$ system in **4**. This is particularly evident from the fact that on going from **4** to **5**, the C(1)−C(2) bond length increases [from 161.2(9) to 165.0(10) pm], the Ir−Se bond lengths grow significantly [from 237.0 (av.) to 247.0 (av.) pm], while the Se−Ir−Se angle decreases [from 93.65(3) to 90.2(1)°]. Compared to **4**, the trimethylphosphane adduct **5** is an ordinary diselenolate chelate complex.

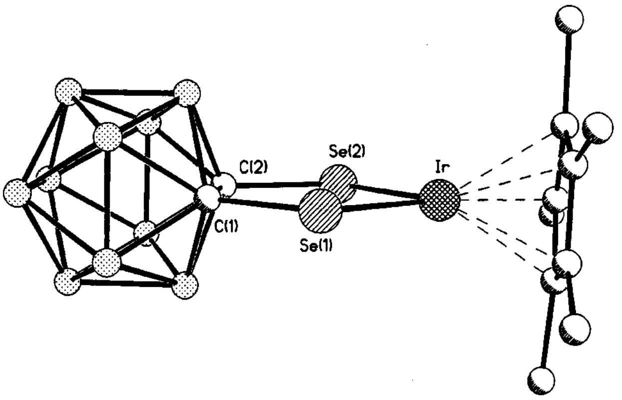

Figure 1. Molecular structure of $[Cp^*Ir(Se_2C_2B_{10}H_{10})]$ (**4**); selected bond lengths [pm] and angles [°]: Ir−Se(1) 237.53(9), Ir−Se(2) 236.56(9), Se(1)−C(1) 194.1(7), Se(2)−C(2) 193.7(7), C(1)−C(2) 161.2(9), Ir−Z(Cp*) 179.4; Se(1)−Ir−Se(2) 93.65(3), Ir−Se(1)−C(1) 104.6(2), Ir−Se(2)−C(2) 105.0(2), Se(1)−C(1)−C(2) 118.5(5), Se(2)−C(2)−C(1) 118.3(5); dihedral angle Se(1)IrSe(2)/Se(1)C(1)C(2)Se(2) 180°

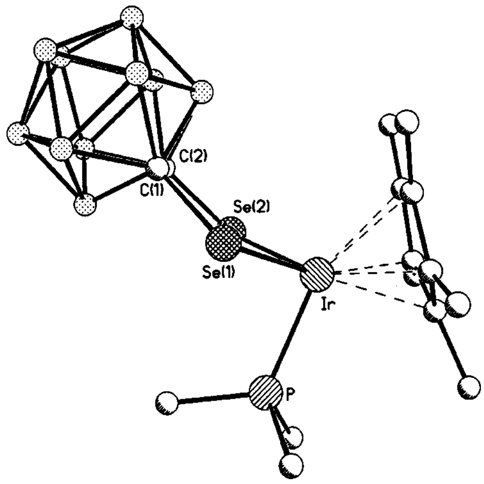

Figure 2. Molecular structure of $[Cp^*Ir(Se_2C_2B_{10}H_{10})(PMe_3)]$ (**5**); selected bond lengths [pm] and angles [°]: Ir−Se(1) 247.3(1), Ir−Se(2) 246.6(2), Ir−P 227.3(2), Se(1)−C(1) 194.9(6), Se(2)−C(2) 195.2(6), C(1)−C(2) 165.0(10), Ir−Z(Cp*) 188.7. Se(1)−Ir−Se(2) 90.2(1), Se(1)−Ir−P 89.1(1), Se(2)−Ir−P 89.1(1), Ir−Se(1)−C(1) 103.1(2), Ir−Se(2)−C(1) 103.9(2), Se(1)−C(1)−C(2) 119.0(4), Se(2)−C(2)−C(1) 117.6(4); dihedral angle Se(1)IrSe(2)/Se(1)C(1)C(2)Se(2) 156.1°

The ^1H-, ^{11}B-, ^{13}C-, ^{31}P-, and ^{77}Se-NMR data (Table 1) of **4** and **5** in solution are in complete agreement with their solid-state structures. In the case of **4**, the C_{2v} symmetry requires four ^{11}B-NMR signals in the intensity ratio of 2:4:2:2, as observed in the 180.5-MHz ^{11}B-NMR spectrum, whereas the C_s symmetry of **5** should give rise to seven ^{11}B-NMR signals in the ratio of 1:1:2:2:1:1:2, of which six are observed. The range of the $\delta^{11}B$-NMR data is similar to that of other 1,2-substituted derivatives of $1,2-C_2B_{10}H_{12}$.[7] There is only one ^{13}C(carborane) signal each for **4** and **5**, as expected, the one of **4** being shifted by 6.8 ppm to lower field relative to that of **5**. The structural changes between **4** and **5** are most strikingly reflected by the ^{77}Se-nuclear deshielding of almost 500 ppm in the 16-electron complex **4** relative to the 18-electron complex **5**. Such a deshielding is typical of ^{77}Se nuclei becoming part of a heteroaromatic system.[8] This effect can be traced to magnetic field induced mixing of electronic ground and energetically low-lying excited states present in such heterocycles. The complexes **4** and **5** are the first examples to compare the influence of electronic structure on ^{77}Se-nuclear shielding in closely related transition metal diselenolene complexes. A similar comparison has been carried out between titanocene diselenolene metallacycles (also 16-electron complexes) and non-cyclic derivatives.[9] However, in these cases the metallacycles are non-planar and the differences in ^{77}Se-nuclear shielding are rather small.

Experimental Section

The starting complexes $[\{Cp^*IrCl_2\}_2]$[10] and $[Cp^*Ir(PMe_3)Cl_2]$[11] were prepared according to established procedures; the *ortho*-carborane $1,2-C_2B_{10}H_{12}$ is commercially available. − NMR measurements: Bruker ARX 250 and DRX 500 spectrometers; chemical shifts are given relative to $CHCl_3/CDCl_3$ (δ^1H = 7.24; $\delta^{13}C$ = 77.0), external Et_2O-BF_3 [$\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 MHz], external 85% aqueous H_3PO_4 [$\delta^{31}P$ = 0 for $\Xi(^{31}P)$ = 40.480747 MHz], external Me_2Se [$\delta^{77}Se$ = 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.

Dilithium 1,2-Dicarba-*closo*-dodecaborane-1,2-diselenolate (3): A solution of $1,2-C_2B_{10}H_{12}$ (0.29 g; 2 mmol) in Et_2O (40 mL) was lithiated by addition of 2.75 mL of 1.6 M butyllithium (4.4 mmol) in hexane. Addition of selenium (0.32 g; 4 mmol) gave a yellow solution of $H_{10}B_{10}C_2(SeLi)_2$ (**3**) in quantitative yield.

Pentamethylcyclopentadienyl-(1,2-dicarba-*closo*-dodecaborane-1,2-diselenolato)iridium ($[Cp^*Ir\{Se_2C_2(B_{10}H_{10})\}]$, 4): A solution of **3** (1 mmol) in Et_2O (60 mL) was added to a solution of $[\{Cp^*IrCl_2\}_2]$ (0.40 g; 0.5 mmol) in THF (60 mL). The colour of the Et_2O/THF solution changed gradually from red to dark green. After 24 h of stirring at ambient temperature, the solvents were evaporated under reduced pressure and the residue chromatographed on silica. Elution with CH_2Cl_2/hexane (5:1) gave a dark green zone which contained 0.57 g (91%) of **4**. Dark green prismatic crystals were grown from CH_2Cl_2/hexane/THF solvent mixtures. − IR (CsI): $\tilde{\nu}$ = 2586 cm^{-1}, ν(B−H). − EI MS (70 eV); *m/z* (%): 628 (100) [M^+], 484 (38) [$M^+ - C_2B_{10}H_{12}$], 143 (100) [$C_2B_{10}H_{11}{}^+$].

(1,2-Dicarba-*closo*-dodecaborane-1,2-diselenolato)(pentamethylcyclopentadienyl)(trimethylphosphane)iridium ($[Cp^*Ir\{Se_2C_2(B_{10}H_{10})\}(PMe_3)]$, 5): Trimethylphosphane (0.10 g, 1.32 mmol) was added to the green solution of **4** (0.30 g; 0.48 mmol) in CH_2Cl_2

Table 1. NMR-spectroscopic data[a] of **4** and **5**

	[Cp*Ir($Se_2C_2B_{10}H_{10}$)] (**4**)	[Cp*Ir($Se_2C_2B_{10}H_{10}$)(PMe_3)] (**5**)
δ^1H	1.83 s Cp*	1.80 (2.1) d Cp*, 1.71 (10.5) d Me_3P
$\delta^{11}B$[b]	−6.0, −7.1, −7.5, −8.4 [ratio 2:4:2:2]	−2.4, −4.2, −6.2, −8.0/−8.4, −10.7 [ratio 1:1:2:4:2]
$\delta^{13}C$	10.6, 90.7 Cp*; 72.8 $C_2B_{10}H_{10}$	9.4 (1.1), 97.0 (3.2) Cp*; 66.1 (3.5) $C_2B_{10}H_{10}$;17.5 (43.3) Me_3P
$\delta^{31}P$	−	−29.3
$\delta^{77}Se$	855.5	363.4 (38.0)[c]

[a] Measured from diluted solutions in $CDCl_3$ at 20 ± 1°C; coupling constants $J(^{31}P,X)$ ($X = {}^1H$, ^{13}C, ^{77}Se), ± 0.5 Hz, are given in parentheses. − [b] The number of boron atoms corresponding to the signals is given in square brackets. − [c] The $\delta^{77}Se$ value depends only slightly on the nature of L in [Cp*Ir($Se_2C_2B_{10}H_{10}$)(L)], e.g. 342.7 (L = CO), 360.0 (L = CN*t*Bu).

(60 mL). The colour turned yellow immediately. The solvent was evaporated, the residue washed with hexane and recrystallized from CH_2Cl_2/hexane mixtures to give 0.31 g (93%) of orange-yellow crystals of **5**. − IR (CsI): $\tilde{\nu} = 2580\ cm^{-1}$, ν(B−H). − EI MS (70 eV); *m*/*z* (%): 620 (43) [$M^+ - PMe_3$], 549 (100) [$M^+ - PMe_3Se$].

X-ray Crystal Structure Analyses of 4 and 5:[12] The intensity data of both compounds were collected with a Siemens P4 diffractometer using Mo-K_α radiation (λ = 71.073 pm, graphite-monochromated). The stability of the primary beam was controlled by monitoring three check reflections every 100 reflections.

4: $C_{12}H_{25}B_{10}IrSe_2$; $M_r = 627.6$; $\rho = 1.954\ g\ cm^{-3}$; black prism of the dimensions 0.12 × 0.15 × 0.20 mm, monoclinic space group $P2_1/c$, with lattice parameters $a = 1478.30(17)$, $b = 1105.57(13)$, $c = 1483.0(2)$ pm, $\beta = 117.990(9)°$ and $Z = 4$; unit cell volume $V = 2140.3(5) \cdot 10^6\ pm^3$, absorption coefficient $\mu = 9.633\ mm^{-1}$. Data collection: Intensity data of 5977 reflections in the range $3° \leq 2\vartheta \leq 55°$ have been measured in the ω-scan mode (measuring temperature 296 K); 4868 ($R_{int} = 0.033$) reflections were unique and assigned to be observed; the data were Lorentz-, polarization-, and absorption-corrected (ψ-scans, min./max. transmission 0.2796/0.4392). Structure solution and refinement: Direct methods (Siemens SHELXTL PLUS v5.01); refinement (against F_o^2) with 222 parameters converged at $R1 = 0.0412$ and $wR2 = 0.0961$ [$I \geq 2\sigma(I)$]; max./min. residual electron density was $1.09/-1.34\ 10^{-6}$ e pm^{-3}.

5: $C_{15}H_{34}B_{10}PIrSe_2$ (CH_2Cl_2); $M_r = 703.6$; $\rho = 1.729\ g\ cm^{-3}$; orange prism with dimensions 0.20 × 0.15 × 0.12 mm, monoclinic space group $C2/c$ with the lattice parameters $a = 24.886(5)$, $b = 17.636(4)$, $c = 14.734(3)$ pm, $\beta = 123.27(3)°$, and $Z = 8$, $V = 5407(2)\ 10^6\ pm^3$, absorption coefficient $\mu = 7.693\ mm^{-1}$. Data collection: Intensity data of 7222 reflections in the range $3° \leq 2\ \vartheta \leq 55°$ have been measured in the ω-scan mode, 6144 reflections were unique ($R_{int} = 0.03$) and 5482 were assigned to be observed [$F_o \geq 2\sigma(F_o)$]; the data were corrected for Lorentz, polarization, and absorption effects (ψ-scans, min./max. transmission 0.4145/0.9647). Structure solution and refinement: Direct methods (Siemens SHELXTL PLUS v4.2), refinement (against F_o) with 277 parameters converged at $R = 0.0383/wR = 0.0325$ [$w^{-1} = \sigma^2(F_o)$]; max./min. residual electron density was $1.22/-2.03 \cdot 10^6\ e \cdot pm^{-3}$.

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[12] 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-112292 (**5**) and -112293 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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