Supporting Information for:

**Low temperature activation of S\textsubscript{8}, Se\textsubscript{8} and α-Te with \([\text{Cp}^{\text{BIG}}\text{Fe(CO)}\text{\textsubscript{2}}]\) radicals**

Sebastian Heinl and Manfred Scheer*

Institute of Inorganic Chemistry, University of Regensburg, 93053 Regensburg, Germany. Fax: +49 941943 4439; Tel: +49 941943 4440; E-mail: manfred.scheer@chemie.uni-regensburg.de

Contents
1. Experimental details
2. NMR spectra
3. Crystallographic details

1. Experimental Details

General Remarks:
All experiments were carried out under an atmosphere of dry argon or nitrogen using glovebox and schlenk techniques. Solvents were purified, dried and degassed prior to use. S\textsubscript{8}, Se\textsubscript{red} and α-Te were available and \([\text{Cp}^{\text{BIG}}\text{Fe(CO)}\text{\textsubscript{2}}]\) was prepared according to literature procedure.\(^{[1]}\) The NMR spectra were measured on a Bruker Avance 300, 400 or 600 spectrometer. FD-MS spectra were measured on a Finnigan MAT 95 mass spectrometer. The elemental analyses were determined on a Vario EL III apparatus. The IR spectra were measured on a VARIAN FTS-800 FT-IR spectrometer.
Synthesis of [(Cp^{BIG}FeCO)]_{2} (2a)

A solution of [Cp^{BIG}Fe(CO)]_{2} (1) (100 mg, 55 µmol) in 5 mL toluene is added to a solution of S8 (14 mg, 55 µmol) in 5 mL toluene and stirred 30 min. The mixture turns into dark red. After removal of the solvent in vacuum, the residue is solved in 3 mL CH2Cl2 and filtered via a cannula. In a thin Schlenk-tube 5 mL CH3CN are layered over the solution. After full diffusion the product crystalizes as red blocks. Yield: 15 mg (15%).

[C_{112}H_{130}Fe_{2}O_{2}S_{4}] calc.: C, 76.95; H, 7.50; S, 7.34. Found: C, 77.23; H, 7.28; S, 8.48. m/z (FD, toluene) 1691.7 (100%, [M – 2 CO]+), 1627.8 (40%, [M – 2 CO - S2]+). IR (toluene, cm⁻¹): νCO 2020 (s), 1980 (s). ¹H NMR (CD2Cl2): δ [ppm] = 0.90 (t, 3JHH = 7.2 Hz, 30H, ^{8}Bu), 1.30 (m, 20H, ^{8}Bu), 1.54 (m, 20H, ^{8}Bu), 2.52 (t, 3JHH = 7.3 Hz, 20H, ^{8}Bu), 6.44 (d, 3JHH = 8.4 Hz, 1H, Ph), 6.53 (d, 3JHH = 7.7 Hz, 1H, Ph), 6.64 (d, 3JHH = 7.7 Hz, 1H, Ph), 6.71 (d, 3JHH = 7.3 Hz, 2H, Ph), 6.88 (m, 35H, Ph). ¹³C{¹H} NMR (CD2Cl2): δ [ppm] = 14.1 (^{8}Bu), 22.7 (^{8}Bu), 33.6 (^{8}Bu), 35.6 (^{8}Bu), 107.2 (Cp), 127.8 (Ph), 128.5 (Ph), 132.8 (Ph), 143.0 (Ph), 210.9 (CO). (Carbonyl C atoms are not detectable)

Synthesis of [(Cp^{BIG}FeCO)]_{2}(µ-Se_{2}) (2b), [(Cp^{BIG}Fe(CO)]_{2}(µ-Se_{2}) (3) and [(Cp^{BIG}FeCO)}{(Cp^{BIG}Fe(CO)]_{2}(µ,η^{2}:1-Se_{2}) (4)

A solution of [Cp^{BIG}Fe(CO)]_{2} (1) (100 mg, 55 µmol) in 5 mL toluene is added to a solution of red selenium (38 mg, 55 µmol) in 5 mL toluene and stirred 30 min. The mixture turns into red/purple. After removal of the solvent in vacuum, the residue is solved in 3 mL CH2Cl2 and filtered via a cannula. In a thin Schlenk-tube 5 mL CH3CN are layered over the solution. After full diffusion the product crystalizes. Sometimes only one distinct, but in other cases multiple compounds are obtained simultaneously.

[(Cp^{BIG}FeCO)]_{2}(µ-Se_{2}) (2b): Yield: 11 mg (10%).
IR (toluene, cm⁻¹): νCO 2016 (s), 1973 (s). ¹H NMR (CD2Cl2): δ [ppm] = 0.90 (br-s, 30H, ^{8}Bu), 1.31 (br-s, 20H, ^{8}Bu), 1.54 (br-s, 20H, ^{8}Bu), 2.52 (br-s, 20H, ^{8}Bu), 6.40 (br-s, 1H, Ph), 6.54 (br-s, 1H, Ph), 6.62 (br-s, 1H, Ph), 6.71 (br-s, 2H, Ph), 6.90 (m, 35H, Ph). ¹³C{¹H} NMR (CD2Cl2): δ [ppm] = 14.1 (^{8}Bu), 22.8 (^{8}Bu), 33.6 (^{8}Bu), 35.6 (^{8}Bu), 106.7 (Cp), 127.9 (Ph), 128.7 (Ph), 132.8 (Ph), 143.1 (Ph), 214.0 (CO). ⁷⁷Se{¹H} NMR (CD2Cl2): δ [ppm] = 1453 (s).

[(Cp^{BIG}Fe(CO)]_{2}(µ-Se_{2}) (3): Yield: 60 mg (59%).
[C_{114}H_{132}Fe_{2}O_{2}Se_{4}] calc.: C, 74.66; H, 7.14. Found: C, 73.89; H, 7.02. m/z (FD, toluene) 1835.0 (100%, [M]+). IR (CH2Cl2, cm⁻¹): νCO 2016 (s), 2003(s), 1969 (s). ¹H NMR (C₆D₆): δ [ppm] = 0.79 (t, 3JHH = 7.3 Hz, 30H, ^{8}Bu), 1.14 (m, 20H, ^{8}Bu), 1.34 (m, 20H, ^{8}Bu), 2.28 (t,
\[J_{HH} = 7.8 \text{ Hz}, \ 20\text{H, }^8\text{Bu}, \ 6.76 \ (d, \ {J_{HH} = 8.2 \text{ Hz}, \ 20\text{H, }\text{Ph}), \ 7.44 \ (d, \ {J_{HH} = 8.2 \text{ Hz}, \ 20\text{H, }\text{Ph}).}\]

\[^{13}\text{C} \ {^1\text{H}}\text{ NMR (C}_6\text{D}_6): \ \delta \ [\text{ppm}] = 14.1 \ (^8\text{Bu}), \ 22.7 \ (^8\text{Bu}), \ 33.1 \ (^8\text{Bu}), \ 35.5 \ (^8\text{Bu}), \ 101.9 \ (\text{Cp}), \ 129.2 \ (\text{Ph}), \ 132.8 \ (\text{Ph}), \ 142.4 \ (\text{Ph}), \ 217.7 \ (\text{CO}), \ \text{one phenyl C atom is superimposed by the solv signal.}\]

\[
[\{\text{Cp}^{\text{BIG}}\text{FeCO}\} \ {\text{Cp}^{\text{BIG}}\text{Fe(CO)}_2\} (\mu,\eta^{2,1}\text{-Se}_2)] (4) \ : \ \text{Yield: 29 mg (27%).}\]

\[\text{[C}_{113}\text{H}_{130}\text{Fe}_2\text{O}_8\text{Se}_2*\text{CH}_2\text{Cl}_2]} \ \text{calc.: C, 72.42; H, 7.04. Found: C, 72.35; H, 7.12.} \ m/z \ (\text{FD, toluene}) 1804.6 \ (100\%, [M]^+)\]. \ \text{IR (toluene, cm}^{-1}) : \nu_{\text{CO}} 2023 \ (s), 1979 \ (s), 1971 \ (s). \ ^1\text{H NMR (CD}_2\text{Cl}_2) : \ \delta \ [\text{ppm}] = 0.91 \ (\text{br-s, 30H, }^8\text{Bu}), 1.31 \ (\text{br-s, 20H, }^8\text{Bu}), 1.53 \ (\text{br-s, 20H, }^8\text{Bu}), 2.52 \ (\text{br-m, 20H, }^8\text{Bu}), 6.88 \ (\text{br-m, 40H, Ph}).\]

\text{Synthesis of } [\{\text{Cp}^{\text{BIG}}\text{FeCO}_2\} (\mu-\text{Te})] (5)

\text{A solution of } [\text{Cp}^{\text{BIG}}\text{Fe(CO)}_2\} (1) \ (50 \ mg, 28 \ \mu\text{mol}) \ in 5 \ mL \ \text{toluene is added powdery Te powder (50 mg, 392 \ \mu\text{mol}). The mixture is put into a ultrasonic bath for 16 h. The remaining Te powder is filtered off via a cannula. The solvent is removed in vacuum and the residue is dissolved in 3 mL CH}_2\text{Cl}_2. \ \text{In a thin Schlenk-tube 5 mL CH}_3\text{CN are layered over the solution. After full diffusion the product crystalizes in dark purple blocks. Yield: 25 mg (47%).}\]

\[\text{[C}_{114}\text{H}_{130}\text{Fe}_2\text{O}_8\text{Te]} \ \text{calc.: C, 75.92; H, 7.26. Found: C, 75.71; H, 7.28.} \ m/z \ (\text{FD, toluene}) 1804.4 \ (100\%, [M]^+)\]. \ \text{IR (toluene, cm}^{-1}) : \nu_{\text{CO}} 2009 \ (s), 1977 \ (s), 1956 \ (s). \ ^1\text{H NMR (CD}_2\text{Cl}_2) : \ \delta \ [\text{ppm}] = 0.91 \ (\text{br-s, 30H, }^8\text{Bu}), 1.32 \ (\text{br-s, 20H, }^8\text{Bu}), 1.55 \ (\text{br-s, 20H, }^8\text{Bu}), 2.53 \ (\text{br-s, 20H, }^8\text{Bu}), 6.87 \ (\text{br-s, 20H, Ph}), 7.06 \ (\text{br-s, 20H, Ph}). \ ^{13}\text{C} \ {^1\text{H}}\text{ NMR (CD}_2\text{Cl}_2) : \ \delta \ [\text{ppm}] = 14.1 \ (^8\text{Bu}), 22.7 \ (^8\text{Bu}), 33.6 \ (^8\text{Bu}), 35.6 \ (^8\text{Bu}), 101.7 \ (\text{Cp}), 127.6 \ (\text{Ph}), 129.2 \ (\text{Ph}), 132.8 \ (\text{Ph}), 142.5 \ (\text{Ph}), 221.8 \ (\text{CO}).\]

\text{Synthesis of } [\{\text{Cp}^{\text{BIG}}\text{Fe}_2(\mu,\eta^{1,1}\text{-Q}_2)(\mu,\eta^{2,2}\text{-Q}_2)] (Q = S \ (6a), \ Se \ (6b))

\text{A solution of } [\text{Cp}^{\text{BIG}}\text{Fe(CO)}_2\} (200 \ mg, 119 \ \mu\text{mol}) \ and \ Q_n (Q_n = S_8: 61 \ mg, 239 \ \mu\text{mol}; Q_n = S_{red}: 151 \ mg, 239 \ \mu\text{mol}) \ in 30 mL \ \text{toluene is refluxed for 1 h. The solvent is removed in vacuum. The residue is purified by column chromatography (10x3 cm, silica, hexane/toluene 3/1). The product is eluted as red band. The solvent is again removed and the crude product is dissolved in 5 mL CH}_2\text{Cl}_2. \ \text{In a thin Schlenk-tube 10 mL CH}_3\text{CN are layered over the solution. After full diffusion the product crystalizes in red blocks.}\]

\[[\{\text{Cp}^{\text{BIG}}\text{Fe}_2(\mu,\eta^{1,1}\text{-S}_2)(\mu,\eta^{2,2}\text{-S}_2)] \ (6a): \ \text{Yield: 160 mg (80%).}\]

\[\text{[C}_{110}\text{H}_{130}\text{Fe}_2\text{S}_4]} \ \text{calc.: C, 78.08; H, 7.74; S, 7.58. Found: C, 78.26; H, 7.72; S, 7.74.} \ m/z \ (\text{FD, toluene}) 1691.5 \ (100\%, [M]^+), 1627.5 \ (40\%, [M - S_2]^+). \ ^1\text{H NMR (CD}_2\text{Cl}_2) : \ \delta \ [\text{ppm}] = 0.92 \ (t,
$^{3}\text{J}_{\text{HH}} = 7.3 \text{ Hz, } 30\text{H, }^{n}\text{Bu}, 1.32 \text{ (sextett, }^{3}\text{J}_{\text{HH}} = 7.3 \text{ Hz, } 20\text{H, }^{n}\text{Bu}), 1.55 \text{ (m, } 20\text{H, }^{n}\text{Bu}, 2.53 \text{ (t, }^{3}\text{J}_{\text{HH}} = 7.7 \text{ Hz, }^{n}\text{Bu}), 6.85 \text{ (m, } 40\text{H, Ph).}$

$^{13}\text{C}\{^1\text{H}\} \text{ NMR (CD}_2\text{Cl}_2): \delta \text{ [ppm] } = 14.1 \text{ (}^{n}\text{Bu), 22.7 }^{(n}\text{Bu), 33.6 }^{(n}\text{Bu), 35.6 }^{(n}\text{Bu), 99.0 \text{ (Cp), 127.5 (Ph), 130.2 (Ph), 133.1 (Ph), 142.1 (Ph).}$

$[\text{(Cp}^{\text{BG}}\text{Fe)}_2(\mu,\eta^{1:1-}\text{Se}_2)(\mu,\eta^{2:2-}\text{Se}_2)] \text{ (6b): Yield: 160 mg (72%).}$

$[\text{C}_{110}\text{H}_{130}\text{Fe}_2\text{Se}_4] \text{ calc.: C, 70.29; H, 6.97. Found: C, 69.74; H, 6.56. m/z (FD, toluene) 1880.0 (100%, [M]^+), 1722.6 (85%, [M - Se}_2]^+).}$

$^1\text{H} \text{ NMR (C}_6\text{D}_6): \delta \text{ [ppm] } = 0.78 \text{ (br-t, }^{3}\text{J}_{\text{HH}} = 7.2 \text{ Hz, 30H, }^{n}\text{Bu}, 1.14 \text{ (m, } 20\text{H, }^{n}\text{Bu}, 1.34 \text{ (m, } 20\text{H, }^{n}\text{Bu), 2.53 \text{ (br-t, }^{3}\text{J}_{\text{HH}} = 7.3 \text{ Hz, } 20\text{H, }^{n}\text{Bu), 6.70 \text{ (d, }^{3}\text{J}_{\text{HH}} = 7.3 \text{ Hz, } 20\text{H, Ph), 7.38 \text{ (d, }^{3}\text{J}_{\text{HH}} = 7.3 \text{ Hz, } 20\text{H, Ph).}$

$^{13}\text{C}\{^1\text{H}\} \text{ NMR (CD}_2\text{Cl}_2): \delta \text{ [ppm] } = 14.1 \text{ (}^{n}\text{Bu), 22.7 }^{(n}\text{Bu), 33.1 }^{(n}\text{Bu), 35.6 }^{(n}\text{Bu), 98.6 \text{ (Cp), 130.9 (Ph), 133.7 (Ph), 141.8 (Ph), one phenyl C atom is overlaid by the solvent signal.}$

$^{77}\text{Se}\{^1\text{H}\} \text{ NMR (C}_6\text{D}_6): \delta \text{ [ppm] } = 2209 \text{ (s).}$
2. NMR spectra

**Fig. S1** $^1$H NMR spectrum of 2a in CD$_2$Cl$_2$.

**Fig. S2** $^{13}$C{$^1$H} NMR spectrum of 2a in CD$_2$Cl$_2$. 
Fig. S3  \(^1\)H NMR spectrum of 2b in CD\(_2\)Cl\(_2\).

Fig. S4  \(^{13}\)C\(^{\{1\}H}\) NMR spectrum of 2b in CD\(_2\)Cl\(_2\).
Fig. S5  $^1$H NMR spectrum of 3 in C$_6$D$_6$.

Fig. S6  $^{13}$C$\{^1$H$\}$ NMR spectrum of 3 in C$_6$D$_6$. 
Fig. S7  $^1$H NMR spectrum of 4 in CD$_2$Cl$_2$. 

Fig. S8  $^1$H NMR spectrum of 5 in CD$_2$Cl$_2$. 
**Fig. S9** $^{13}$C\{$^1$H\} NMR spectrum of 5 in CD$_2$Cl$_2$.

**Fig. S10** $^1$H NMR spectrum of 6a in CD$_2$Cl$_2$. 
Fig. S11 $^{13}\text{C}^{1}\text{H}$ NMR spectrum of 6a in CD$_2$Cl$_2$.

Fig. S12 $^1\text{H}$ NMR spectrum of 6b in C$_6$D$_6$. 
Fig. S13 \( ^{13}\text{C}\{^1\text{H}\} \) NMR spectrum of 6b in C\(_6\)D\(_6\).
3. Crystallographic details

The crystal structure analyses were performed either on an Oxford Diffraction Gemini R Ultra CCD diffractometer (2a, 2b, 3, 4·0.5(CH₂Cl₂)·0.5(CH₃CN), 5·0.5(CH₂Cl₂), 6a) or an Oxford Diffraction SuperNova diffractometer (6b·2(CH₂Cl₂)·0.75(CH₃CN)). For all compounds an analytical absorption correction was carried out. The structures were solved by direct methods either of the program SIR-92 or SUPERFLIP and refined with least square method on F² employing SHELXL-97 with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model.

Several nBu groups of the CpBIG ligands show disorder in crystal structures. In most cases a reasonable refinement was only possible by using restraints for interatomic distances and/or for displacement parameters. The used restraints in SHELXL-97 are: SAME, SADI, ISOR, SIMU and DELU.

With the aid of PLATON six solvent accessible areas were found in the crystal structure of 6b·2(CH₂Cl₂)·0.75(CH₃CN), but it was impossible to refine any reasonable molecules from difference Fourier peaks. Therefore the midpoints, the sizes and the numbers of electrons in the voids were refined and the contribution to the calculated structure factors of the disordered solvent is taken into account by back-Fourier transformation with the program SQUEEZE (Sluis and Spek, 1990). The voids are found around (0.365 0.335 0.910), (0.500 0.000 0.000) and (0.635 0.665 0.089) the sizes are 91, 117 and 91 Å³, and 23, 30 and 23 e⁻ respectively were detected (whole cell). This electron number corresponds roughly to three acetonitrile molecules.

CCDC-996971 (2a), CCDC-996972 (2b) and CCDC-996973 (3), CCDC-996974 (4·0.5(CH₂Cl₂)·0.5(CH₃CN)), CCDC-996975 (5·0.5(CH₂Cl₂)), CCDC-996976 (6a) and CCDC-996977 (6b·2(CH₂Cl₂)·0.75(CH₃CN)) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
Crystal data for [(Cp^BIG)FeCO]_2(µ-S2)2 (2a): C_{112}H_{130}Fe_2O_2S_4, M = 1748.14, space group P2_1/c (no.14), a = 13.5054(3) Å, b = 28.7294(5) Å, c = 13.3073(3) Å, β = 114.321(3)°, V = 4705.0(2) Å³, Z = 2, μ = 3.683 mm^{-1}, F(000) = 1868, T = 123 K, 26963 reflections measured, 8085 unique (R_int = 0.0341), R_1 = 0.0516, wR_2 = 0.0924 for I > 2σ(I); CCDC-996971.

Fig. S14  Molecular structure of 2a in the crystal. For clarity reasons H atoms are omitted and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level.
Crystal data for [(Cp^BiG)FeCO]_2(µ-Se_2)] (2b): C_{112}H_{130}Fe_2O_2Se_4, \( M = 1935.70 \), space group \( P2_1/c \) (no.14), \( a = 13.4614(1) \) Å, \( b = 28.5802(2) \) Å, \( c = 13.7406(1) \) Å, \( \beta = 114.394(1)^\circ \), \( V = 4814.48(7) \) Å\(^3\), \( Z = 2 \), \( \mu = 4.518 \) mm\(^{-1}\), \( F(000) = 2012 \), \( T = 123 \) K, 20789 reflections measured, 8255 unique (\( R_{int} = 0.0224 \)), \( R_I = 0.0556 \), \( wR_2 = 0.1479 \) for I > 2\( \sigma(I) \); CCDC-996972.

Fig. S15 Molecular structure of 2b in the crystal. For clarity reasons H atoms are omitted and in case of disorder only the main part is shown.
Crystal data for \([\text{Cp}^2\text{Fe}^\text{II}(\text{CO})_3\{\mu-\text{Se}_2\}]\) (3): \(\text{C}_{114}\text{H}_{130}\text{O}_{4}\text{Fe}_2\text{Se}_2\), \(M = 1833.80\), space group \(P\overline{1}\) (no.2), \(a = 13.7339(4)\) Å, \(b = 14.0008(4)\) Å, \(c = 14.5709(4)\) Å, \(\alpha = 105.226(3)^\circ\), \(\beta = 92.080(2)^\circ\), \(\gamma = 114.452(3)^\circ\), \(V = 2427.2(2)\) Å\(^3\), \(Z = 1\), \(\mu = 3.648\) mm\(^{-1}\), \(F(000) = 966\), \(T = 123\) K, 15903 reflections measured, 8357 unique \((R_{int} = 0.0207), R_I = 0.0919, wR_2 = 0.2423\) for \(I > 2\sigma(I)\); CCDC-996973.

**Fig. S16** Molecular structure of 3 in the crystal. For clarity reasons H atoms are omitted and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level.

**Fig. S17** Disordered central structure of 3 in the crystal. Different parts are colored differently.
Crystal data for [{\(\text{Cp}^{\text{BIG}}\text{FeCO}\)}{\(\text{Cp}^{\text{BIG}}\text{Fe(CO)\}}\}}{\(\mu,\eta^{2:1}\text{Se}_2\)}\} \cdot 0.5(\text{CH}_2\text{Cl}_2) \cdot 0.5(\text{CH}_3\text{CN})
(4 \cdot 0.5(\text{CH}_2\text{Cl}_2) \cdot 0.5(\text{CH}_3\text{CN}))]: \text{C}_{114.3}\text{H}_{132.5}\text{ClFe}_2\text{NO}_3\text{Se}_2, \text{M} = 1868.79, \text{space group } P\overline{T} \text{ (no.2),}
\quad a = 14.1706(4) \text{ Å, } b = 19.5430(6) \text{ Å, } c = 19.6307(5) \text{ Å, } \alpha = 74.040(3)^\circ, \beta = 82.507(2)^\circ, \gamma = 75.027(3)^\circ,
\quad V = 5039.1(3) \text{ Å}^3, \quad Z = 2, \quad \mu = 3.755 \text{ mm}^{-1}, \quad F(000) = 1968, \quad T = 123 \text{ K, 38843 reflections measured, 17180 unique (R}_{int} = 0.0318),}

\quad R_I = 0.0714, \quad wR_2 = 0.1634 \text{ for } I > 2\sigma(I); \quad \text{CCDC-996974.}

**Fig. S18**  Molecular structure of 4 in the crystal. For clarity reasons H atoms are omitted and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level.

**Fig. S19**  Disordered central structure of 4 in the crystal. Different parts are colored differently. The hatched globes belong to both parts.
Crystal data for [(Cp^BisFeCO_2)_2(µ-Te)]·0.5(CH_2Cl_2)·(5·0.5(CH_2Cl_2))]: C_{114.5}H_{131}ClFe_2O_4Te, $M = 1845.95$, space group $Pca2_1$ (no.29), $a = 25.3317(2)$ Å, $b = 27.1293(2)$ Å, $c = 28.8386(2)$ Å, $V = 19818.8(3)$ Å$^3$, $Z = 8$, $\mu = 5.261$ mm$^{-1}$, $F(000) = 7768$, $T = 123$ K, 107769 reflections measured, 35108 unique ($R_{int} = 0.0368$), $R_I = 0.0534$, $wR_2 = 0.1279$ for $I > 2\sigma(I)$; CCDC-996975.

**Fig. S20** Molecular structure of 5 in the crystal. For clarity reasons H atoms are omitted and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level.
Crystal data for [(Cp\textsuperscript{Bi}Fe)\textsubscript{2}(\mu,\eta\textsubscript{1:1}^{}\cdot S\textsubscript{2}^{})(\mu,\eta\textsubscript{2:2}^{}\cdot S\textsubscript{2}^{})] (6a): C\textsubscript{110}H\textsubscript{130}Fe\textsubscript{2}S\textsubscript{4}, M = 1692.13, space group \textit{P1} \textbar (no. 2), a = 14.1813(1) Å, b = 15.5102(1) Å, c = 23.3895 (1) Å, \( \alpha = 107.255(1)^\circ \), \( \beta = 101.438(1)^\circ \), \( \gamma = 95.228(1)^\circ \), \( V = 4753.33(6) \) Å\textsuperscript{3}, \( Z = 2 \), \( \mu = 3.612 \) mm\textsuperscript{-1}, \( F(000) = 1812, T = 123 \) K, 66247 reflections measured, 16722 unique (R\textsubscript{int} = 0.0295), \( R_1 = 0.0335, wR_2 = 0.0784 \) for I > 2\( \sigma \)(I); CCDC-996976.

\textbf{Fig. S21}  Molecular structure of 6a in the crystal. For clarity reasons H atoms are omitted and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level.
Crystal data for [(Cp^{BIG}Fe)_{2}(\mu,\eta^{1:1}\text{-Se}_{2})(\mu,\eta^{2:2}\text{-Se}_{2})]\cdot 2(\text{CH}_{2}\text{Cl}_{2})\cdot 0.75(\text{CH}_{3}\text{CN}) (6b\cdot 2(\text{CH}_{2}\text{Cl}_{2})\cdot 0.75(\text{CH}_{3}\text{CN})): C_{113.5}H_{136.25}Cl_{4}Fe_{2}N_{0.75}Se_{4}, M = 2049.54, space group \text{PT} (no.2), a = 22.1190(4) \text{ Å}, b = 22.2233(5) \text{ Å}, c = 23.0616(3) \text{ Å}, \alpha = 90.382(1)^{\circ}, \beta = 92.790(1)^{\circ}, \gamma = 112.446(2)^{\circ}, V = 10460.9(4) \text{ Å}^3, Z = 4, \mu = 5.090 \text{ mm}^{-1}, F(000) = 4248, T = 128 \text{ K}, 38150 reflections measured, 14553 unique (R_{int} is not given because SQUEEZE was used. Otherwise it would be 0.0383), \( R_{I} = 0.0749, wR_{2} = 0.1608 \) for \( I > 2\sigma(I) \); CCDC-996977.

**Fig. S22** Molecular structure of 6b in the crystal. For clarity reasons H atoms are omitted and in case of disorder only the main part is shown. Thermal ellipsoids are drawn with 50% probability level.

---

**References**


GPSS-2014-0019


