Synthesis and Reactivity of Triiron Complexes Containing Selenide and Diselenide Bridging Ligands: X-ray Structure of $[Cp^*_3Fe_3(\mu_2\text{-}Se)(\mu_3\text{-}Se_2)_2](PF_6)$ ($Cp^*=\eta^5\text{-}C_5Me_5$)

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Reaction of $Cp^*_2Fe_2(CO)_4$ with red selenium (Se_8) afforded an unexpected selenium-rich triiron complex $Cp^*_3Fe_3Se_5$ (**1**). Air oxidation of **1** in the presence of NH_4PF_6 gave the monocationic complex $[Cp^*_3Fe_3Se_5](PF_6)$ (**2**). An X-ray crystal structure analysis of **2** revealed that an Fe_3Se_5 core consists of three iron atoms, one μ_2-selenide ligand, and two μ_3-diselenide ligands with a side-on manner. Reactions of **2** with some simple reagents were also examined.

Thermal reaction of transition metal carbonyl complexes containing cyclopentadienyl ligands with elemental chalcogens is one of the typical methods for synthesizing metal-chalcogen clusters with cyclopentadienyl ligands.[1-3]

Reaction of $Cp_2Fe_2(CO)_4$ with elemental sulfur gives a mixture of tetrairon clusters (eq 1).[4-6]

$$2Cp_2Fe_2(CO)_4 + n/8S_8 \xrightarrow[\text{reflux}]{\text{toluene}} Cp_4Fe_4S_n\ (n = 4 - 6) \quad (1)$$

Similarly, treatment of $Cp_2Fe_2(CO)_4$ with Se_8 (red selenium) gives a cubane type cluster $Cp_4Fe_4Se_4$ in high yield (eq 2).[7]

$$2Cp_2Fe_2(CO)_4 + 1/2Se_8 \xrightarrow[\text{reflux}]{\text{toluene}} Cp_4Fe_4Se_4 \quad (2)$$

On the other hand, the reaction between sulfur and $Cp'_2Fe_2(CO)_4$ containing bulky cyclopentadienyl derivatives affords a diiron complex (eq 3).[8,9]

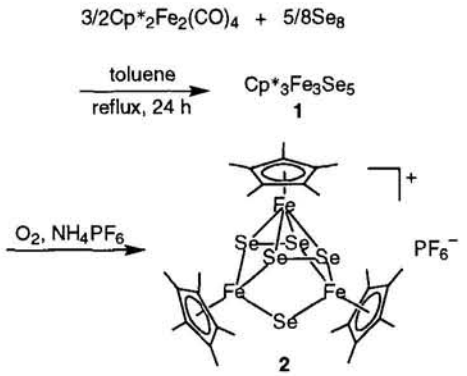
$$Cp'_2Fe_2(CO)_4 + 1/2S_8 \xrightarrow[\text{reflux}]{\text{toluene}} Cp'_2Fe_2S_4 \quad (3)$$

$Cp' = Cp^*$, 1,3-$C_5H_3(SiMe_3)_2$

This paper describes the synthesis of $Cp^*_3Fe_3Se_5$ (**1**) and related complexes. A toluene solution (20 ml) containing $Cp^*_2Fe_2(CO)_4$ (203 mg, 0.411 mmol) and Se_8 (269 mg, 0.426 mmol) was refluxed for 24 h under a dry nitrogen atmosphere. After filtration, the solvent was removed in vacuo. The residue was washed with pentane (20 ml x 3) to give $Cp^*_3Fe_3Se_5$ (**1**) (122 mg, 46%) as a brown solid.[10] Complex **1** is paramagnetic and extremely sensitive to air.

Freshly prepared complex **1** (1.32 g, 1.36 mmol) was suspended in acetonitrile (30 ml) in the presence of NH_4PF_6 (542 mg, 3.32 mmol). The suspension was exposed to the air with stirring for 25 min at room temperature. After filtration, the solvent was evaporated to dryness. The residue was washed with water to remove excess NH_4PF_6 and was heated in vacuo at 80°C (1 mmHg) for 2 h to give $[Cp^*_3Fe_3Se_5](PF_6)$ (**2**) (1.00 g, 66%) as a brown solid (Scheme 1).[11]

The structure of **2** was determined by the X-ray diffraction study.[12] An ORTEP drawing of the cationic moiety of **2** is shown in Figure 1. The Fe_3Se_5 core consists of three iron atoms, one μ_2-selenide ligand, and two μ_3-diselenide ligands and is surrounded by three Cp* ligands. Each μ_3-Se_2 ligand is coordinated to the three iron atoms in a side-on manner.[13] The interatomic distances of Se(1)-Se(2) and Se(3)-Se(4) (2.388(3) and 2.376(3) Å, respectively) indicate the existence of single bonds between two selenium atoms: These distances are very close to that of Se_2^{2-} (2.38(5) Å) having single bond character[14] and much longer than that of Se_2 molecule (2.19(3) Å) having double bond character.[15] On the other hand, the Se(1)---Se(4) and Se(2)---Se(3)



Scheme 1.

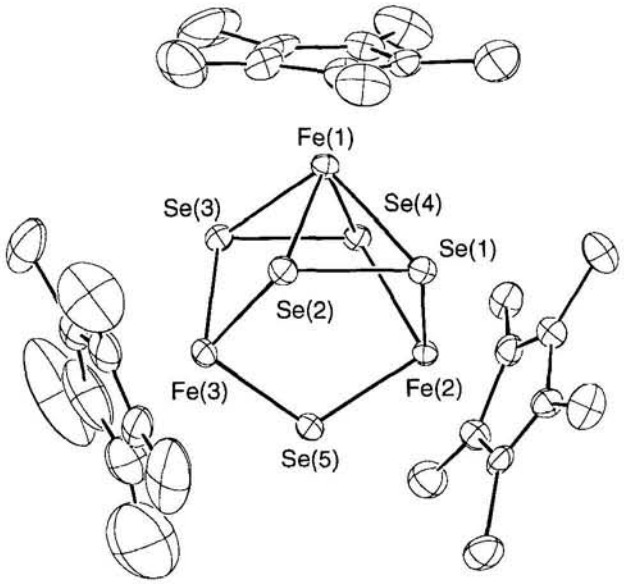
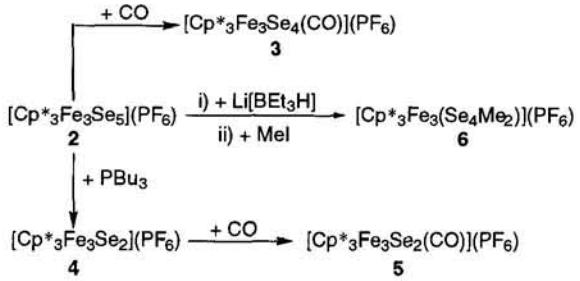


Figure 1. ORTEP drawing of the cationic moiety of $[Cp^*_3Fe_3Se_5]$ (PF_6) (**2**). Important bond distances (Å): Fe(1)···Fe(2), 3.591(4); Fe(2)···Fe(3), 3.803(4); Fe(1)···Fe(3), 3.589(4); Se(1)-Se(2), 2.388(3); Se(3)-Se(4), 2.376(3).

separations are very long (3.047(3) and 3.044(3) Å, respectively), which means no bonding interaction. Complex **2** has an Fe_3Se_5 core with pseudo C_{2v} symmetry. In solution, chemical environments of Fe(2) and Fe(3) are identical, because ^1H NMR spectrum of **2** shows two singlet signals assignable to the methyl groups of Cp* ligands with 1:2 intensity ratio. The three Fe-Fe separations of **2** range from 3.589(4) to 3.803(4) Å which indicates the absence of Fe-Fe bond. This is consistent with the electron counting rule because **2** has 54 cluster valence electrons and is regarded as the electron precise cluster without Fe-Fe bond.

Complex **2** is the first cluster containing M_3Se_5 core and provides rich chemistry (Scheme 2):



Scheme 2.

Complex **2** reacts with CO to give $[Cp^*_2Fe_3Se_4(CO)](PF_6)$ (**3**).[16] Reaction of **2** with a dechalcogen agent PBu_3 gives $[Cp^*_3Fe_3Se_2](PF_6)$ (**4**) which is the complex having a triplet ground state.[17] Complex **4** reacts with CO to give $[Cp^*_3Fe_3Se_2(CO)](PF_6)$ (**5**).[19] Treatment of **2** with Li[BEt3H] and then MeI afforded a paramagnetic complex, $[Cp^*_3Fe_3(Se_4Me_2)](PF_6)$ (**6**).[20]

References and Notes

1 Abbreviations used in this paper: Cp = C_5H_5, Cp* = C_5Me_5, MeCp = C_5MeH_4, and Cp' = general expression for Cp and substituted cyclopentadienyl ligands.

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10 Data for **1**: ^1H NMR ($CDCl_3$, 300 MHz): δ 0.3 (br, 30H, CH_3, $W_{1/2}$ = 164 Hz), 1.2 (br, 15H, CH_3, $W_{1/2}$ = 76 Hz). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 973 (100, M^+), 893 (7, M^+ - Se), 838 (9, M^+ - Cp*), 758 (12, M^+ - Cp* - Se), 678 (35, M^+ - Cp* - 2Se).

11 Data for **2**: ^1H NMR ($CDCl_3$, 300 MHz): δ 1.51 (s, 30H, CH_3), 1.56 (s, 15H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 10.4 [$C_5(CH_3)_5$], 11.6 [$C_5(CH_3)_5$], 99.0 [$C_5(CH_3)_5$], 104.7 [$C_5(CH_3)_5$]. IR (KBr pellet, cm^{-1}): 839 (ν_{PF}), 557 (δ_{PF}). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 973 (100, M^+), 893 (6, M^+ - Se), 838 (22, M^+ - Cp*), 758 (8, M^+ - Cp* - Se), 678 (32, M^+ - Cp* - 2Se). Anal. Found: C, 32.66; H, 4.12%. Calcd for $C_{30}H_{45}F_6Fe_3PSe_5$: C, 32.37; H, 4.08%.

12 Crystal data for **2**: formula $C_{30}H_{45}F_6Fe_3PSe_5$, triclinic, space group $P\bar{1}$, a = 13.584(5) Å, b = 15.651(7) Å, c = 9.208(4) Å, α = 98.82(4)°, β = 98.53(5)°, γ = 100.34(6)°, V = 1872(1) $Å^3$, Z = 2, and d_{calcd} = 1.98 g cm^{-3}. X-ray diffraction data were collected on a Rigaku AFC-6A diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 20°C. The structure was solved by the direct method (MULTAN). All non-hydrogen atoms were refined by the block-diagonal least-squares method with anisotropic thermal parameters to converge R = 0.079 for 4587 reflections [$|F_o| > 3\sigma(F_o)$].

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16 An acetone solution (20 ml) of **2** (210 mg, 0.189 mmol) was heated in an autoclave under a CO atmosphere (5.9 MPa) at 100°C for 24 h. The solvent was evaporated to dryness and the residue was dissolved in dichloromethane. Layering the solution with hexane afforded reddish brown $[Cp^*_3Fe_3Se_4(CO)](PF_6)$ (**3**) (175 mg, 87%). Data for **3**: ^1H NMR ($CDCl_3$, 300 MHz): δ 1.37 (s, 15H, CH_3), 1.52 (s, 15H, CH_3), 1.54 (s, 15H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 10.0 [$C_5(CH_3)_5$], 11.4 [$C_5(CH_3)_5$], 12.1 [$C_5(CH_3)_5$], 94.2 [$C_5(CH_3)_5$], 100.4 [$C_5(CH_3)_5$], 101.1 [$C_5(CH_3)_5$], 212.2 (CO). IR (KBr pellet, cm^{-1}): 1930 (ν_{CO}), 841 (ν_{PF}), 557 (δ_{PF}). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 921 (100, M^+), 893 (56, M^+ - CO), 758 (64, M^+ - CO - Cp*), 678 (9, M^+ - CO - Cp* - Se). Anal. Calcd for $C_{31}H_{45}F_6Fe_3PSe_4O$: C, 35.06; H, 4.27%. Found: C, 35.09; H, 4.13%.

17 A dichloromethane solution (20 ml) of **2** (331 mg, 0.297 mmol) and PBu_3 (0.45 ml, 1.8 mmol) was stirred for 2 h at room temperature. After removal of solvent, the residue was washed with hexane (5 ml) and then dissolved in acetone. Layering the solution with diethyl ether afforded $[Cp^*_3Fe_3Se_2](PF_6)$ (**4**) as a reddish brown solid (227 mg, 87%). Data for **4**: ^1H NMR ($CDCl_3$, 300 MHz): δ -8.12 (br, 45H, CH_3, $W_{1/2}$ = 17 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 46.6 [$C_5(CH_3)_5$], 218.8 [$C_5(CH_3)_5$]; IR (KBr pellet, cm^{-1}): 839 (ν_{PF}), 557 (δ_{PF}). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 733 (100, M^+), 598 (17, M^+ - Cp*), 542 (6, M^+ - Cp* - Fe), 463 (17, M^+ - 2Cp*), 328 (40, M^+ - 3Cp*). Anal. Found: C, 41.27; H, 5.01%. Calcd for $C_{30}H_{45}F_6Fe_3PSe_2$: C, 41.13; H, 5.18%. Magnetic susceptibility measurement of **4** in $CDCl_3$ containing 6% $CHCl_3$ by Evans method[18] gave an effective magnetic moment of 2.95 μ_B at 20°C.

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19 An acetone solution (20 ml) of **4** (202 mg, 0.231 mmol) was heated in an autoclave under a CO atmosphere (5.9 MPa) at 70°C for 18 h. After removal of solvent, the residue was washed with hexane. Layering a dichloromethane solution of the residue with diethyl ether afforded $[Cp^*_3Fe_3Se_2(CO)](PF_6)$ (**5**) (163 mg, 78%) as a brown solid. Data for **5**: ^1H NMR ($CDCl_3$, 300 MHz): δ 1.44 (s, 30H, CH_3), 1.65 (s, 15H, CH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 11.5 [$C_5(CH_3)_5$], 13.3 [$C_5(CH_3)_5$], 94.9 [$C_5(CH_3)_5$], 102.9 ($C_5(CH_3)_5$), 246.0 (CO). IR (KBr pellet, cm^{-1}): 1795 (ν_{CO}), 839 (ν_{PF}), 557 (δ_{PF}). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 761 (89, M^+), 733 (100, M^+ - CO), 598 (41, M^+ - CO - Cp*), 542 (17, M^+ - CO - Cp* - Fe), 463 (37, M^+ - CO - 2Cp*), 328 (35, M^+ - CO - 3Cp*). Anal. Calcd for $C_{31}H_{45}F_6Fe_3PSe_2O$: C, 41.18; H, 5.02%. Found: C, 41.12; H, 4.83%.

20 Suspension of $[Cp^*_3Fe_3Se_5](PF_6)$ (**2**) (85 mg, 7.6 x 10^{-5} mol) in THF (10 ml) was treated with 0.1 M THF solution of Li[BEt3H] (0.40 ml, 4.0 x 10^{-4} mol) and then with 0.32 M THF solution of MeI (1.2 mL, 3.8 x 10^{-3} mol) at -41°C. After removal of the solvent, the residue was dissolved in acetone. Layering the solution with hexane afforded a powdery solid. Layering the dichloromethane solution of the solid with hexane afforded purple-brown $[Cp^*_3Fe_3(Se_4Me_2)](PF_6)$ (**6**) (17 mg, 21%). The product was found to be a mixture of two isomers **6a** and **6b**. Data for **6**: ^1H NMR ($CDCl_3$, 300 MHz) for **6a**: δ -1.91 (br, 30H, CH_3), 1.35 (br, 15H, CH_3); for **6b**: δ -1.91 (br, 30H, CH_3), 0.92 (br, 15H, CH_3). IR (KBr pellet, cm^{-1}): 839 (ν_{PF}), 557 (δ_{PF}). MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe): *m/z* 923 (50, M^+), 908 (100, M^+ - Me), 893 (20, M^+ - 2Me), 788 (10, M^+ - Cp*), 773 (8, M^+ - Me - Cp*), 758 (20, M^+ - 2Me - Cp*). Anal. Found: C, 35.66; H, 5.01%. Calcd for $C_{32}H_{51}F_6Fe_3PSe_4$: C, 36.12; H, 4.83%.