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Sulphur-Sulphur, Sulphur-Selenium, Selenium-Selenium and Selenium-Carbon Bond Activation Using  $Fe_3(CO)_{12}$ : An Unexpected Formation of a  $Fe_2(CO)_6$  Complex Containing a  $\mu^2, \kappa^3$ -C,O,Se-Ligand

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# Abstract

Three diiron hexacarbonyl complexes containing dithiolato (5), diselenolato (6), and selenolatothiolato ligands (7), respectively have been prepared as [FeFe]-hydrogenase mimics. Treatment of Fe<sub>3</sub>(CO)<sub>12</sub> with one equivalent of the corresponding 5-membered heterocycles **1**, **3** and **4** in toluene at reflux afforded the corresponding complexes **5-7**. The reaction of 5,5bis(bromomethyl)-2,2-dimethyl-1,3-dioxane with an *in situ* generated Na<sub>2</sub>Se<sub>2</sub> results in the formation of 8,8-dimethyl-7,9-dioxa-2,3-diselenaspiro[4.5]decane (**1**) and traces of 7,7-dimethyl-6,8-dioxa-2-selenaspiro[3.4]nonane (**2**). Alternatively, 5,5-bis(bromomethyl)-2,2-dimethyl-1,3dioxane reacts with an *in situ* generated Na<sub>2</sub>Se yielding compound **2** in 26% yield. When Fe<sub>3</sub>(CO)<sub>12</sub> reacts under reflux with the selenaspiro compound **2** in toluene, the unique diiron complex [Fe<sub>2</sub>(CO)<sub>6</sub>{( $\mu^2,\kappa^3$ -Se,C,O-SeCH<sub>2</sub>C<sub>7</sub>H<sub>12</sub>O<sub>2</sub>}] (**8**) is obtained as a result of an initial

selenium-carbon bond activation. Compounds **5**, **6**, **7**, and **8** were characterized by IR, <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>77</sup>Se{<sup>1</sup>H} NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray single-crystal structure analysis. The chiral complex **8** shows a coordination of the O atom at the dioxane ring to one Fe atom and the O-CH<sup>-</sup> carbanionic group to the other Fe atom. Furthermore, we investigated the redox properties and the catalytic behaviour of complexes **5-8** in the presence of AcOH as a source of protons. The reduction of complexes **5-7** is accompanied by a chemical process resulting in an overall two-electron transfer at their primary reduction wave. This observation is consistent with an ECE reduction (E = electrochemical process, C = chemical process), while each reduction event in the case of complex **8** involves simple transfer of one electron. Moreover, high level DFT calculations were performed on neutral **8** and its reduction products **8**<sup>-</sup> and **8**<sup>2-</sup>.

# Introduction

The global demand for energy is of continuous increase in step with economic development and population growth while the limited quantities of fossil fuel have begun to diminish. Since several years an ongoing challenge for scientists and engineers has been the development of technologies for power generation from renewable resources. Hydrogen, which can be produced via water electrolysis, is an eco-friendly energy carrier owing to its clean cold combustion in fuel cells.<sup>1-4a</sup> Moreover, hydrogen is an important starting material for the synthesis of fertilizers (e.g., potassium nitrate or ammonium nitrate production), where ammonia is produced via the Haber-Bosch process.<sup>4b</sup> Therefore, many studies have entirely devoted to development of an economically feasible production of hydrogen via proton reduction, which requires an electrocatalyst as an alternative to the platinum.<sup>5</sup> In fact, the process of proton reduction into hydrogen occurs in nature through enzymes known as [FeFe]-hydrogenases, which efficiently catalyse this process (ca. 10<sup>4</sup> turnover per s).<sup>4,6</sup> Crystallographic and spectroscopic studies have shown that the active site of these enzymes contains an organometallic cluster, the H-cluster, that consists of two Fe atoms making Fe-Fe bond, dithiolato bridge between these Fe atoms forming a butterfly structure of the [2Fe2S] core, two unusual types of ligands (CO, CN-) in the coordination sphere of each Fe atom and a [4Fe4S] cluster bonded to one Fe atom (Figure 1, left).<sup>7</sup> The bridgehead of the dithiolato linker has been recently proven to be a NH group.<sup>8</sup> The activity of the H-cluster in catalyzing the reduction of protons is attributed to three functional moieties: (i) a redox functionality ([4Fe4S] cluster), (ii) a pendant base in the dithiolate bridge, playing the role of proton relay to the iron core and (iii) a vacant site at the Fe atom located under the amine group where the H<sup>+</sup>/H<sub>2</sub> conversion occurs as shown in Figure 1 (left).<sup>9</sup>



**Figure 1.** The active site of the [FeFe]-Hydrogenase (H-cluster) (left) and the model complexes used in this study (right).

With these functional moieties in mind, a remarkable number of diiron dithiolato complexes mimicking the butterfly [2Fe2S] core of the H-cluster has been synthesized and tested as electrocatalysts.<sup>5,10</sup> Moreover, modifications have been performed by introducing the heavier selenium or tellurium atoms instead of sulfur.<sup>11</sup> Nonetheless, these mimics catalyse the reduction of protons in non-aqueous solvents with low turnover numbers and large overpotentials compared to the H-cluster.<sup>5a</sup>

Although the reversible  $H^+/H_2$  conversion is apparently a simple reaction, the mechanism of proton reduction catalysed by the H-cluster mimics may follow different pathways. The catalytic pathway may be initiated with either protonation or reduction depending on the structural features of the catalyst or the strength of the acid used as a proton source.<sup>5a,12,13</sup> These structural features include the basicity of the diiron units, the nature of the dithiolato ligand and the presence of an internal basic site. Indeed, studying the protonation properties as well as the redox features of any complex is essential for obtaining a clear picture of its mechanistic pathway for H<sub>2</sub> production from protons.

One focus of our group is an investigation of the impact of the dithiolato ligand on the physical, redox and electrocatalytical properties of the diiron core of the [FeFe]-hydrogenase H-cluster models. Moreover, we have incorporated selenium atoms into artificial mimics of the H-cluster since the presence of selenium enhances the catalytic activity of the enzymes.<sup>14,15</sup> Furthermore,

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H-cluster model complexes featuring [2Fe2Se] cluster reveal less negative reduction potentials compared with those featuring [2Fe2S] core.<sup>16,17</sup>

Herein, we report syntheses of H-cluster model complexes **5**,  $6^{18}$  and **7** (Figure 1) obtained by activation of Se-Se, Se-S and S-S bonds in dioxane-containing molecules **1**, **3** and  $4^{19}$ , respectively. Moreover, we describe the reaction of 7,7-dimethyl-6,8-dioxa-2-selenaspiro[3.5]nonane (**2**) with Fe<sub>3</sub>(CO)<sub>12</sub> that is initiated with Se-C bond activation affording an unexpected formation of complex **8** (Figure 1). In this report, we compare the molecular structures of these complexes and illustrate their structure-property relationship in terms of redox reactions as well as electrocatalysis of H<sub>2</sub> production using acetic acid, AcOH, as a proton source.

# **Results and discussion**

# Synthesis and characterization of 8,8-dimethyl-7,9-dioxa-2,3-diselenaspiro[4.5]decane (1) and 7,7-dimethyl-6,8-dioxa-2-selenaspiro[3.4]nonane (2)

The reaction of 5,5-bis(bromomethyl)-2,2-dimethyl-1,3-dioxane with an *in situ* generated Na<sub>2</sub>Se<sub>2</sub> results in the formation of 8,8-dimethyl-7,9-dioxa-2,3-diselenaspiro[4.5]decane (1) and traces of 7,7-dimethyl-6,8-dioxa-2-selenaspiro[3.4]nonane (2) as shown in Scheme 1. Alternatively, 5,5-bis(bromomethyl)-2,2-dimethyl-1,3-dioxane reacts with an *in situ* generated Na<sub>2</sub>Se leading to generation of compound 2 in 26% yield (Scheme 1). Compounds 1 and 2, have been characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>1</sup>H<sup>77</sup>Se-HMBC NMR spectroscopic techniques, mass spectrometry and elemental analysis as well as X-ray crystallography for compound 2.



Scheme 1. Synthesis of 8,8-dimethyl-7,9-dioxa-2,3-diselenaspiro[4.5]decane (1) and 7,7-dimethyl-6,8-dioxa-2-selenaspiro[3.4]nonane (2).

The <sup>1</sup>H NMR spectrum of compound **1** exhibits singlets at 3.81, 3.23 and 1.41 ppm for the hydrogen atoms in CH<sub>2</sub>O, CH<sub>2</sub>Se and CH<sub>3</sub> moieties, respectively. The singlets due to the hydrogen atoms of CH<sub>2</sub>O (3.80 ppm), CH<sub>2</sub>Se (2.84 ppm) and CH<sub>3</sub> (1.35 ppm) moieties in compound **2** are slightly shifted upfield in comparison to their corresponding hydrogen atoms in compound **1**. The CH<sub>2</sub>Se singlets in compounds **1** and **2** show <sup>77</sup>Se-satellites with coupling constant  ${}^{2}J_{\text{H-Se}} = 15.43$  Hz (for compound **1**) and 8.70 Hz (for compound **2**).

The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound **1** displays singlets for the carbon atoms in OCCH<sub>3</sub> (98.77 ppm), CCH<sub>2</sub>O (67.10 ppm), CCH<sub>2</sub>O (51.71 ppm), CH<sub>2</sub>Se (36.17 ppm) and CH<sub>3</sub> (23.53 ppm) moieties that are slightly shifted downfield with respect to their corresponding carbon atoms in compound **2**; OCCH<sub>3</sub> (97.89 ppm), CCH<sub>2</sub>O (67.06 ppm), CCH<sub>2</sub>O (42.22 ppm), CH<sub>3</sub> (23.50 ppm) and CH<sub>2</sub>Se (17.10 ppm). The CH<sub>2</sub>Se singlets in compounds **1** and **2** show <sup>77</sup>Se-satellites with coupling constant <sup>1</sup>*J*<sub>C-Se</sub> = 68.44 Hz (for compound **1**) and 12 Hz (for compound **2**). In the <sup>1</sup>H<sup>77</sup>Se HMBC NMR spectrum of compound **1**, a singlet is observed at 276.40 ppm that is significantly shifted downfield compared to that detected in the spectrum of compound **2** (144.48 ppm). While attempts to crystallize compound **1** has led only to a structural motif (not shown), suitable crystals for molecular structure determination has been obtained for compound **2** by sublimation method (Figure S1 in the Supporting Information).

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# Synthesis and characterization of 8,8-dimethyl-7,9-dioxa-2-selena-3-thiaspiro[4.5]decane (3)

8,8-Dimethyl-7,9-dioxa-2-selena-3-thiaspiro[4.5]decane (**3**) has been synthesized following a standard multistep procedure described previously (Scheme 2).<sup>20-23</sup> The reaction between 5,5-bis(bromomethyl)-2,2-dimethyl-1,3-dioxane and potassium thioacetate (KSAc) in equimolar amounts results in formation of 5-bromomethyl-5-acetylthiomethyl-2,2-dimethyl-1,3-dioxane (**A**).<sup>23</sup> Subsequently, the resulting product **A** is reacted with potassium selenocyanate to afford 5-selenocyanatomethyl-5-acetylthiomethyl-2,2-dimethyl-1,3-dioxane (**B**).<sup>24</sup> In the final step, compound **B** is reacted with NaBH<sub>4</sub> followed by oxidative ring closure using elemental iodine to give compound **3** in 51% yield. Compounds **A**, **B** and **3** have been characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>1</sup>H<sup>77</sup>Se HMBC NMR spectroscopic techniques, mass spectrometry and elemental analysis.



Scheme 2. Synthesis of 8,8-dimethyl-7,9-dioxa-2-selena-3-thiaspiro[4.5]decane (3).

The synthetic procedures and characterizations of **A** and **B** are described in the Supporting Information. The hydrogen atoms of the  $CH_2O$  moiety in compound **3** resonate as multiplet in the range 3.75-3.82 ppm in the <sup>1</sup>H NMR spectrum whereas singlets were detected for the hydrogen atoms of  $CH_2Se$  and  $CH_2S$  at 3.15 ppm and 3.14 ppm, respectively. The signal due to the CH<sub>2</sub>Se shows <sup>77</sup>Se-satellites with coupling constant <sup>2</sup> $J_{H-Se} = 15.14$  Hz. Moreover, the <sup>1</sup>H NMR spectrum confirms the chemical nonequivalency of the two  $CH_3$  groups in compound **3** where two singlets are detected at 1.42 ppm and 1.40 ppm. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of compound **3**, the carbon atoms of OCCH<sub>3</sub>, CCH<sub>2</sub>O and CCH<sub>2</sub>O resonate as singlets at 98.62 ppm, 66.12 ppm and 51.08 ppm, respectively. Further singlets are detected for the CH<sub>2</sub>S and CH<sub>2</sub>Se moieties at 45.67 ppm and 34.96 ppm, respectively. The singlet observed at 34.96 ppm features <sup>77</sup>Se-satellites with coupling constant <sup>1</sup> $J_{C-Se} = 66.77$  Hz. The carbon atoms of the two

nonequivalent  $CH_3$  groups result in two singlets at 24.44 ppm and 22.72 ppm. The  ${}^{1}H^{77}Se$  HMBC NMR spectrum of compound **3** displays a singlet at 410.13 ppm owing to the  $CH_2Se$  moiety.

#### Synthesis of the diiron complexes 5-8.

Treatment of  $Fe_3(CO)_{12}$  with 8,8-dimethyl-7,9-dioxa-2,3-dithiaspiro[4.5]decane,  $4^{19}$ , or compound 1 and 3 in toluene under reflux affords the diiron complexes  $[Fe_2(CO)_6]\mu$ - $(S(CH_2)_2S)C(C_5H_{10}O_2)$  (5),  $[Fe_2(CO)_6\{\mu-(Se(CH_2)_2Se)C(C_5H_{10}O_2)\}]$  (6) and  $[Fe_2(CO)_6\{\mu-(Se(CH_2)_2Se)C(C_5H_{10}O_2)\}]$  $(Se(CH_2)_2S)C(C_5H_{10}O_2)$ ] (7), respectively (Scheme 3). Complex 6 was previously synthesized by reacting Fe<sub>3</sub>(CO)<sub>12</sub> with 2,2-dimethyl-5,5-bis(selenocyanatomethyl)-1,3-dioxane.<sup>18</sup> When  $Fe_3(CO)_{12}$  is refluxed with compound 2 in toluene, a unique diiron product 8 is obtained. In the dashed box in Scheme 4, a mechanism is proposed for the formation of the chiral complex 8. As shown in Scheme 4, formation of complex 8 is initiated by activation of the Se-C bond in 2 through oxidative addition to Fe(0) carbonyl species. Indeed, examples for the activation of C-X  $(X = S \text{ or } Se)^{25-27}$  by iron carbonyl complexes has been reported by us and others. This oxidative addition step would afford an intermediate in which the Se atom bridges the two Fe atoms and the CH<sub>2</sub> group is involved in a 3c-2e bond; Fe-CH<sub>2</sub>-Fe. One O atom in the dioxane ring coordinates then to one Fe atom, leading to localization of the two bonding electrons of the Fe-CH<sub>2</sub>-Fe core between the other Fe atom and the CH<sub>2</sub> carbon atom. Subsequently, scission of the Fe-CH<sub>2</sub> bonding takes place that is successively followed by a transfer of proton from the αcarbon of the dioxane ring to the carbonionic C-CH<sub>2</sub> group. In the final step, complex 8 is formed upon coordination of the O-CH<sup>-</sup> carbanionic group with the Fe atom. Indeed, an alternative mechanism (Scheme S1) might involve homolytic Fe-CH<sub>2</sub> bond scission leading to a radical intermediate in which the hydrogen atom of the O-CH<sub>2</sub> group is transferred to the radical CH<sub>2</sub> substituent. Subsequently, cyclization takes place through formation of Fe-CH bond to afford complex 8.

Complexes **5-8** have been characterized by  ${}^{1}H$ ,  ${}^{13}C{}^{1}H$  and  ${}^{1}H^{77}Se$  HMBC NMR spectroscopic techniques, mass spectrometry and elemental analysis as well as X-ray crystallography.



Scheme 3. Synthetic pathway of obtaining complexes 5-7.



Scheme 4. Synthesis of complex 8. A tentative mechanism for the formation of complex 8 is shown between brackets.

In the <sup>1</sup>H NMR spectra of complexes **5** and **6**, the hydrogen atoms of  $CH_2O$  resonate as singlets at 3.53 ppm (for **5**) and 3.50 ppm (for **6**) whereas the spectrum of complex **7** displays a multiplet (3.48-3.56 ppm) for the hydrogen atoms of  $CH_2O$ . Furthermore, the <sup>1</sup>H NMR spectrum of complex **5** shows a singlet (2.23 ppm) due to the hydrogen atoms of the  $CH_2S$  moiety that is slightly shifted downfield in comparison to the singlet (2.16 ppm) of the  $CH_2S$  hydrogen atoms in the spectrum of complex **7**. The hydrogen atoms of the  $CH_2S$  moiety appear in the <sup>1</sup>H NMR spectrum of complex **6** as singlet at 2.25 ppm. In comparison, the <sup>1</sup>H NMR spectrum of complex **7** exhibits a singlet, with <sup>77</sup>Se-satellites (<sup>2</sup> $J_{H-Se} = 17.5Hz$ ), for the hydrogen atoms of the  $CH_2Se$ 

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moiety that is slightly shifted downfield, 2.31 ppm. The hydrogen atoms of the  $CH_3$  groups in complexes 5-7 resonate with the same chemical shift of 1.31 ppm in the <sup>1</sup>H NMR spectra. The <sup>13</sup>C{<sup>1</sup>H} NMR spectra exhibit singlets at 207.31 ppm, 208.20 ppm and 207.75 ppm for the carbonyl carbon atoms CO of complexes 5, 6 and 7, respectively. The quaternary carbon atoms of the OCCH<sub>3</sub> moiety resonate as singlets in the  ${}^{13}C{}^{1}H$  NMR spectra at 98.84 ppm (for 5), 98.87 ppm (for 6) and 98.88 ppm (for 7). The  ${}^{13}C{}^{1}H$  NMR spectra of these complexes also show singlets at 68.09 ppm (for 5), 66.95 ppm (for 6) and 67.59 ppm (for 7) due to the carbon atoms in CH<sub>2</sub>O moieties. The quaternary carbon atoms of the CCH<sub>2</sub>O moieties appear at 35.79 ppm (for 5), 35.25 ppm (for 6) and 35.61 ppm (for 7). Moreover, singlets due to the CH<sub>2</sub>S carbon atoms in complexes 5 and 7 appear at 26.75 ppm and 28.10 ppm, respectively. In comparison to these CH<sub>2</sub>S singlets, the CH<sub>2</sub>Se carbon atoms are shifted upfield, 17.94 ppm (for 6) and 16.91 ppm (for 7). These CH<sub>2</sub>Se singlets features <sup>77</sup>Se-satellites with coupling constant  ${}^{1}J_{C-Se} = 85.5$  Hz (for 6) and 83.1 Hz (for 7). The  $CH_3$  groups in complex 7 are chemically non-equivalent resulting in two singlets in the  ${}^{13}C{}^{1}H$  NMR spectrum at 24.00 ppm and 23.34 ppm. For complex 5 or 6, one singlet is detected at 23.34 ppm or 23.33 ppm, respectively, due to their CH<sub>3</sub> carbon atoms. The  ${}^{1}\text{H}^{77}$ Se HMBC NMR spectrum of complex 6 shows a singlet at 69.73 ppm due to the selenium atom of CH<sub>2</sub>Se, which is shifted downfield in comparison to that singlet (56.01 ppm) in the spectrum of complex 7.

In the <sup>1</sup>H NMR spectrum of complex **8**, a singlet is detected at 5.30 ppm and assigned for the hydrogen atom of the *CH*Fe core. The <sup>1</sup>H NMR spectrum of complex **8** also shows the splitting pattern of an AB spin system at 3.38 ppm and 2.74 ppm for the diastereotopic methylene hydrogen atoms of the *CH*<sub>2</sub>Se moiety. Moreover, the methylene hydrogen atoms in the dioxane ring resonate also as doublets at 3.45 ppm and 3.30 ppm. The observed geminal coupling constants in all case are comparable;  ${}^{2}J_{H-H} = 11.3-11.5$  Hz. In addition, the <sup>1</sup>H NMR spectrum of complex **8** displays two singlets at 1.25 ppm and 1.20 ppm for the diastereotopic OCC*H*<sub>3</sub> methyl groups as well as a singlet at 0.59 ppm for the methyl group of the CH<sub>2</sub>C*CH*<sub>3</sub> moiety. In the <sup>13</sup>C{<sup>1</sup>H}</sup> NMR spectrum of complex **8**, the carbonyl carbon atoms resonate as singlets at 215.52 ppm, 212.19 ppm and 209.88 ppm. Furthermore, additional singlets are detected at 107.53 ppm, 102.30 ppm, 67.28 ppm and 52.91 ppm for the carbon atoms of *C*HFe, OCCH<sub>3</sub>, *C*H<sub>2</sub>O and *C*CHFe moieties, respectively. The carbon atom of the *C*H<sub>2</sub>Se moiety resonates as a singlet at 32.80 ppm with <sup>77</sup>Se-satellite, where <sup>1</sup>J<sub>C-Se</sub> = 59.0 Hz. The carbon atoms of the methyl groups in

the OCCH<sub>3</sub> moieties resonate as singlets at 28.72 ppm and 18.43 ppm while the methyl group in  $CH_2CCH_3$  core leads to a singlet at 21.92 ppm. The <sup>1</sup>H<sup>77</sup>Se HMBC NMR spectrum of complex **8** shows a singlet at 31.49 ppm owing to the selenium atom of the CH<sub>2</sub>Se core.

The IR spectra of the complexes **5-8** exhibit absorption bands for the terminal CO ligands (Table 1). It is evident from these data that the v(CO) wavenumbers are shifted to lower values upon systematic replacement of the S atoms by Se ongoing from **5** through **7** to **6**. This finding can be rationalized in terms of increasing back-donation to CO due to the stronger  $\sigma$ -donor capability of Se compared to S. Obviously, the electron density at the diiron core of complex **8** is the highest among the complexes owing to the presence of the carbanionic ligand coordinated at one Fe centre.

**Table 1**. Wavenumbers of the carbonyl ligands, v(CO) in cm<sup>-1</sup>, in the IR spectra of complexes **5**-**8** (ATR, neat solid).

Complex	v(CO), cm <sup>-1</sup>
5	2073 (s), 2029 (s), 2015 (s), 1997(s), 1981 (s), 1971 (s), 1960 (bs)
6	2064 (s), 2021 (s), 1999 (s), 1979 (s), 1970 (s), 1948 (bs)
7	2069 (s), 2025 (s), 2004 (s), 1982 (s), 1972 (s), 1950 (bs)
8	2059 (s), 2008 (s), 1978 (s), 1956 (s), 1931 (bs)

#### **Molecular Structures**

Suitable crystals for single-crystal X-ray analysis were accessible by slow evaporation of a saturated solution of complexes **5-8** in hexane at 7 °C. The molecular structures of complexes **5, 6** and **8** are shown in Figure 2. Indeed, the (S, Se) position in 7 is superimposed, where the (S, Se) is disordered between the locations of the chalcogen atoms (Figure S2, supporting information). In complexes **5-7**, each iron atom of the Fe-Fe bond coordinates to three terminal CO ligands in facial fashion as well as two chalcogen (X = S and/or Se) atoms that bridge both iron atoms. The bicyclic [2Fe2X] structure in these complexes reveals a butterfly conformation.

In a similar way, all CO ligands in complex **8** are terminally bound in a facial manner at the iron centres. Additionally, the two iron sites are bridged by one Se atom as well as the dioxane ring through a carbanionic and O donor sites.



Figure 2. Molecular structures (50% probability) of one isomer of complex 5 and complexes 6 and 8. Hydrogen atoms are omitted for clarity.

Table 2 display some structural features of these complexes. The Fe-Fe distance increases slightly as the size of the bridging chalcogen atoms increases on going from **5** to **6**. Replacing one bridging Se atom in **6** by O,C-donor sites of the dioxane ring in complex **8** explains the longer Fe-Fe distance in the latter complex compared to the former. The Fe-Se distances in complexes **6** and **8** are comparable. In a similar way, complex **5** shows slight difference in the Fe-S distances. The Fe-C<sub>Carbanion</sub> distance in complex **8** (2.050(2) Å) is comparable to that in structurally related complexes.<sup>25</sup> Interestingly, the torsion angle in the symmetrically independent molecules **5A** (17.50°) and **5B** (30.27°) even though these two molecules have similar flap angles; 141.0° (for **5A**) and 141.8° (for **5B**). Only complex **6** shows an almost eclipsed conformation of its two Fe(CO)<sub>3</sub> units as indicated by the torsion angle, C<sub>ap</sub>-Fe-Fe-C<sub>ap</sub>, of 1.04°.

	5(A)	5(B)	6	8
Fe-Fe [Å]	2.4982(4)	2.5034(4)	2.5432(4)	2.5623(4)
Fe-S/Se [Å]	2.2575(5)	2.2579(5)	2.3789(3)	2.3631(4)
Fe-C <sub>Carbanion</sub> [Å]	_	_	_	2.050(2)
Fe-O [Å]	_	—	_	2.0579(14)
C <sub>ap</sub> -Fe-Fe-C <sub>ap</sub> [°] <sup>[a]</sup>	17.50	30.27	1.04	20.47
Flap angle, α [°][ <sup>b]</sup>	141.0	141.8	131.6	_

Table 2. Selected bond lengths [Å] and angles [°] in complexes 5, 6 and 8.

[a] Dihedral twist angle (torsion angle) of the apical carbonyl carbon atoms across the Fe-Fe bond. [b] Refers to angle between plane made from bridgehead carbons-elbow carbons and the plane made from the elbow carbons-S/Se.

#### **Redox Properties**

Table 3 summarizes the redox potentials (referenced to ferrocenium/ferrocene couple; Fc<sup>+</sup>/Fc) of complexes **5-8** in MeCN-[n-Bu<sub>4</sub>N][BF<sub>4</sub>] obtained by cyclic voltammetry. The cyclic voltammetry of complexes **5-7** shows one reduction event at half-wave potentials  $E_{1/2}$  of -1.51, - 1.48 and -1.49 V, respectively as shown in Figure 3a-c. In comparison, two reduction events are observed in the cyclic voltammogram of complex **8** at  $E_{1/2}$  of -1.13 V and -1.77 V (Figure 3d).

**Table 3**. Summary of the redox features of complexes **5-8** in MeCN-[n-Bu<sub>4</sub>N][BF<sub>4</sub>] (0.1 M) measured at 0.2 V·s<sup>-1</sup> using glassy carbon disk (diameter = 1.6 mm). Potentials *E* are given in volts (V) and referenced to Fc<sup>+</sup>/Fc.

Complex	$E_{\rm red}{}^{1[a]}$	$E_{1/2}^{1[b]}$	$E_{\rm red}^2$	$E_{1/2}{}^{2[b]}$	$E_{\rm ox}^{1[c]}$	$E_{\mathrm{ox}}^{2\mathrm{[d]}}$	$E_{\rm ox}^{3}$
5	$-1.54 (E_{pc}^{1}), -1.48 (E_{pa}^{1})$	-1.51	_	-	+0.22	+0.73	+0.79 <sup>[e]</sup>
6	$-1.51 (E_{pc}^{1}), -1.46 (E_{pa}^{1})$	-1.48	-	-	+0.17	+0.65	_
7	$-1.51 (E_{pc}^{1}), -1.47 (E_{pa}^{1})$	-1.49	-	-	+0.19	+0.69	-
8	$-1.21 (E_{pc}^{1}), -1.06 (E_{pa}^{1})$	-1.13	-1.81 $(E_{pc}^{1})$ , -1.73 $(E_{pa}^{1})$	-1.77	+0.03	+0.52	_

[a]  $E_{red}^1$  and  $E_{red}^2$  are the potentials for the first and the second reductions, where  $E_{pc}$  and  $E_{pa}$  are the cathodic and anodic scan peak potentials. [b]  $E_{1/2}^1$  and  $E_{1/2}^2$  are the half-wave potentials for the first and second reduction events, respectively. [c]  $E_{ox}^1$  is the potential of a very weak oxidation peak attributed to an initial oxidation to a rotated structure as discussed previously for complexes structurally related to those of 5-7.<sup>[5b,17]</sup> [d]  $E_{ox}^2$  is the potential of the primary oxidation peak. The oxidation of only

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complex 6 ( $E_{pa} = +0.65$  V) is characterized by a small cathodic event at  $E_{pc} = +0.45$  V observed in the return sweep of the cyclic voltammogram. [e] This oxidation event is characterized by a small cathodic event at  $E_{pc} = +0.72$  V observed in the return sweep of the cyclic voltammogram. Increasing the scan rate results in an overlap of  $E_{ox}^2$  and  $E_{ox}^3$  of complex 5.



**Figure 3.** Cyclic voltammetry of 1.0 mM a) complex **5**, b) complex **6**, c) complex **7** and d) complex **8** in MeCN-[*n*-Bu<sub>4</sub>N][PF<sub>4</sub>] (0.1 M) solutions at different scan rates using glassy carbon disk (d = 1.6 mm). The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the Fc<sup>+</sup>/Fc couple.

The oxidation of complexes **5-8** shows a very weak anodic wave  $E_{ox}^{1}$  in the vicinity of +0.17 to +0.22 V (for complexes **5-7**) and at +0.03 V (for complex **8**) while the primary oxidation events occur at more positive potentials  $E_{ox}^{2}$  and  $E_{ox}^{3}$  as given in Table 3. The primary oxidation potential  $E_{ox}^{2}$  shows an anodic shift on going from complex **8** to complex **6** to complex **7** to

complex 5, which is consistent with the order of electron richness of the diiron core of these complexes indicated by their relative v(CO) wavenumbers (Table 1). While  $E_{ox}^2$  values and the v(CO) wavenumbers are directly proportional to the electron density at the diiron carbonyl core, other factors may tune the reduction potentials.<sup>5b,17</sup> In spite of the fact that complex 8 features the highest electron richness at the diiron core, the first reduction potential of this complex  $E_{1/2}^1$  is the least negative in Table 3. The observed trend in the reduction potentials could be related to the number of polarizable atoms coordinated at the diiron site, such that the soft S- and Se-donor atoms are more capable of moderating the increase in the electron density upon reduction than the hard oxygen- or the carbanionic-donor sites in complex 8.

According to our previous photoelectron spectroscopic studies and calculations of ionization energies of complexes structurally related to those of 5-7,<sup>5b,17</sup> the primary oxidation event of 5, 6 or 7 at  $E_{ox}^2$  could be attributed to an initial oxidation forming a cationic species with all-terminal CO ligands similar to the structure of their neutral state. Also similar to these studies, the very weak oxidation events of 5-7 that are observed in the vicinity of +0.17 to +0.22 V could arise from an oxidation leading to a cationic species featuring one inverted Fe(CO)<sub>3</sub> unit and a bridging CO ligand.

An insight on the reduction mechanism at a given potential can be obtained by comparing the value of the current function  $i_{pc} / c \cdot v^{1/2}$  ( $i_{pc}$  = cathodic peak current, c = concentration and v = scan rate) of that reduction at various scan rates.<sup>5b,28-30</sup> The current function is given by Randles-Sevcik equation:<sup>29,30</sup>

$$i_{\rm pc} / {\rm c} \cdot v^{1/2} = (2.69 \times 10^5) \cdot A \cdot D^{1/2} \cdot n^{3/2}$$

where *A*, *D* and *n* are the surface area of the electrode, the diffusion coefficient and the number of electrons responsible for the reduction event, respectively. In principle, in the absence of chemical complications the current function  $i_{pc} / c \cdot v^{1/2}$  of a reduction peak should remain constant at all scan rates because  $(2.69 \times 10^5) \cdot A \cdot D^{1/2} \cdot n^{3/2}$  is constant. Nonetheless, a chemical process may accompany the electron transfer in an ECE mechanism of reduction (E = electrochemical process, C = chemical process) making the second electron reduction thermodynamically favoured over the first electron reduction; i.e. potential inversion. This intervening chemical process to take place and hence the second electron transfer will not occur. Simply stated,

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 $i_{\rm pc}^{\rm c}/{\rm c.v}^{1/2}$ (µA.V<sup>-1/2</sup>.S<sup>1/2</sup>.mM<sup>-1</sup>)

performing the voltammetric experiment at fast scan rates prevents the intervening chemical process and alters the redox mechanism from ECE (n = 2) to a simple E process (n = 1). Therefore, a decrease of  $i_{pc} / c \cdot v^{1/2}$  at fast scan rates suggests an ECE mechanism while a constant value of  $i_{pc} / c \cdot v^{1/2}$  at slow and fast scan rates is indicative of an uncomplicated one-electron transfer. Whereas the current function of the reduction of complexes 5-7 decreases towards a constant value as the scan rate increases, both reduction events of complex 8 show no dependency of their current function on the scan rate (Figure 4). These observations are consistent with an ECE reduction in the case of complexes 5-7 while each reduction event in the case of complex 8 involves simple transfer of one electron. As shown in Figure 4, the scan rate dependence of the current function of the reduction of complexes 5-7 is similar to that in the case of  $[Fe_2(CO)_6(bdt)]^{31}$  (bdt =  $\mu$ -benzenedithiolato), which is known to undergo two-electron reduction with potential inversion. The chemical process intervening in the reduction of a dianionic species featuring semi-bridging CO ligand in a similar manner described for  $[Fe_2(CO)_6(bdt)]^{31}$ 



**Figure 4.** Scan rate dependence of the current function of the reduction events of complexes **5-8** in comparison to that of the reduction of  $[Fe_2(CO)_6 {bdt}]^{31}$  under the same conditions.

# Electrocatalysis

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The electrocatalytic proton reduction by complexes **5-8** using acetic acid (AcOH,  $pK_a^{MeCN} = 22.6)^{32}$  as a source of protons is shown in Figure 5. It is evident from Figure 5 that complexes **5**-7 exhibit two potential-dependent catalytic processes in the vicinities of -1.9 to -2.1 V (for process I) and -2.1 to -2.3 V (for process II), respectively. In comparison, only one catalytic process is observed at -1.84 V by the cyclic voltammetry of complex **8**.

The electrocatalytic reduction of AcOH by complexes 5-7 is similar to that in the case of their analogues complexes  $[Fe_2(CO)_6{\mu-(XCH_2)_2CMe_2}]$  (X = S or Se).<sup>28</sup> In the presence of various equivalents of AcOH, the current of the two-electron reduction waves of complexes 5-7, that is observed in the absence of acid, remains unaffected, but the reduction peaks show small anodic shifts of 10-30 mV. Protonation of the dianionic species of complexes 5-7 accounts for these



Figure 5. Cyclic voltammetry of 1.0 mM a) complex 5, b) complex 6, c) complex 7 and d) complex 8 in MeCN-[n-Bu<sub>4</sub>N][PF<sub>4</sub>] (0.1 M) solutions at 0.2 V s<sup>-1</sup> in the presence of different

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concentration of AcOH using glassy carbon disk (d = 1.6 mm). The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the  $Fc^+/Fc$  couple.

anodic shifts.<sup>31,33</sup> Reduction of the resulting protonated species  $HA^-$  (A = 5-7) that is followed by a protonation step would lead to H<sub>2</sub> release from an H<sub>2</sub>A<sup>-</sup> species in process I (Scheme 5, green arrow). As shown in Scheme 5, the catalytic process I of complexes 5-7 levels off at higher acid concentrations while process II dominates upon a further reduction step affording H<sub>2</sub>A<sup>2-</sup> species. In the case of complex 8, neither the current nor the potential of its first one-electron reduction is affected by the presence of AcOH. Furthermore, the first reduction wave of complex 8 remains reversible at all acid concentrations (Figure S3, see Supporting Information). These observations indicate that the monoanionic species 8<sup>-</sup> is not basic enough to undergo protonation. As evident from Figure 5d, the catalytic process is triggered upon reduction of 8<sup>-</sup> affording the more basic species 8<sup>2-</sup> that undergoes protonation to give 8H<sup>-</sup>. A second protonation step would then lead to formation of H<sub>2</sub> as shown in Scheme 5 (blue arrows).



Scheme 5. Tentative mechanism for the proton reduction cycle catalyzed by complexes 5-8 in the presence of AcOH.

## **DFT Investigations**

Cyclovoltammetric measurements have revealed that catalytic hydrogen production occurs from dianionic species derived from **8** upon two reduction steps. In order to get some insight into this catalytic process high level DFT calculations were performed on neutral **8** and its reduction products **8**<sup>-</sup> and **8**<sup>2</sup>. In addition, corresponding calculations have been performed for diiron carbonyl complexes produced from **8**<sup>2</sup> by the addition of one or two protons. Calculations were performed applying the B3LYP/6-311++G(d,p) functional and basis set as it is implemented in *Gaussian09*.<sup>34,35,36</sup> Moreover, relativistic ECPs of the Stuttgart-Dresden groups were used for iron and selenium atoms.<sup>36</sup> Besides, a continuum solvent model for acetonitrile was applied to the calculations since it has been shown that this is crucial to obtain results that correspond to the experimental outcome of electrochemical investigations.<sup>37</sup> As the addition of protons represent bimolecular reactions, thermal and entropic corrections were considered. All energy values E<sub>corr</sub> as well as the results of frequency calculations are summarized in Table S1 (Supporting Information). Vibrational analysis for all calculated molecules show that they represent minimum structures on the hypersurface (NImag = 0).

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**Figure 6.** Calculated molecular structures of **8**, **8**<sup>-</sup> and **8**<sup>2</sup>- (upper row from left to right) as well as the protonated species **H8**<sup>-</sup>**1**, **H8**<sup>-</sup>**2** and **H**<sub>2</sub>**8** (lower row from left to right).

The molecular structure of **8** was calculated starting with the geometry of the molecule as it has been the result of an X-ray structural analysis, which remains almost unchanged in the theoretical investigation. **8** is a diiron hexacarbonyl compound with a bridging selenium atom and another organic ligand coordinating via formally anionic C1 and one of the ether oxygen atoms of the cyclic acetal. By the two latter interactions the organic ligand also adopts a position bridging both iron atoms. The iron selenium bond toward the iron that is coordinated by the acetal oxygen atom next to three CO ligands is about 6 pm longer than the other iron selenium distance. If **8** is reduced, the anionic complex **8**- is formed upon a single electron transfer. The most significant structural effects caused by the enhanced number of electrons is the elongation of the iron iron distance by more than 40 pm as well as the breakage of the bonding interaction between Fe2 and O1. In addition, the bridging position of the selenium atom now is almost symmetrical due to an elongation of the Fe1-Se bond. Moreover, also the interaction between C1

and Fe1 obviously is slightly weakened upon reduction of **8** since this bond distance also is elongated. Interestingly, upon a second electron transfer the iron iron distance in the resulting dianion **8**<sup>2-</sup> is not further elongated compared to **8**<sup>-</sup> but is calculated to be more than 10 pm shorter. Concurrently, the selenium bridge gets unsymmetrical again, although in contrast to the starting compound **8** in **8**<sup>2-</sup> Fe2-Se is significantly shorter than Fe1-Se. On the other hand, the bond between Fe1 and C1 is further elongated compared to the situation in **8**<sup>-</sup>. There are no semibridging CO ligands observed in the calculated structure of **8**<sup>2-</sup>. All Fe-C-O bond angles are above 170° and the distances between CO carbon atoms and the second iron atom are well above 300 pm. Nevertheless, it is noticeable, that Fe-C-O bond angles in **8**<sup>2-</sup> in average are only slightly above 170° whereas for all other compounds they are generally observed between 175° and 180°. So the second reduction step seems to lead to a situation in which  $\pi$ -backbonding into  $\pi^*$  orbitals of coordinated CO ligands is quite effective leading to a slight bending of all CO ligands rather than to another shortening of the Fe-Fe distance.

	8	8-	<b>8</b> <sup>2-</sup>	H8 <sup>-</sup> _1	H8 <sup>-</sup> _2	H <sub>2</sub> 8
Fe1-Fe2	257.8	299.0	286.2	277.2	270.8	285.9
Fe1-Se	241.1	245.3	246.4	241.9	245.5	244.0
Fe2-Se	247.0	247.5	240.8	241.0	245.4	244.0
Fel-Cl	206.3	209.8	212.4	212.5	211.3	211.0
Fe2-O1	211.0	-	-	-	-	-
Fe1-H2	-	-	-	-	167.5	167.6
Fe2-H1	-	-	-	152.5	-	151.3
Fe2-H2	-	-	-	-	165.1	166.2

Table 4. Selected bond lengths and distances [pm] of the calculated compounds

If a proton is added to  $8^{2}$ - the number of electrons in the protonated species is identical to the number of electrons in 8<sup>2-</sup> which means that H8<sup>-</sup> 1 and H8<sup>-</sup> 2 both are monoanions. It was one of the goals of this theoretical investigation to see at which iron atom the first protonation will take place. So we started the geometry optimization from three different situations: two starting geometries with hydride ligands attached either to Fe1 or Fe2 and a situation with a bridging hydride. By this methodology we were able to observe two minimum structures on the hypersurface. In H8-1 a hydride ligand coordinates to Fe2 whereas starting from a hydride at Fe1 or with a bridging hydride in both cases ends up in the same minimum structure  $H8^{-2}$  with the hydride adopting a symmetrical bridging position. The bonding situation in H8-2 is stabilized relative to the one in H8<sup>-</sup> 1 by 29.6 kJ/mol. In both isomers the position of the selenium atom is almost perfectly symmetrical although the iron selenium bonds in H8<sup>-</sup> 2 are slightly longer than the respective bond lengths in the other isomer. In both compounds the iron iron distance is significantly shorter than in 1<sup>2-</sup> with the effect being even more pronounced in H8-2 with the bridging hydride ligand. The interaction between Fe1 and C1 is almost not affected by protonation of  $8^{2-}$ . If a second protonation occurs the resulting compound is a neutral species. We were only able to identify one single minimum on the hypersurface because independently of the position of the second hydrogen atom in the starting geometry, optimization of the structure always leads to  $H_28$ . This is true for the second hydrogen atom being placed as  $\eta^{1}$ -hydride ligand at Fe1 or as a bridging ligand in starting geometries produced from H8<sup>-</sup> 1 or as a n<sup>1</sup>-hydride ligand at Fe2 in starting geometries produced from H8<sup>-</sup> 2. Iron hydrogen distances in all protonated species are almost identical for  $\eta^1$ -hydrides on one side and for bridging hydrides on the other side. Nevertheless, there is one significant difference in the coordination of the bridging hydride in  $H8^-$  2 compared to  $H_28$ . The former shows a typical butterfly arrangement with an angle of 57.9° between the planes Fe1-Fe2-Se and Fe1-Fe2-H2, whereas in the latter the corresponding angle measures to 29.15° which means that the arrangement of these 4 atoms in  $H_28$  is closer to planarity than in  $H8^-$  2. This also leads ton elongation of the iron iron distance which in  $H_28$  is 15 pm longer than in  $H8^-$  2. In addition, in H<sub>2</sub>8 the selenium bridge is perfectly symmetrical and Fe-Se bond lengths as well as the Fe1-C1 interaction are observed with very similar values compared to the situation in H8<sup>-</sup>\_2.

#### Conclusion

Activation of the chalcogen-chalcogen bonds in compounds 1, 3 or 4 by  $Fe_3(CO)_{12}$  result in the formation of complexes 6, 7 or 5, respectively (Scheme 3). Unexpectedly, refluxing compound 2 with Fe<sub>3</sub>(CO)<sub>12</sub> starts with an activation of the Se-C bond, but this oxidative addition is followed by rearrangement steps leading to unexpected formation of complex 8 (Scheme 4). The electron density at the diiron core of the complexes in this study decreases on going from 8 to 6 to 7 to 5 as evident from their v(CO) wavenumbers (Table 1) as well as the oxidation potentials  $E_{ox}^2$ (Table 3). This trend reflects the  $\sigma$ -donor ability of the ligands in these complexes, where the ligand set in complex 8 inductively increases the electron richness of the diiron units compared to the ligands in complexes 5-7. Despite this order of electron density at the diiron core of these complexes, their reduction potentials  $E_{1/2}$  (Table 3) follow an opposite trend owing to the polarizability of the donor atoms coordinated at the Fe atom. The reduction of complexes 5-7 is accompanied by a chemical process resulting in an overall two-electron transfer at their primary reduction wave, which afford their dianionic form at  $E_{1/2}$  shown in Table 3. Uncommonly, the cyclic voltammetry of complex 8 reveals reversibility of two well-separated cathodic events for 8/8<sup>-</sup> and 8<sup>-</sup>/8<sup>2-</sup> redox couples having  $E_{1/2}$  of -1.13 V and -1.77 V, respectively. The electrocatalytic reduction of protons, using AcOH as a proton source, requires an initial reduction of the complexes. The dianionic species of complexes 5-7 undergoes protonation in the presence of AcOH, but further reduction is required for catalysis. In the case of complex 8, catalysis takes place once the dianionic species  $8^{2-}$  is formed leading to H<sub>2</sub> formation at potential lower than that required in the case of complexes 5-7.

## Experimental

#### Materials and techniques.

All reactions were performed using standard Schlenk and vacuum-line techniques under an inert gas (nitrogen). The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>77</sup>Se{<sup>1</sup>H} and <sup>1</sup>H <sup>77</sup>Se HMBC NMR spectra were recorded with a Bruker Avance 400 or 600 MHz spectrometer. Chemical shifts are given in parts per million with references to internal SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C) or to Me<sub>2</sub>Se (<sup>77</sup>Se, <sup>1</sup>H <sup>77</sup>Se HMBC). The mass spectrum was recorded with Finnigan MAT SSQ 710 instrument. The IR spectra were recorded with a Bruker Equinox 55 spectrometer equipped with an ATR unit. Elemental analysis was

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performed with a Leco CHNS-932 apparatus. TLC was performed by using Merck TLC aluminum sheets (Silica gel 60 F254). Solvents from Fisher Scientific and other chemicals from Acros and Aldrich were used without further purification. All solvents were dried and distilled prior to use according to standard methods. The compound 8,8-dimethyl-7,9-dioxa-2,3-dithiaspiro[4.5]decane, **4**, was synthesized according to the known literature methods.<sup>19</sup>

#### Electrochemistry

Corrections for the *iR* drop were performed for all experiments. Cyclic voltammetric measurements were conducted in three-electrode technique [glassy carbon disk (diameter = 1.6 mm) as working electrode, Ag/Ag<sup>+</sup> in MeCN as reference electrode, Pt wire as counter electrode] using a Reference 600 Potentiostat (Gamry Instruments). All experiments were performed in MeCN solutions (concentration of the complexes 1.0 mM) containing 0.1 M [*n*-Bu<sub>4</sub>N][BF<sub>4</sub>] at room temperature. The solutions were purged with N<sub>2</sub> and a stream of it was maintained over the solutions during the measurements. The vitreous carbon disk was polished on a felt tissue with alumina before each measurement. All potential values reported in this paper are referenced to the potential of the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple.

#### **Theoretical Calculations**

Full geometry optimizations (i. e. without symmetry constraints) were carried out with the GAUSSIAN09 program package using throughout the hybrid Hartree-Fock-DFT approach (B3LYP/6-311++G(d,p)).<sup>34,35,36</sup> The B3LYP functional has previously been found to be of suitable theoretical level for the study of iron and ruthenium carbonyl complexes.<sup>38</sup> For iron and selenium atoms we used a relativistic ECP of the Stuttgart-Dresden group (SDD).<sup>36</sup> Stationary points were rigorously characterized as minima according to the number of imaginary modes by applying a second-order derivative calculation (vibrational analysis). Zero point energy (ZPE) corrections have been applied. Solvent effects were addressed by performing a polarizable continuum model calculation for CH<sub>3</sub>CN using the CPCM model.<sup>37</sup>

#### **Crystal structure determination**

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K<sub> $\alpha$ </sub> radiation. Data were corrected for Lorentz and polarization effects; absorption was considered on a semi-empirical basis using multiple-scans.<sup>39-</sup>

<sup>41</sup> The structures were solved by direct methods (SHELXS)<sup>41</sup> and refined by full-matrix least squares techniques against Fo<sup>2</sup> (SHELXL-97).<sup>42</sup> The hydrogen atoms of 7 were included at calculated positions with fixed thermal parameters. All other hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All non-disordered, non-hydrogen atoms were refined anisotropically.<sup>42</sup> In the crystal of complex 7, the sulfur and selenium atoms can occupy the same lattice sites. As a result, the diffraction pattern is a superposition of four compounds or isomers: the pure S-S complex and / or the pure Se-Se complex; as well as the S-Se and / or Se-S complex. This is associated with a disorder. Although the disorder of S and Se could be resolved, the s.u. of the sulfur and selenium distances are so large that these are not discussed in this paper (e.g., Fe1-S (1) 2.211 (1) or Fe1-Se1 2.398 (15)Å). Crystallographic data as well as structure solution and refinement details are summarized in Table S2 in the Supporting Information. MERCURY<sup>43</sup> was used for structure representations.

## Synthesis of 8,8-dimethyl-7,9-dioxa-2,3-diselenaspiro[4.5]decane (1)

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162 mg (4.28 mmol) of NaBH<sub>4</sub> and 473 mg (6.00 mmol) of selenium were initially introduced into a Schlenk flask, and the mixture was cooled down to 0 °C before the addition of 20 mL ethanol. After the initial reaction had subsided, the mixture was stirred and heated at reflux for 2 h with N<sub>2</sub> passing into the liquid in order to dissolve the Se and eject H<sub>2</sub>Se. The resulting deepred ethanolic solution of Na<sub>2</sub>Se<sub>2</sub> was cooled down again to 0 °C before the addition of the 5,5bis(bromomethyl)-2,2-dimethyl-1,3-dioxane (604 mg, 2.00 mmol) dissolved in 15 mL ethanol. The ice-bath was removed, and the mixture stirred for 24 h at room temperature. Water was added, extracted three times with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic phases were washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed in vacuo. After purification by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub> / hexane 3: 1) it was possible to isolate a red-brown solid which, however, contained in a small amount the corresponding compound 2. Suitable crystals for single-crystal X-ray analysis could be obtained by slowly evaporating a solution of the compound in hexane. Yield: 29% (173 mg, 0.58mmol). Elemental analysis for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>Se<sub>2</sub>: calc.: C 32.02; H 4.70 found.: C 32.50; H 4.74. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$  = 3.81 (s, 4H, CH<sub>2</sub>O), 3.23 (s, with <sup>77</sup>Se satellite,  ${}^{2}J_{H-Se} = 15.43$  Hz, 4H, CH<sub>2</sub>Se), 1.41 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$  = 98.8 (s, OCCH<sub>3</sub>), 67.1 (s, CCH<sub>2</sub>O), 51.7 (s,

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CCH<sub>2</sub>O), 36.8 (s, with <sup>77</sup>Se satellite, <sup>1</sup> $J_{C-Se} = 68.44$  Hz, CH<sub>2</sub>Se), 23.5 (s, CH<sub>3</sub>). <sup>1</sup>H<sup>77</sup>Se HMBC NMR (600 MHz, 114 MHz, CDCl<sub>3</sub>, 23°C):  $\delta = 276.40$  (s, CH<sub>2</sub>Se). DEI-MS: m/z = 302 [M]<sup>+</sup>.

## Synthesis of 7,7-Dimethyl-6,8-dioxa-2-selenaspiro[3.4]nonane (2)

400 mg (10.57 mmol) of NaBH<sub>4</sub> and 473 mg (5.99 mmol) of elemental selenium were initially introduced into a Schlenk flask, and the mixture was cooled down to 0 ° C before the addition of 20 mL ethanol. After the initial reaction had subsided, the mixture was stirred and heated at reflux for 2 h with N<sub>2</sub> passing into the liquid in order to dissolve the Se and eject H<sub>2</sub>Se. The resulting deep-red ethanolic solution of Na<sub>2</sub>Se<sub>2</sub> was cooled down again to 0 °C before the addition of the 5,5-bis(bromomethyl)-2,2-dimethyl-1,3-dioxane (2.50 g, 8.28 mmol) dissolved in 20 ml of ethanol. After the reaction mixture had slowly warmed to room temperature, stirring was continued overnight and then refluxed for a further two hours. The bulk of the ethanol was removed in vacuo, water was added to the remaining solution and extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. After washing the combined organic phases with water, drying over Na<sub>2</sub>SO<sub>4</sub> and removal of the solvent in vacuo, the residue thus obtained was purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub> / hexane 3: 1). The desired product was obtained as a white solid, and suitable crystals for single-crystal X-ray diffraction analysis were obtained by sublimation under normal pressure at 60 ° C. Yield: 26% (483 mg, 2.18 mmol). Elemental analysis for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>Se: calc: C 43.45; H 6.38 found: C 43.66; H 6.29. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$  = 3.80 (s, 4H, CH<sub>2</sub>O), 2.84 (s, with <sup>77</sup>Se satellite, <sup>2</sup>J<sub>H-Se</sub> = 8.70 Hz, 4H, CH<sub>2</sub>Se), 1.5 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 97.9 (s, OCCH<sub>3</sub>), 69.1 (s, OCH<sub>2</sub>), 42,2 (s, CCH<sub>2</sub>O), 23.5 (s, CH<sub>3</sub>), 17.1 (s, with <sup>77</sup>Se satellite  ${}^{1}J_{C-Se} = 12$  Hz, CH<sub>2</sub>Se).  ${}^{1}H^{77}Se$ HMBC NMR (600 MHz, 114 MHz, CDCl<sub>3</sub>, 24°C):  $\delta = 144.48$  (s, CH<sub>2</sub>Se). DEI-MS: m/z = 207[M-CH<sub>3</sub>]<sup>+</sup>.

#### Synthesis of 8,8-Dimethyl-7,9-dioxa-2-selena-3-thiaspiro[4.5]decane (3)

In a Schlenk falsk, 75 mg (0.23 mmol) of 5-selenocyanatomethyl-5-acetylthiomethyl-2,2dimethyl-1,3-dioxane which was prepared following the same procedure reported for similar compounds<sup>23</sup> were placed under nitrogen atmosphere and dissolved in 10 ml of ethanol. After addition of 86 mg (2.27 mmol) NaBH<sub>4</sub>, the reaction mixture was stirred overnight at room temperature and washed with 20 mL water, 3 mL Glacial acetic acid and 20 mL CHCl<sub>3</sub> was added. The above solution together with a solution of I<sub>2</sub> dissolved in CHCl<sub>3</sub> were added dropwise and simultaneously to a solution made of 40 mL of CHCl<sub>3</sub> and 10 mL of triethylamine under a nitrogen atmosphere. Upon complete addition, the reaction mixture was washed with water, dried with Na<sub>2</sub>SO<sub>4</sub> and the solvent removed in vacuo. The resulting residue was purified by column chromatography (eluent: hexane / CH<sub>2</sub>Cl<sub>2</sub> 4:1) to give an orange solid. Yield: 51% (30 mg, 0.12 mmol). Elemental analysis for C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>SSe: Calc.: C 28.17; H 4.73; S 15.04. found: C 28.41; H 4.81; S 15.22. <sup>1</sup>H NMR (400 MHz, acetone-d<sup>6</sup>, 24°C):  $\delta$  = 4.09 (t, 2H, <sup>3</sup>J<sub>H-H</sub> = 5.36 Hz, OH), 3.61-3.71 (m, 4H, CH<sub>2</sub>OH), 3.23 (s, with <sup>77</sup>Se satellite <sup>2</sup>J<sub>H-Se</sub> = 15.26 Hz, 2H, CH<sub>2</sub>Se), 3.10 (s, 2H, CH<sub>2</sub>S). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, acetone-d<sup>6</sup>, 24°C):  $\delta$  = 64.64 (s, CH<sub>2</sub>OH), 59.56 (s, CCH<sub>2</sub>OH), 45.11 (s, CH<sub>2</sub>S), 35.10 (s, with <sup>77</sup>Se satellite <sup>1</sup>J<sub>C-Se</sub> = 65.27 Hz, CH<sub>2</sub>Se). <sup>1</sup>H<sup>77</sup>Se HMBC NMR (400 MHz, 76 MHz, CDCl<sub>3</sub>, 24°C):  $\delta$  = 412.95 (s, CH<sub>2</sub>Se). DEI-MS: *m*/*z* = 253 [M]<sup>+</sup>.

#### General procedure for the synthesis of the diiron complexes 5-8.

A solution of  $Fe_3(CO)_{12}$  (200 mg, 0.40 mmol) and compounds 1-4, respectively, (0.40 mmol) in toluene (30 mL) was heated at reflux for 2 h under N<sub>2</sub>. The green solution turned deep-red and the solvent was removed under reduced pressure. The residue was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>-hexane mixture (2: 3) to isolate a red solid. Suitable crystals for single-crystal X-ray analysis were accessible by slow evaporation of a solution of the compound in hexane at 7 °C.

[Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu$ -(S(CH<sub>2</sub>)<sub>2</sub>S)C(C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>)}] (5). Yield: 57% (110 mg, 226 mmol). Elemental analysis for C<sub>14</sub>H<sub>14</sub>Fe<sub>2</sub>O<sub>8</sub>S<sub>2</sub>: Calc.: C 34.59; H 2.90; S 13.19 found: C 34.83; H 2.92; S 13.25. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$  = 3.53 (s, 4H, CH<sub>2</sub>O), 2.23 (s, 4H, CH<sub>2</sub>S), 1.31 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 23°C):  $\delta$  = 207.3 (s, CO), 98.8 (s, OCCH<sub>3</sub>), 68.1 (s, CCH<sub>2</sub>O), 35.8 (s, CCH<sub>2</sub>O), 26.8 (s, CH<sub>2</sub>S), 23.3 (s, CH<sub>3</sub>). IR ( $\nu$ <sub>CO</sub>, cm<sup>-1</sup>): 2073 (s), 2029 (s), 2015 (s), 1997(s), 1981 (s), 1971 (s), 1960 (bs). DEI-MS: m/z = 486 [M]<sup>+</sup>, 458 [M-CO]<sup>+</sup>, 430 [M-2CO]<sup>+</sup>, 402 [M-3CO]<sup>+</sup>, 374 [M-4CO]<sup>+</sup>, 346 [M-5CO]<sup>+</sup>, 318 [M-6CO]<sup>+</sup>.

[Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu$ -(Se(CH<sub>2</sub>)<sub>2</sub>Se)C(C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>)}] (6). Yield: 54% (125 mg, 0.22 mmol). Elemental analysis for C<sub>14</sub>H<sub>14</sub>Fe<sub>2</sub>O<sub>8</sub>Se<sub>2</sub>: Calc.: C 29.0; H 2.43 found.: C 29.49; H 2.44. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 3.50 (s, 4H, CH<sub>2</sub>O), 2.25 (s, 4H, CH<sub>2</sub>Se), 1.31 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 208.2 (s, CO), 98.9 (s; OCCH<sub>3</sub>), 66.9 (s, CCH<sub>2</sub>O), 35.3 (s, CCH<sub>2</sub>O), 23.3 (s, CH<sub>3</sub>), 17.9 (s, with <sup>77</sup>Se satellite <sup>1</sup>J<sub>C-Se</sub> = 85.53 Hz, CH<sub>2</sub>Se). <sup>1</sup>H<sup>77</sup>Se HMBC

NMR (400 MHz, 76 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 69.73$  (s, CH<sub>2</sub>Se). IR: ( $v_{CO}$ , cm<sup>-1</sup>): 2064 (s), 2021 (s), 1999 (s), 1979 (s), 1970 (s), 1948 (bs). DEI-MS: m/z = 582 [M]<sup>+</sup>, 554 [M-CO]<sup>+</sup>, 526 [M-2CO]<sup>+</sup>, 498 [M-3CO]<sup>+</sup>, 470 [M-4CO]<sup>+</sup>, 442 [M-5CO]<sup>+</sup>, 414 [M-6CO]<sup>+</sup>.

[Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu$ -(Se(CH<sub>2</sub>)<sub>2</sub>S)C(C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>)} (7). Yield: 59% (126 mg, 0.236 mmol). Elemental analysis for C<sub>14</sub>H<sub>14</sub>Fe<sub>2</sub>O<sub>8</sub>SSe: Calc: C 31.55; H 2.65; S 6.02 found.: C 31.70; H 2.70; S 6.00. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 24°C):  $\delta$  = 3.48-3.56 (m, 4H, CH<sub>2</sub>O), 2.31 (s, with <sup>77</sup>Se satellite <sup>2</sup>J<sub>H-Se</sub> = 17.48 Hz, 2H, CH<sub>2</sub>Se), 2.16 (s, 2H, CH<sub>2</sub>S), 1.31 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 207.8 (s, CO), 98.9 (s, OCCH<sub>3</sub>), 67.6 (s, CCH<sub>2</sub>O), 35.6 (s, CCH<sub>2</sub>O), 28.1 (s, CH<sub>2</sub>S), 24.0 (s, CH<sub>3</sub>), 23.3 (s, CH<sub>3</sub>), 16.9 (s, with <sup>77</sup>Se satellite <sup>1</sup>J<sub>C-Se</sub> = 83.12 Hz, CH<sub>2</sub>Se). <sup>1</sup>H<sup>77</sup>Se HMBC NMR (400 MHz, 76 MHz, CDCl<sub>3</sub>, 24°C):  $\delta$  = 56.01 (s, CH<sub>2</sub>Se). IR ( $\nu$ <sub>CO</sub>, cm<sup>-1</sup>): 2069 (s), 2025 (s), 2004 (s), 1982 (s), 1972 (s), 1950 (bs). DEI-MS: *m*/*z* = 534 [M]<sup>+</sup>, 506 [M-CO]<sup>+</sup>, 478 [M-2CO]<sup>+</sup>, 450 [M-3CO]<sup>+</sup>, 422 [M-4CO]<sup>+</sup>, 394 [M-5CO]<sup>+</sup>, 366 [M-6CO]<sup>+</sup>.

**[Fe<sub>2</sub>(CO)<sub>6</sub>{(\mu^2,\kappa^3-Se,C,O-SeCH<sub>2</sub>C<sub>7</sub>H<sub>12</sub>O<sub>2</sub><b>]**] (8). Yield: 42% (84 mg, 0.168 mmol). Elemental analysis for C<sub>14</sub>H<sub>14</sub>Fe<sub>2</sub>O<sub>8</sub>Se: Calc.: C 33.57; H 2.82 found: C 33.50; H 2.66. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 24°C):  $\delta$  = 5.30 (s, 1H, CHFe), 3.45 (d, <sup>2</sup>J<sub>H-H</sub> = 11.46 Hz, 1H, CH<sub>2</sub>O), 3.38 (d, <sup>2</sup>J<sub>H-H</sub> = 11.31 Hz. 1H, CH<sub>2</sub>Se), 3.30 (d, <sup>2</sup>J<sub>H-H</sub> = 11.39 Hz, 1H, CH<sub>2</sub>O), 2.74 (d, <sup>2</sup>J<sub>H-H</sub> = 11.42 Hz, 1H, CH<sub>2</sub>Se), 1.25 (s, 3H, OCCH<sub>3</sub>), 1.20 (s, 3H, OCCH<sub>3</sub>), 0.59 (s, 3H, CH<sub>2</sub>CCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>, 25°C):  $\delta$  = 215.5 (s, CO), 212.2 (s, CO), 209.9 (s, CO), 107.5 (s, CHFe), 102.3 (s, OCCH<sub>3</sub>), 67.3 (s, CH<sub>2</sub>O), 52.9 (s, CCHFe), 32.8 (s, with <sup>77</sup>Se satellite <sup>1</sup>J<sub>C-Se</sub> = 59.04 Hz. CH<sub>2</sub>Se), 28.7 (s, OCCH<sub>3</sub>), 21.9 (s, CH<sub>2</sub>CCH<sub>3</sub>), 18.4 (s, OCCH<sub>3</sub>). <sup>1</sup>H<sup>77</sup>Se HMBC NMR (600 MHz, 114 MHz, CDCl<sub>3</sub>, 24°C):  $\delta$  = 31.49 (s, CH<sub>2</sub>Se). IR (*v*<sub>CO</sub>, cm<sup>-1</sup>): 2059 (s), 2008 (s), 1978 (s), 1956 (s), 1931 (bs). DEI-MS: *m*/*z* = 502 [M]<sup>+</sup>, 474 [M-CO]<sup>+</sup>, 446 [M-2CO]<sup>+</sup>, 418 [M-3CO]<sup>+</sup>, 388 [M-3CO-2CH3]<sup>+</sup>, 360 [M-4CO-2CH3]<sup>+</sup>, 332 [M-5CO-2CH3]<sup>+</sup>, 304 [M-6CO-2CH3]<sup>+</sup>.

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