Supporting Information

Steric Effect of the Dithiolato Linker on the Reduction Mechanism of $[Fe_2(CO)_6\{\mu\text{-}(XCH_2)_2CRR'\}]$ Hydrogenase Models (X = S, Se)

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Synthesis and Spectroscopic Data of Compounds **1-4**, **7-10**, **12** and **13**

1,3-dichloro-2-methylpropane (7)[1,2]

A mixture of 54.07 g (0.60 mol) 2-methyl-1,3-propanediol and 3.55 g (12.75 mmol) triphenylphosphine oxide were placed in a flask and at 80 °C 77.33 g (0.65 mol) thionyl chloride was added dropwise within two hours under stirring. The temperature was raised to 100 °C and further thionyl chloride (101.12 g, 0.85 mol) was added dropwise within two hours. To complete the reaction the whole mixture was additionally stirred at 130 °C for three hours. After cooling to room temperature water was carefully added followed by a concentrated solution of $NaHCO_3$ up to neutral reaction. The mixture was extracted three times with CH_2Cl_2, the combined organic phases were washed with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by distillation (135–137 °C) at normal pressure to yield a colourless liquid. Yield: 61.1 g (0.481 mol, 80.2 %). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 3.58 (dd, $^2J_{H\text{-}H}$ = 11.0 Hz, $^3J_{H\text{-}H}$ = 5.0 Hz, 2 H, C*H*$_2$Cl), 3.53 (dd, $^2J_{H\text{-}H}$ = 11.0 Hz, $^3J_{H\text{-}H}$ = 6.2 Hz, 2 H, C*H*$_2$Cl), 2.15-2.23 (m, 1 H, C*H*), 1.07 (d, $^3J_{H\text{-}H}$ = 7.0 Hz, 3 H, C*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 25 °C): δ = 47.06 (s, *C*H$_2$Cl), 37.56 (s, *C*H), 15.69 (s, *C*H$_3$).

1,3-dichloro-2,2-dimethylpropane (9)[2]

This compound was prepared following the same procedure as for 1,3-dichloro-2-methylpropane using 41.66 g (0.400 mol) 2,2-dimethyl-1,3-propanediol, 2.37 g (8.50 mmol) triphenylphosphine oxide and 119.00 g (1.056 mol) thionyl chloride. Distillation at normal pressure (145–149 °C) gave the product as a colourless liquid. Yield: 48.10 g (0.341 mol, 85.3 %). ^{1}H NMR (200 MHz, $CDCl_3$, 23 °C): δ = 3.45 (s, 4 H, C*H*$_2$Cl), 1.07 (s, 6 H, C*H*$_3$). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$, 24 °C): δ = 51.91 (s, *C*H$_2$Cl), 37.29 (s, *C*CH$_3$), 23.39 (s, *C*H$_3$). DEI-MS: *m/z* = 91 [M - CH_2Cl]$^+$.

2-methylpropane-1,3-dithiol (8)[3-5]

A mixture of 33.63 g (0.14 mole) $Na_2S{\cdot}9\ H_2O$ and 4.49 g (0.14 mol) sulfur was suspended in 200 mL DMF. 1,3-dichloro-2-methylpropane (**7**, 17.78 g, 0.14 mol) was added dropwise under stirring and the mixture was heated to 130 °C for 16 hours. After cooling to room temperature, water was added and the reaction mixture was extracted three times with CH_2Cl_2. The solvent was removed from the combined organic phases and 200 mL of ethanol (96 %) was added. Within two hours 6.00 g (0.159 mol) of $NaBH_4$ was added in small portions and the mixture was allowed to stir for one hour at room temperature. An excess of diluted sulfuric acid was added and the mixture was extracted three times with pentane. The combined organic phases were washed with water, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. Distillation at 6.2 mbar (58-62 °C) gave the product as colourless liquid. Yield: 12.60 g (0.103 mol, 73.6 %). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ = 2.49-2.63 (m, 4 H, C*H*$_2$SH), 1.70-1.82 (m, 1 H, C*H*), 1.23 (t, $^3J_{H\text{-}H}$ = 8.4 Hz, 2 H, S*H*), 1.01 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 3 H, C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 24°C): δ = 38.46 (s, *C*H), 29.27 (s, *C*H$_2$SH), 17.72 (s, *C*H$_3$). DEI-MS: *m/z* = 122 $[M]^+$.

4,4-dimethyl-1,2-dithiolane (10)[6-8]

In a schlenk vessel 5.11 g (21.27 mmol) $Na_2S{\cdot}9\ H_2O$ and 682 mg (21.27 mmol) sulfur were placed and suspended in 25 mL DMF. 3.00 g (21.27 mmol) 1,3-dichloro-2,2-dimethylpropane (**9**) was added and the mixture was stirred at 80-85 °C for three days. After cooling to room temperature water was added and the mixture was extracted three times with CH_2Cl_2, the combined organic phases were washed with water and the solvent was removed under reduced pressure. Purification was done by column chromatography (eluent: hexane) and gave a yellow oil. Yield: 860 mg (6.41 mmol, 30.1 %). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ = 2.85 (s, 4 H, SC*H*$_2$), 1.22 (s, 6 H, C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 24 °C): δ = 51.33 (s, S*C*H$_2$), 47.31 (s, *C*CH$_3$), 27.03 (s, *C*H$_3$). DEI-MS: *m/z* = 134 $[M]^+$.

4,4-dimethyl-1,2-diselenolane (12)[9-12]

A Schlenk vessel was charged with 3.55 g (45.00 mmol) powdered selenium and 1.21 g (32.09 mmol) $NaBH_4$. After cooling down to 0 °C 50 mL of ethanol (96 %) was added, the mixture was warmed to room temperature and additionally refluxed for two hours. Ethanol was removed by a stream of nitrogen at room temperature and 15 mL of DMF was added followed by 2.12 g (15.00 mmol) of 1,3-dichloro-2,2-dimethylpropane (**9**). This mixture was stirred for 30 minutes at 130-140 °C. After cooling down to room temperature 100 mL of water was added and the mixture was three times extracted with hexane. The combined organic phases were washed with water, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was recrystallized from hexane to give **12** as red-brown crystals. Yield: 2.10 g (9.21 mmol, 61.4 %). ^{1}H NMR (400 MHz, $CDCl_3$, 24°C): δ = 3,08 (s with ^{77}Se satellites, $^2J_{H\text{-}Se}$ = 15.6 Hz, 4 H, SeC*H*$_2$), 1.26 (s, 6 H, C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 24°C): δ = 49.20 (s, *C*CH_3), 44.42 (s with ^{77}Se satellites, $^1J_{C\text{-}Se}$ = 66.8 Hz, Se*C*H_2), 26.51 (s, *C*H_3). ^{1}H^{77}Se HMBC NMR (400 MHz, 76 MHz, $CDCl_3$, 24°C): δ = 278.5 (s, *Se*CH_2).

[$Fe_2(CO)_6${μ-$(SCH_2)_2CH_2$}] (1)[13,14]

This complex was prepared according to the general procedure in the Experimental Part using 1.01 g (2.00 mmol) $Fe_3(CO)_{12}$ and 216 mg (2.00 mmole) propane-1,3-dithiol. Yield: 510 mg (1.32 mmol, 67.4 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 2.07-2.18 (m, 4 H, SC*H*$_2$), 1.74-1.84 (m, 2 H, SCH_2C*H*$_2$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 24 °C): δ = 207.71 (s, *C*O), 30.34 (s, SCH_2*C*H_2), 23.20 (s, S*C*H_2). IR: υ(CO) = 2070, 2032 (b), 1982, 1945 (b). DEI-MS: *m/z* = 386 $[M]^+$, 358 $[M - CO]^+$, 330 $[M - 2CO]^+$, 302 $[M - 3CO]^+$, 274 $[M - 4CO]^+$, 246 $[M - 5CO]^+$, 218 $[M - 6CO]^+$, 176 $[Fe_2S_2]^+$. Elemental analysis for $C_9H_6Fe_2O_6S_2$: calculated C 28.01, H 1.57, S 16.62; found C 28.48, H 1.56, S 16.96.

$[Fe_2(CO)_6\{\mu\text{-}(SCH_2)_2CHMe\}]$ (2)[15]

This complex was prepared according to the general procedure in the Experimental Part using 412 mg (0,818 mmol) $Fe_3(CO)_{12}$ and 100 mg (0.818 mmol) 2-methylpropane-1,3-dithiol (**8**). Yield: 180 mg (0.450 mmol, 55.0 %). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ = 2.45-2.65 (m, 2 H, SC*H*$_2$), 1.16-1.41 (m, 3 H, SC*H*$_2$ and C*H*), 0.77-0.98 (m, 3 H, C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 24 °C): δ = 207.88 (s, *C*O), 207.57 (s, *C*O), 38.06 (s, *C*H), 30.12 (s, S*C*H$_2$), 22.52 (s, *C*H$_3$). IR: υ(CO) = 2079, 2070 (b), 2024 (b), 1992 (b), 1980, 1956 (b). DEI-MS: *m/z* = 400 $[M]^+$, 372 $[M - CO]^+$, 344 $[M - 2CO]^+$, 316 $[M - 3CO]^+$, 288 $[M - 4CO]^+$, 260 $[M - 5CO]^+$, 232 $[M - 6CO]^+$, 176 $[Fe_2S_2]^+$. Elemental analysis for $C_{10}H_8Fe_2O_6S_2$: calculated C 30.03, H 2.02, S 16.03; found C 30.29, H 1.98, S 16.05.

$[Fe_2(CO)_6\{\mu\text{-}(SCH_2)_2CMe_2\}]$ (3)[16,17]

This complex was prepared according to the general procedure in the Experimental Part using 593 mg (1.177 mmol) $Fe_3(CO)_{12}$ and 158 mg (1.177 mmol) 4,4-dimethyl-1,2-dithiolane (**10**). Yield: 330 mg (0.797 mmol, 67.7 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 2.06 (s, 4 H, SC*H*$_2$), 0.96 (s, 6 H, C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 24 °C): δ = 207.67 (s, *C*O), 33.37 (s, S*C*H$_2$), 33.24 (s, *C*CH$_3$), 30.35 (s, *C*H$_3$). IR: υ(CO) = 2077, 2068, 2020 (b), 1991 (b), 1953 (b). DEI-MS: *m/z* = 414 $[M]^+$, 386 $[M - CO]^+$, 358 $[M - 2CO]^+$, 330 $[M - 3CO]^+$, 302 $[M - 4CO]^+$, 274 $[M - 5CO]^+$, 246 $[M - 6CO]^+$, 190 $[Fe_2S_2CH_2]^+$, 176 $[Fe_2S_2]^+$. Elemental analysis for $C_{11}H_{10}Fe_2O_6S_2$: calculated C 31.91, H 2.43, S 15.49; found C 32.12, H 2.37, S 15.40.

$[Fe_2(CO)_6\{\mu\text{-}(SeCH_2)_2CH_2\}]$ (4)[18,19]

This complex was prepared according to the general procedure in the Experimental Part using 300 mg (0.595 mmol) $Fe_3(CO)_{12}$ and 150 mg (0.595 mmol) 1,3-diselenocyanatopropane. Yield: 114 mg (0.238 mmole, 39.9 %). ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 2.08-2.31 (m, 4 H, SeC*H*$_2$), 1.54-1.71 (m, 2 H, SeCH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 23 °C):

δ = 208.73 (s, *C*O), 30.08 (s, $SeCH_2CH_2$), 14.52 (s with ^{77}Se satellites, $^1J_{C\text{-}Se}$ = 76.9 Hz, $SeCH_2$). $^1H^{77}Se$ HMBC NMR (600 MHz, 114 MHz, $CDCl_3$, 25 °C) δ = 143.9 (s, *Se*CH_2). IR: υ(CO) = 2062, 2026 (b), 1976 (b), 1942 (b). DEI-MS: *m/z* = 482 $[M]^+$, 454 $[M - CO]^+$, 426 $[M - 2CO]^+$, 398 $[M - 3CO]^+$, 370 $[M - 4CO]^+$, 342 $[M - 5CO]^+$, 314 $[M - 6CO]^+$, 286 $[Fe_2Se_2CH_2]^+$, 272 $[Fe_2Se_2]^+$, 192 $[Fe_2Se]^+$. Elemental analysis for $C_9H_6Fe_2O_6Se_2$: calculated C 22.53, H 1.26; found C 22.44, H 1.16.

$[Fe_2(CO)_6\{\mu\text{-bdt}\}]$ (bdt = benzenedithiolato) (13)[20,21]

This complex was prepared according to the general procedure in the Experimental Part using 319 mg (0.633 mmol) $Fe_3(CO)_{12}$ and 90 mg (0.633 mmol) 1,2-benzenedithiol. Yield: 150 mg (0.357 mmol, 56.4 %). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.07-7.16 (m, 2 H, SCC*H*), 6.57-6.66 (m, 2 H, SCCHC*H*). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, 25 °C): δ = 207.47 (s, *C*O), 147.45 (s, S*C*), 127.95 (s, SC*C*H), 126.79 (s, SCCH*C*H). IR: υ(CO) = 2077, 2074, 2050, 2031, 2001, 1991, 1980, 1960 (b). DEI-MS: *m/z* = 420 $[M]^+$, 392 $[M - CO]^+$, 364 $[M - 2CO]^+$, 336 $[M - 3CO]^+$, 308 $[M - 4CO]^+$, 280 $[M - 5CO]^+$, 252 $[M - 6CO]^+$, 176 $[Fe_2S_2]^+$. Elemental analysis for $C_{12}H_4Fe_2O_6S_2$: calculated C 34.32, H 0.96, S 15.27; found C 34.41, H 0.84, S 15.39.

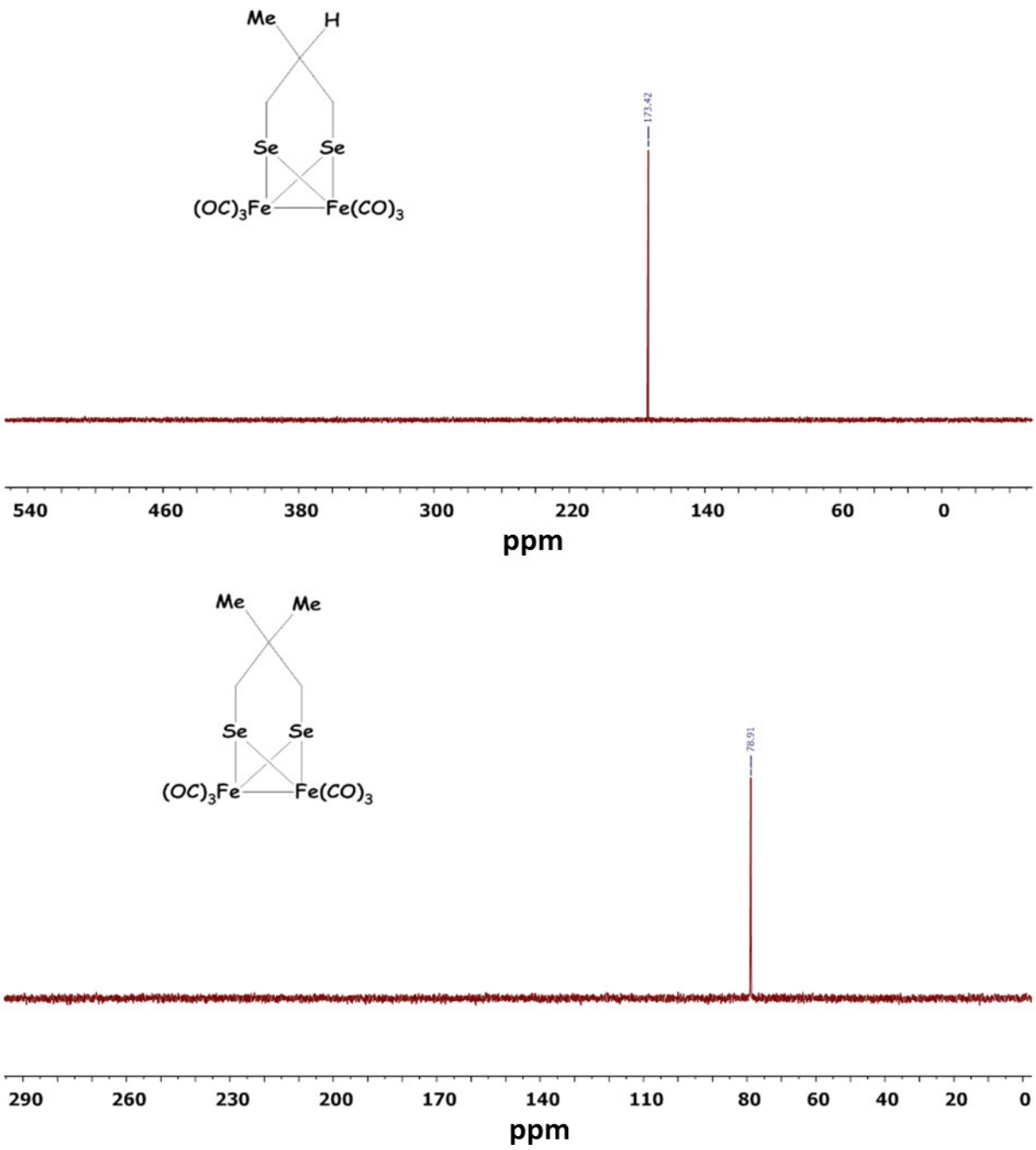


Figure S1. ^{77}Se NMR spectra (400 MHz, 76 MHz, $CDCl_3$, 24 °C) of complexes **5** (δ = 173.42 ppm, above) and **6** (δ = 78.91 ppm, below).

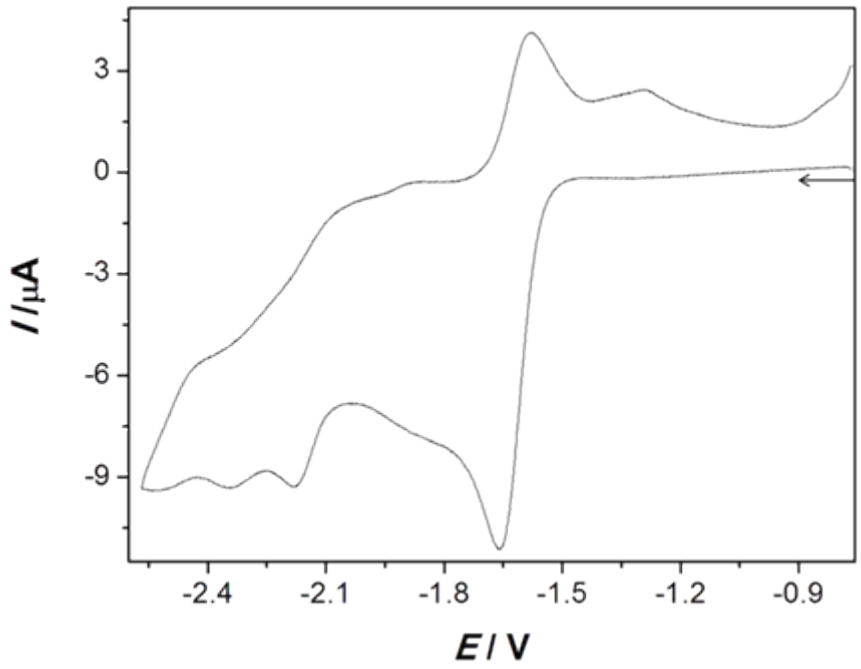
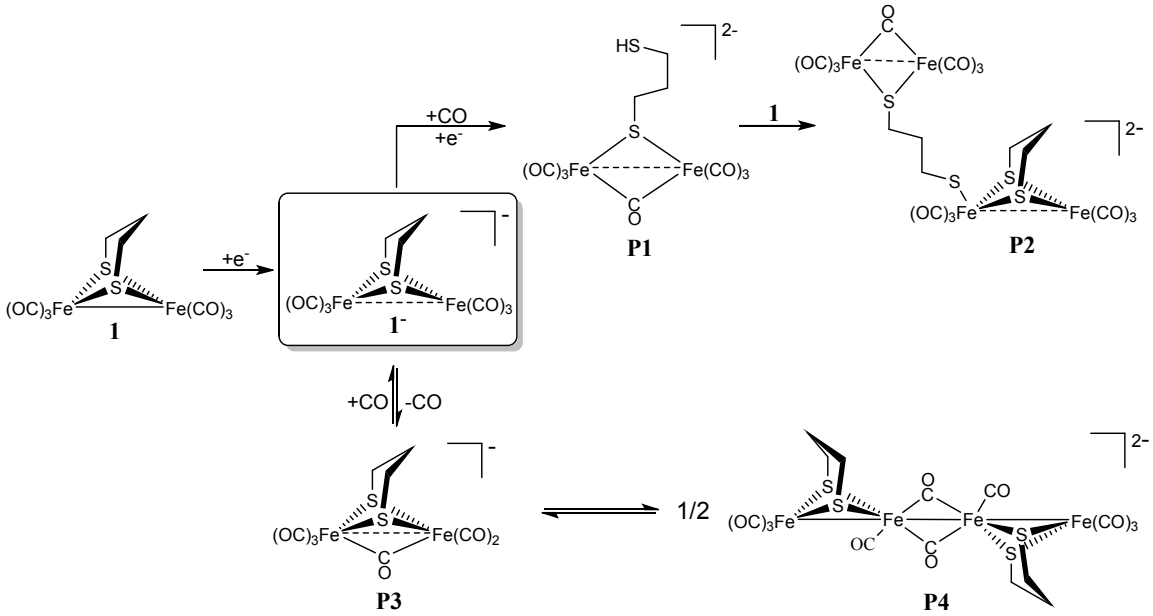


Figure S2. Cyclic voltammetry of 1.0 mM **1** in MeCN-[*n*-Bu_4N][BF_4] (0.1 M) solutions at v = 0.2 $V \cdot s^{-1}$. Glassy carbon disk (d = 1.6 mm). The arrow indicates the scan direction. The potentials E is given in V and referenced to the ferrocenium/ferrocene couple.

Scheme S1. Pathways of decomposition of the monoanion **1**$^-$ during the voltammetric experiment.



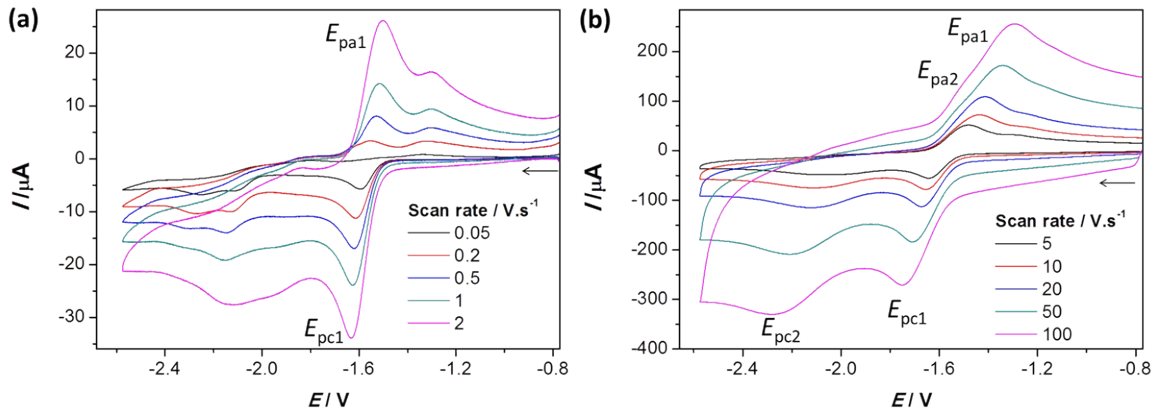


Figure S3. Cyclic voltammetry of 1.0 mM **4** in MeCN-[*n*-Bu_4N][BF_4] (0.1 M) solution at 0.05 V·s^{-1} ≥ *v* ≥ 100 V·s^{-1}. Glassy carbon disk (*d* = 1.6 mm). The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the ferrocenium/ferrocene couple.

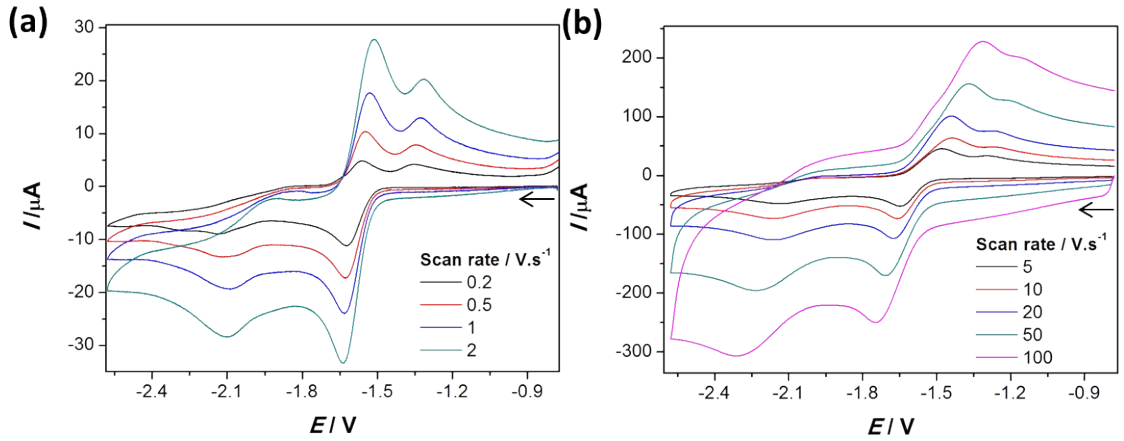


Figure S4. Cyclic voltammetry of 1.0 mM **5** in MeCN-[*n*-Bu_4N][BF_4] (0.1 M) solution at 0.2 V·s^{-1} ≥ *v* ≥ 100 V·s^{-1}. Glassy carbon disk (*d* = 1.6 mm). The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the ferrocenium/ferrocene couple.

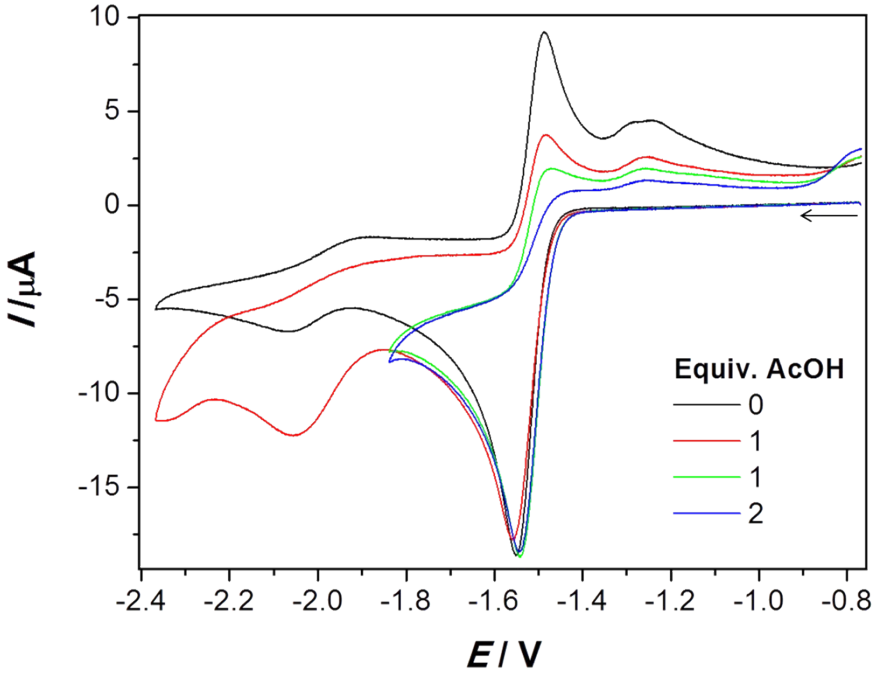


Figure S5. Cyclic voltammetry of 1.0 mM **6** in MeCN-[*n*-Bu_4N][BF_4] (0.1 M) solution at 0.2 $V \cdot s^{-1}$ in the absence and presence of 1 and 2 equiv. AcOH. Glassy carbon disk (d = 1.6 mm). The arrow indicates the scan direction. The potentials E are given in V and referenced to the ferrocenium/ferrocene couple.

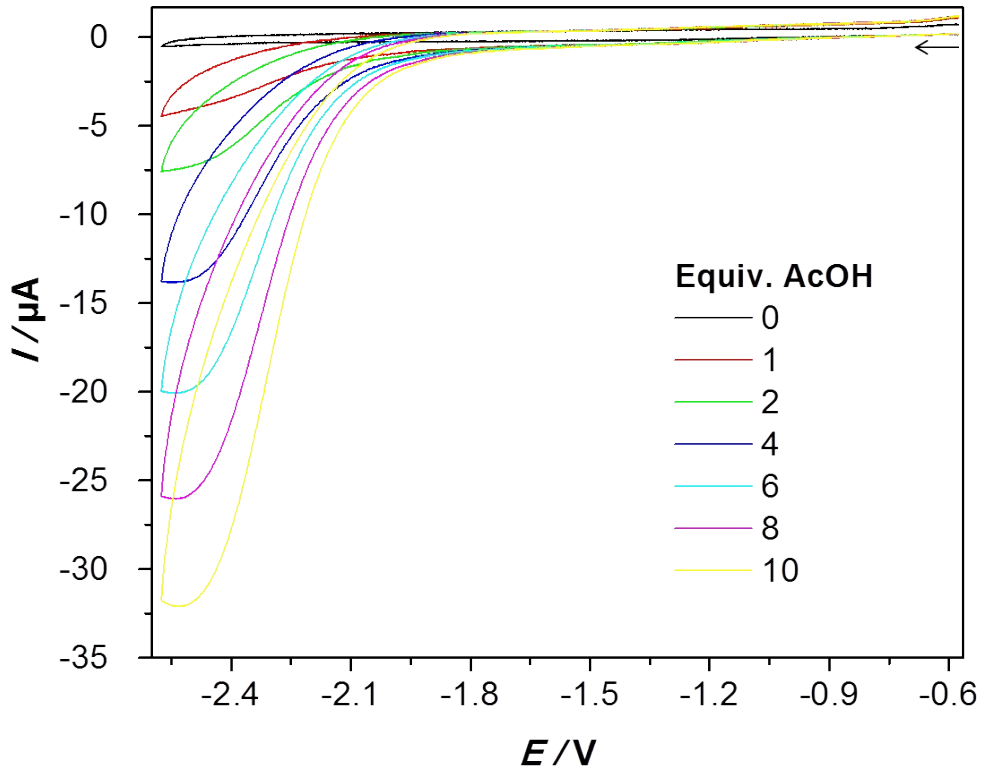


Figure S6. Cyclic voltammetry of various equivalents of AcOH MeCN-[*n*-Bu_4N][BF_4] (0.1 M) solution at 0.2 $V \cdot s^{-1}$ in the absence of catalyst (model complex). Glassy carbon disk (*d* = 1.6 mm). The arrow indicates the scan direction. The potentials *E* are given in V and referenced to the ferrocenium/ferrocene couple.

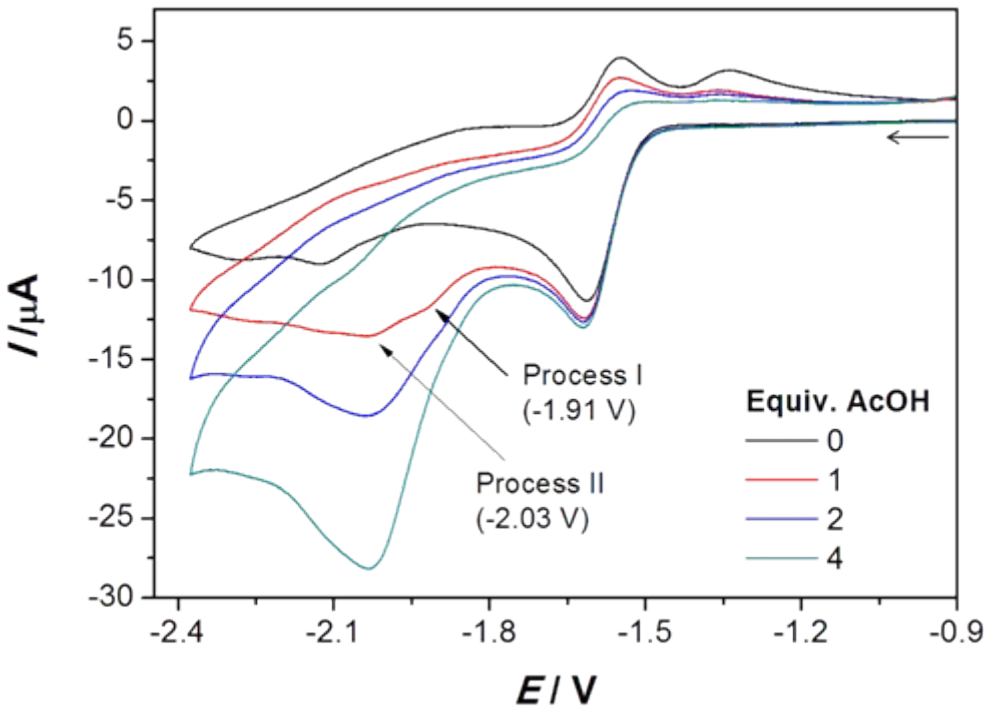


Figure S7. Cyclic voltammetry of 1.0 mM complex **6** in MeCN-[*n*-Bu_4N][BF_4] (0.1 M) at 0.2 $V \cdot s^{-1}$ in the presence of 1-4 equiv. AcOH. Glassy carbon disk (d = 1.6 mm). The arrow indicates the scan direction. The potentials E are given in V and referenced to the ferrocenium/ferrocene couple.

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