Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Material

Selenium makes the difference: Protonation of [FeFe]-hydrogenase mimics with diselenolato ligands

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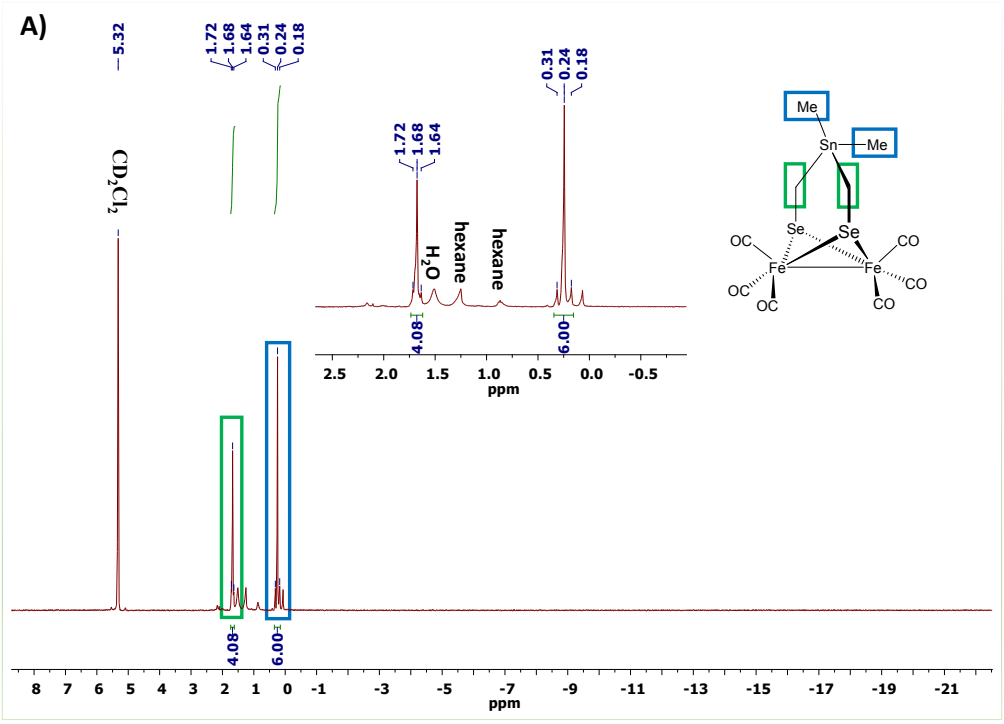
Figure S1. A) ^{1}H NMR spectrum (CD_2Cl_2) of complex **4** without $HBF_4{\cdot}Et_2O$. **B)** ^{1}H NMR spectrum (CD_2Cl_2) of complex **4** with (100 equiv.) $HBF_4{\cdot}Et_2O$. (●) peaks of Et_2O in the acid.



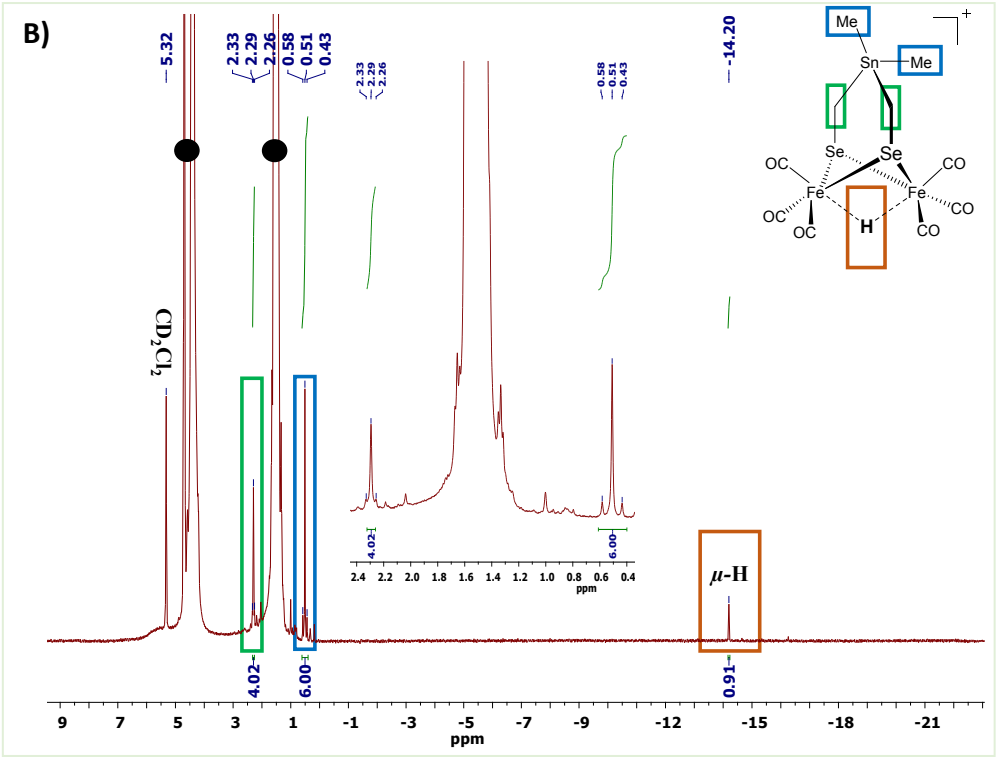


Figure S2. The ^{1}H, $^{77}Se\{H\}$ HMBC NMR spectrum of **4μH^{+}** in CD_2Cl_2.

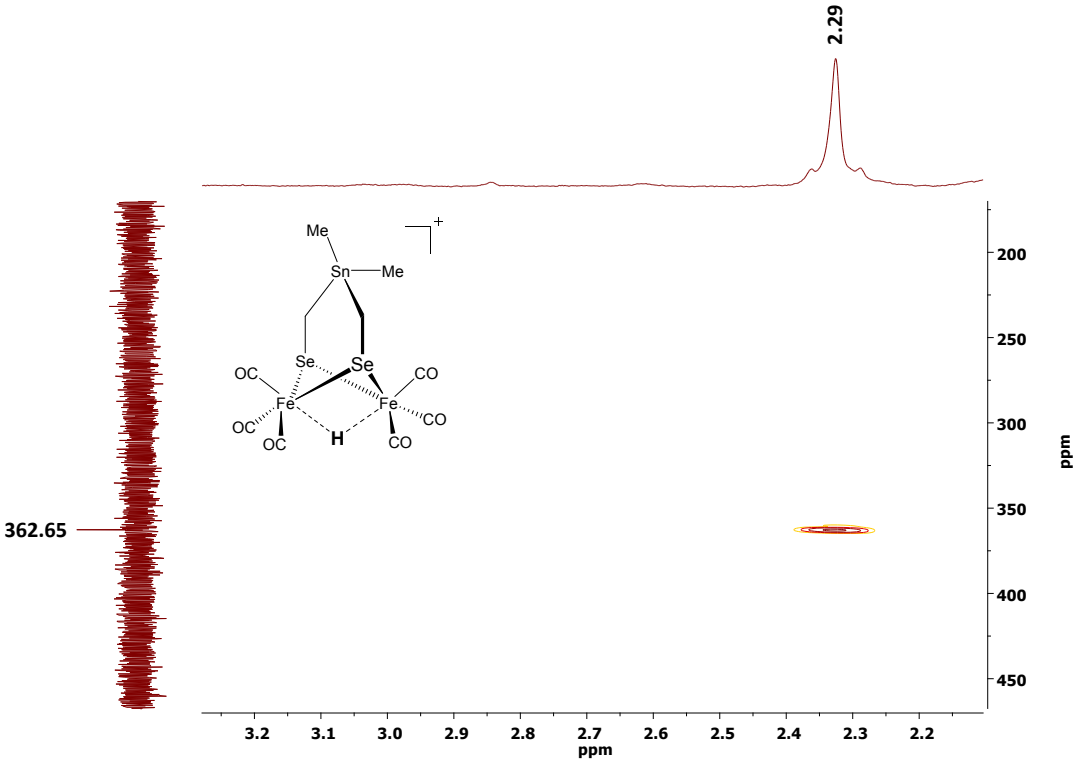


Figure S3. The high field ^{1}H NMR spectrum (CD_2Cl_2) of complexes **7** (blue), **8** (green) and **9** (red) with 100 equiv. $HBF_4 \cdot Et_2O$.

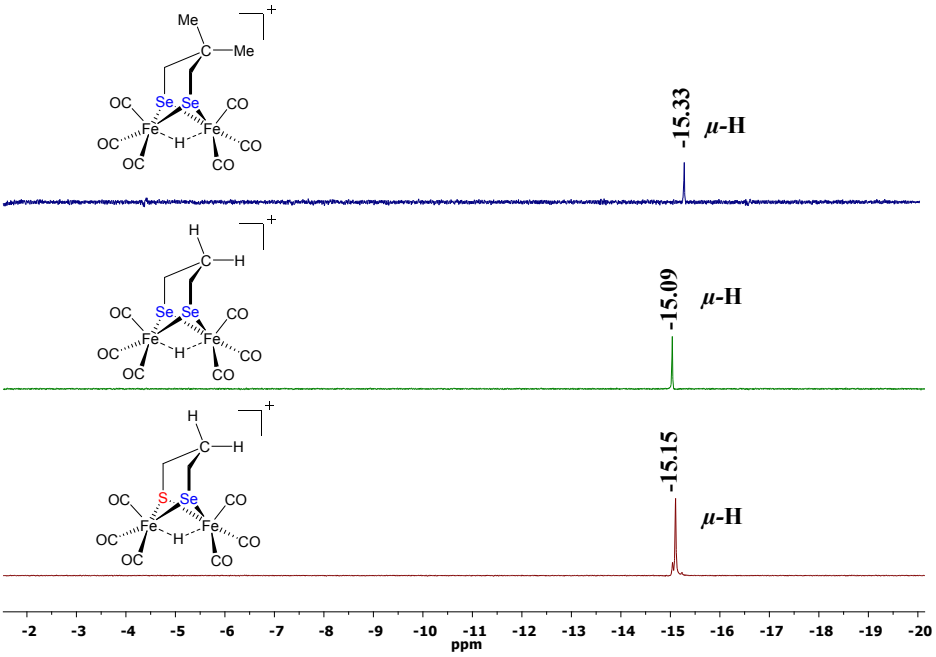


Figure S4. ^{1}H NMR spectrum (CD_2Cl_2) of complex **4** with 100 equiv. CF_3CO_2H (top) and ^{77}Se{H} NMR spectrum (CD_2Cl_2) of complex **4** with 100 equiv. CF_3CO_2H (bottom). (▼) Signals for the new CH_2 (2.33 ppm) and CH_3 (0.59 ppm) moieties. (●) Signals for the CH_2 and CH_3 in the parent complex.

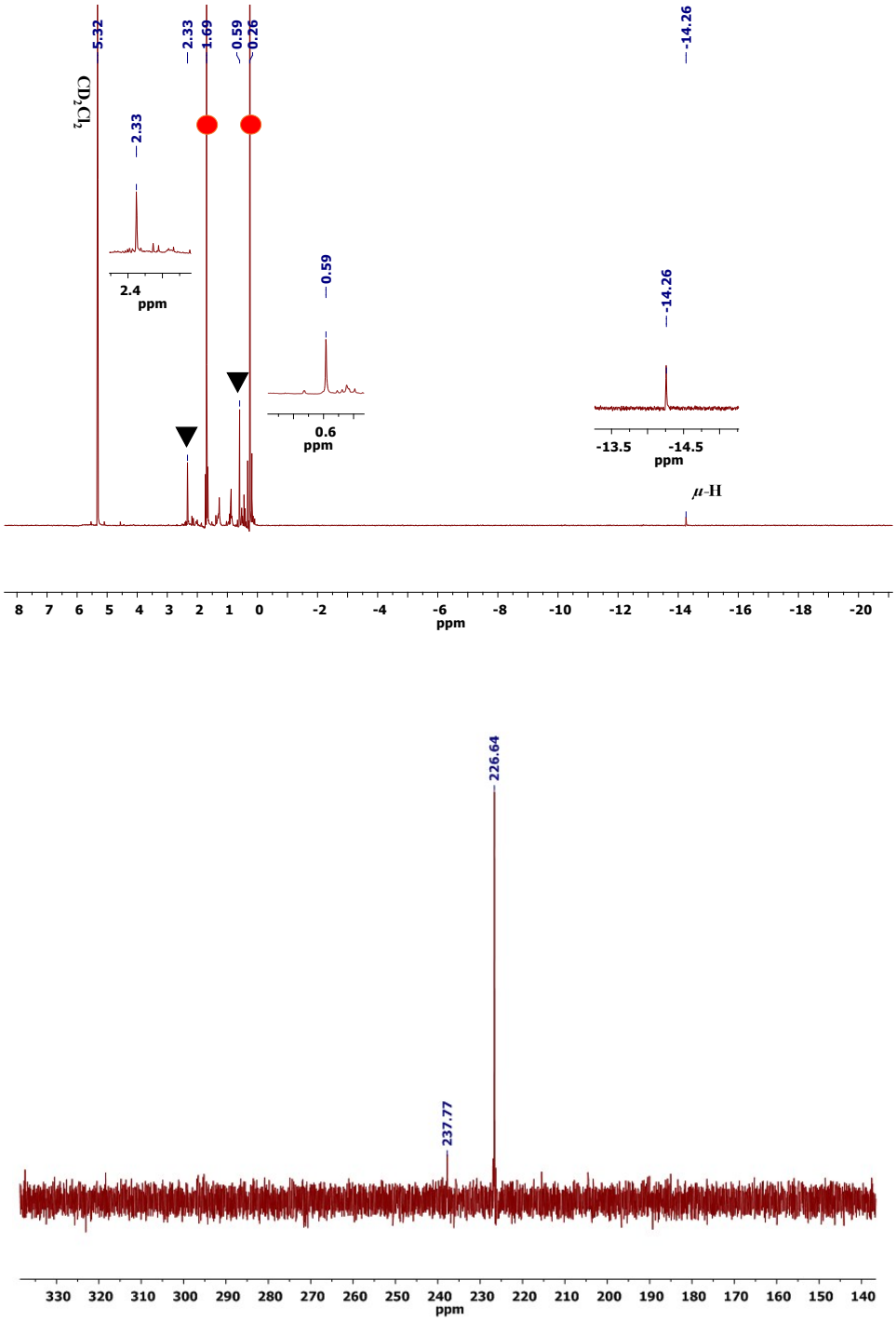
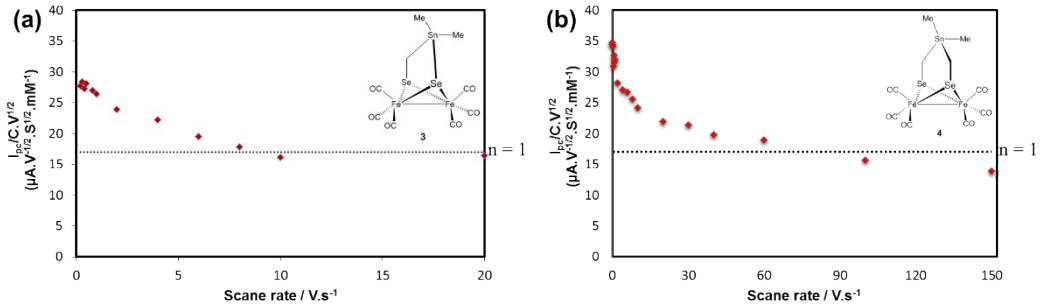


Figure S5. The scan rates dependence of the current function of the primary reduction peaks of (a) 0.87 mM complex **3** and (b) 1.0 mM complex **4** in CH_2Cl_2-[*n*-Bu_4N][PF_4] (0.1 M) solutions. Glassy carbon electrode (A = 0.0206 cm^2). The dashed line represents the current function expected for a one electron process assuming $D \approx 9 \times 10^{-6}$ cm^2 S^{-1}, a value calculated for various [FeFe]-Hydrogenase models.



The current function ($I_{pc}/C.v^{1/2}$) is given by the equation $I_{pc}/C.v^{1/2}$ = (2.69 x 10^5)$\cdot A \cdot D^{1/2} \cdot n^{3/2}$, where I_{pc} is the cathodic peak current in µA, C is the bulk concentration of the complex in mM, A is the surface area of the electrode in cm^2, $D \approx 9 \times 10^{-6}$ cm^2 s^{-1} and n is the number of electrons responsible for the reduction event. In general, when the reduction process does not have any chemical route (simple E mechanism, n =1), the current function of this reduction process should remain constant at all scan rates since 2.69 x 10^5)$\cdot A \cdot D^{1/2} \cdot n^{3/2}$ is constant. In contrast, when an ECE mechanism (n = 2) in which a chemical process takes place, the current function of this reduction process decreases significantly toward that expected for a one electron as the scan rates increase. This means, at higher scan rates there is no enough time for such a chemical process to occur and thus the second electron transfer will not take place (i.e. conversion the mechanism from ECE to simple E process).

Figure S6. Cyclic voltammogam of 1 mM complexes $[Fe_2(CO)_6\{\mu\text{-}(SCH_2)_2SnMe_2\}]$, **4S**, (black line) and **4** (red line) in CH_2Cl_2-[*n*-Bu_4N][PF_4] (0.1 M) solution at 0.2 V s^{-1} scan rate. The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the Fc^+/Fc couple.

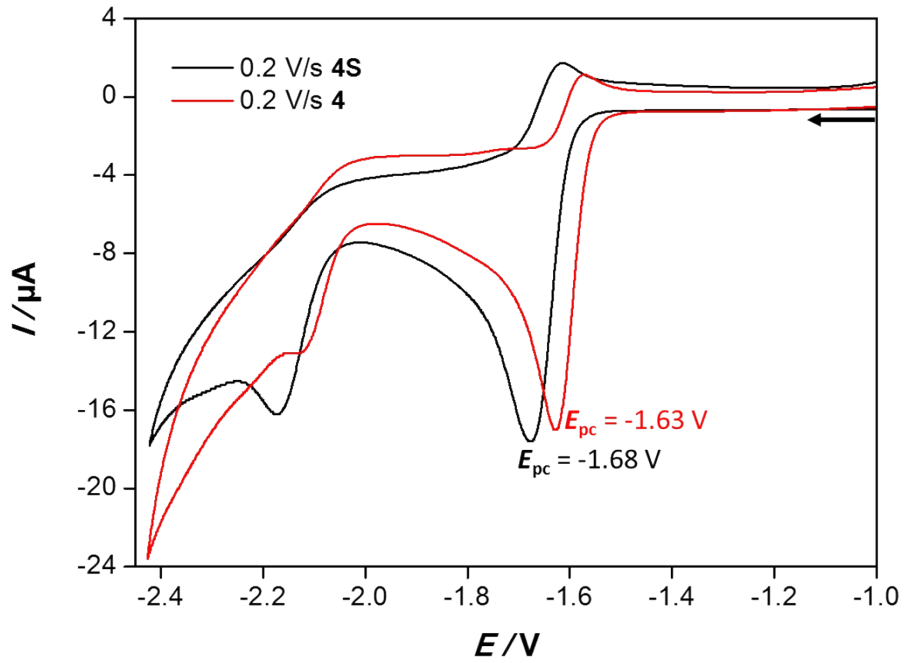


Figure S7. Cyclic voltammogam of various concentration of AcOH in CH_2Cl_2-[*n*-Bu_4N][PF_4] (0.1 M) solution at 0.2 V s^{-1} scan rate in the absence of catalyst (mdel complexes). The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the Fc^+/Fc couple.