

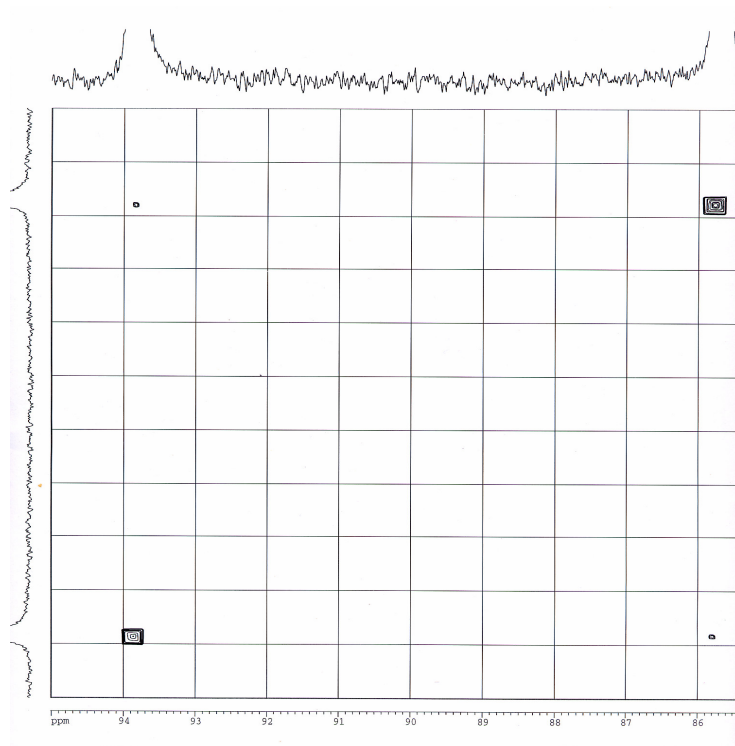
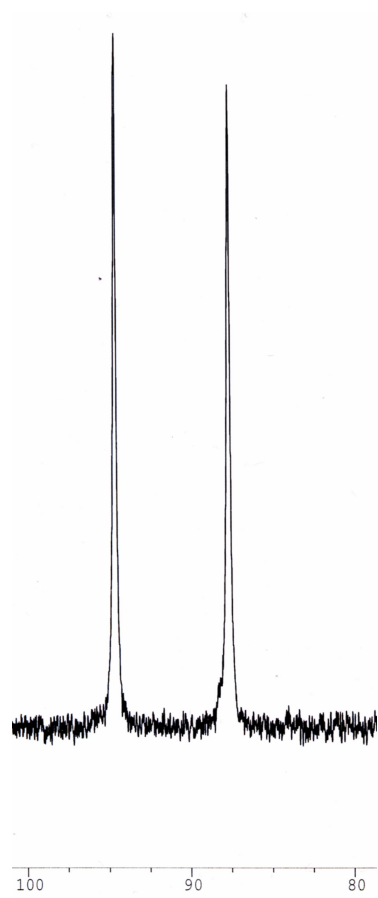
Synthesis of 2

1.384 g of $[\text{Fe}_2\{\mu\text{-SCH}_2\text{N}(\text{iPr})\text{CH}_2\text{S}\}(\text{CO})_6]$ was heated in refluxing toluene with 2 eq of 1,10-phenanthroline monohydrate (1.163 g) until gas evolution stopped. After filtration, the solvent was removed *in vacuo* and the product was purified by column chromatography on silica gel with CH_2Cl_2 as eluent and washed with pentane. Suitable single crystals for X-Ray diffraction were grown at room temperature from hexane/ CH_2Cl_2 solution. Yield : 0.378 g, 22 %. IR (CH_2Cl_2) : ν_{CO} 2008, 1938, 1895 cm^{-1} , RMN ^1H : (300 MHz, CD_2Cl_2) : 9.00 (d, 2H, $J_{\text{HH}} = 4.3$ Hz, phen), 8.24 (d, 2H, $J_{\text{HH}} = 6.8$ Hz, phen), 7.89 (s, 2H, phen), 7.60 (dd, 2H, $J_{\text{HH}} = 5.5$ Hz, $J_{\text{HH}} = 6.2$ Hz, phen), 3.33 (d, 2H, $J_{\text{HH}} = 11$ Hz, $\text{N}(\text{CH}_2)_2\text{S}_2$), 2.88 (spt, 1H, $J_{\text{HH}} = 6.5$ Hz, $\text{NCH}(\text{CH}_3)_2$), 2.76 (d, 2H, $J_{\text{HH}} = 11$ Hz, $\text{N}(\text{CH}_2)_2\text{S}_2$), 0.95 (d, 6H, $J_{\text{HH}} = 6.6$ Hz, $\text{NCH}(\text{CH}_3)_2$) ; RMN $^{13}\text{C}\{^1\text{H}\}$ (300 MHz, CD_2Cl_2) : 217.2 (s, CO), 214.4 (s, CO), {151.1, 148.0, 132.8, 130.0, 127.0, 122.7} (phen), 18.9 (s, $\text{NCH}(\text{CH}_3)_2$), 50.3 (s, $\text{N}(\text{CH}_2)_2\text{S}_2$), 56.5 (s, $\text{NCH}(\text{CH}_3)_2$)

Table 1

Isomer a ($\approx 70\%$)	Isomer b ($\approx 30\%$)
8.94 (d, 2H, $J_{\text{HH}} = 5.2$ Hz ,phen)	8.91 (d, 2H, $J_{\text{HH}} = 4.8$ Hz ,phen)
8.69 (d, 2H, $J_{\text{HH}} = 8.1$ Hz ,phen)	8.69 (d, 2H, $J_{\text{HH}} = 8.1$ Hz ,phen)
8.22 (s, 2H, phen)	8.22 (s, 2H, phen)
7.93 (dd, 2H, nr, phen)	7.93 (dd, 2H, nr, phen)
4.25 (d, 2H, $J_{\text{HH}} = 12.0$ Hz , $\text{N}(\text{CH}_2)_2\text{S}_2$)	4.43 (d, 2H, $J_{\text{HH}} = 12.2$ Hz , $\text{N}(\text{CH}_2)_2\text{S}_2$)
3.96 (spt, 1H, $J_{\text{HH}} = 6.7$ Hz, $\text{NCH}(\text{CH}_3)_2$)	3.96 (spt, 1H, $J_{\text{HH}} = 6.7$ Hz, $\text{NCH}(\text{CH}_3)_2$)
3.12 (d, 2H, $J_{\text{HH}} = 12.0$ Hz , $\text{N}(\text{CH}_2)_2\text{S}_2$)	3.34 (d, 2H, $J_{\text{HH}} = 12.2$ Hz , $\text{N}(\text{CH}_2)_2\text{S}_2$)
1.49 (d, 6H, $J_{\text{HH}} = 6.85$ Hz, $\text{NCH}(\text{CH}_3)_2$)	1.48 (d, 6H, $J_{\text{HH}} = 6.6$ Hz, $\text{NCH}(\text{CH}_3)_2$)

Figure a



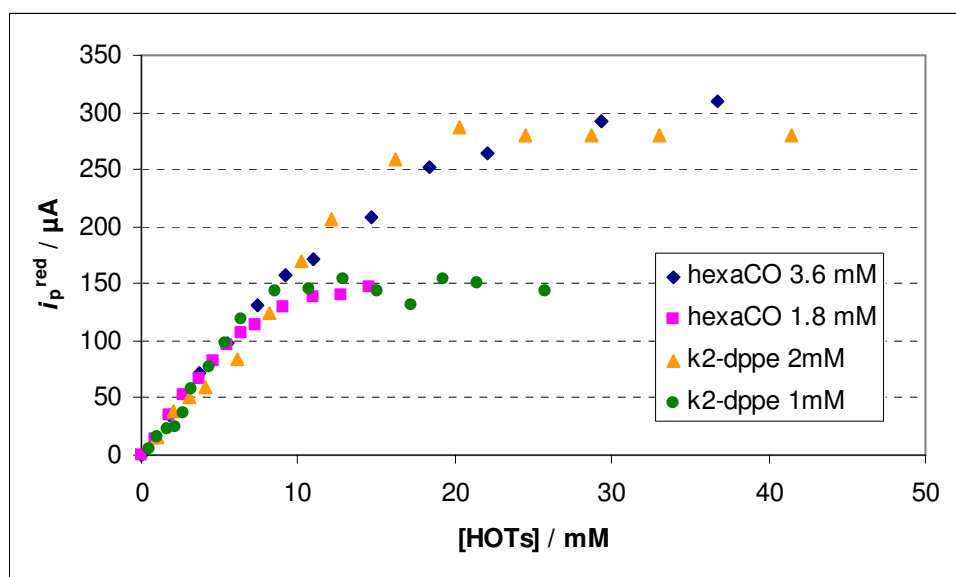


Figure b : Acid-dependence of the reduction current for $[\text{Fe}_2(\text{CO})_4(\kappa^2\text{-dppe})\{\mu\text{-SCH}_2\text{N}(\text{iPr})\text{CH}_2\text{S}\}]$ (**1**) and for $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SCH}_2\text{N}(\text{iPr})\text{CH}_2\text{S}\}]$; the concentrations of complex (k2-dppe = **1** and hexaCO = $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SCH}_2\text{N}(\text{iPr})\text{CH}_2\text{S}\}]$) are indicated on the diagram; the currents (i_p^{red}) were measured by cyclic voltammetry at a scan rate of 0.2 V s^{-1} at the peak potential of process A for both complexes; the data for $[\text{Fe}_2(\text{CO})_6\{\mu\text{-SCH}_2\text{N}(\text{iPr})\text{CH}_2\text{S}\}]$ were taken from reference 24.