# Nitric Oxide activation facilitated by cooperative multimetallic electron transfer within an iron-functionalized polyoxovanadate-alkoxide cluster

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**Supporting Information Table of Contents:**

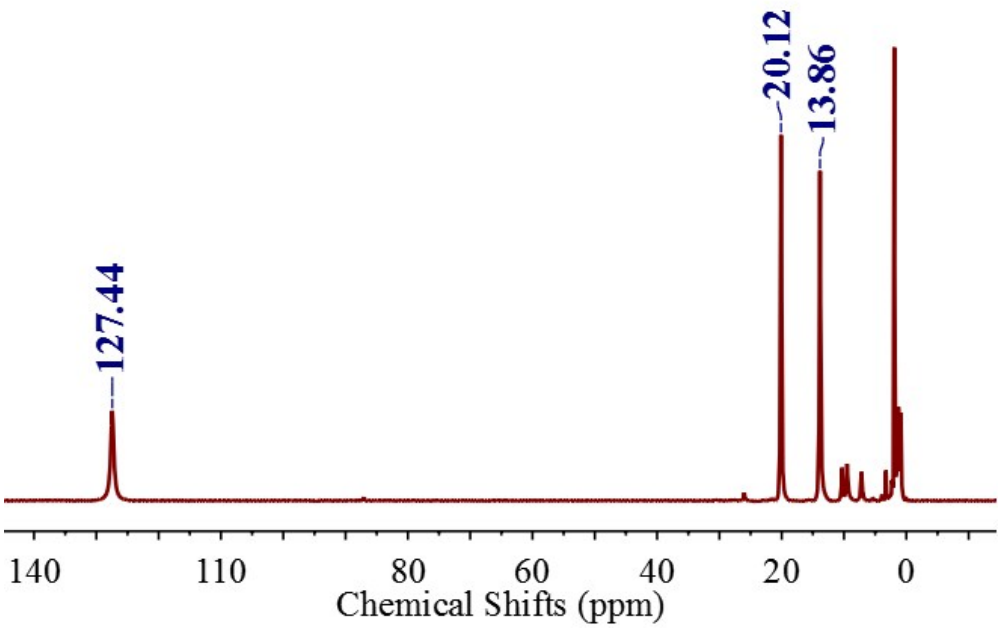


**Figure S1.** $^{1}$H NMR (500 MHz) spectrum of **2-$V_5$FeNO** ($CD_3CN$, 21 °C).

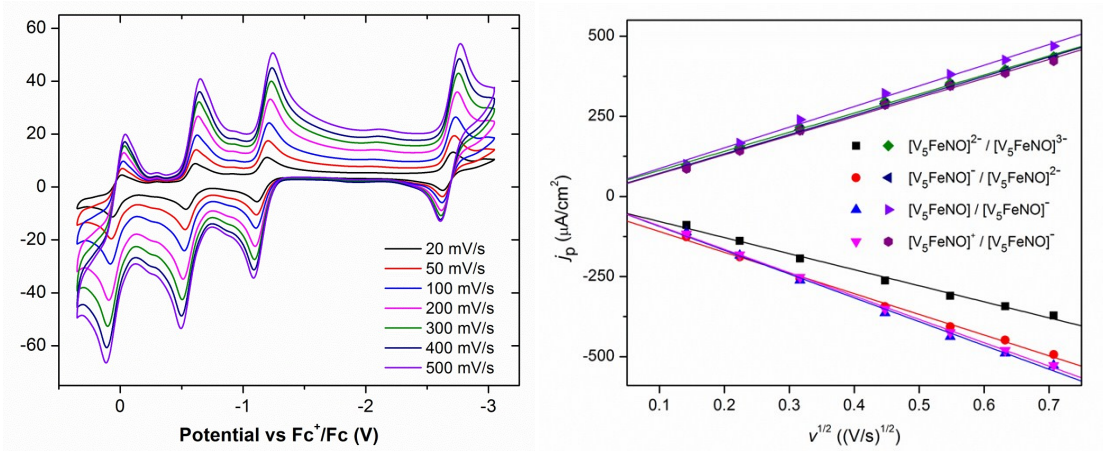


**Figure S2.** Electrochemical data to test the reversibility of redox couples observed for complex **2-$V_5$FeNO**. a.) Cyclic voltammetry of **2-$V_5$FeNO** (2 mM) taken at scan rates ranging from 20 to 500 mV/s in THF with a 0.4 M $[Bu_4N][PF_6]$ as the supporting electrolyte. b.) Plot of current density ($j_p$) vs the square root of the scan rate ($v^{1/2}$) for complex **2-$V_5$FeNO.**

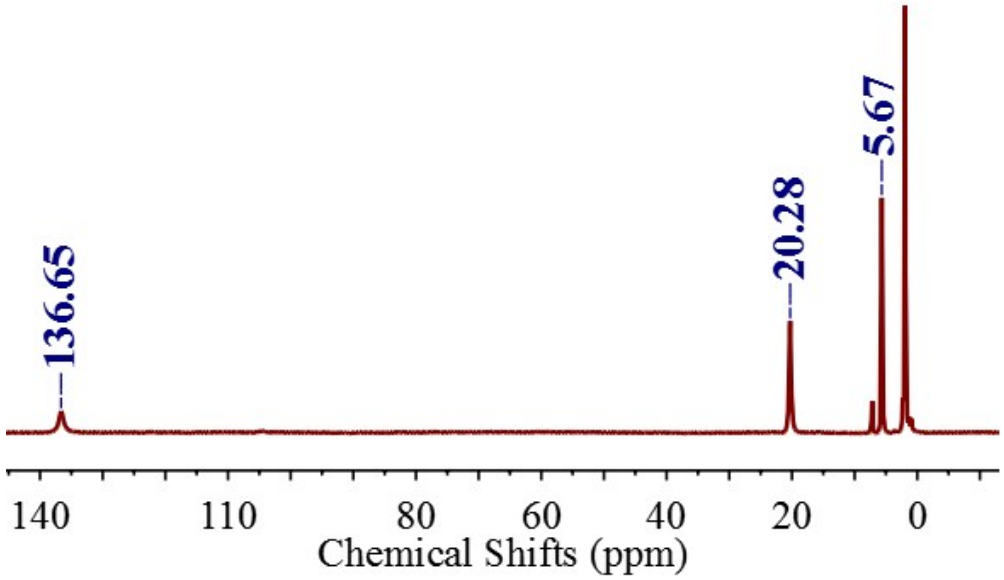


**Figure S3.** $^{1}$H NMR (500 MHz) spectrum of **3-$CoCp_2V_5FeNO$** ($CD_3CN$, 21 °C).

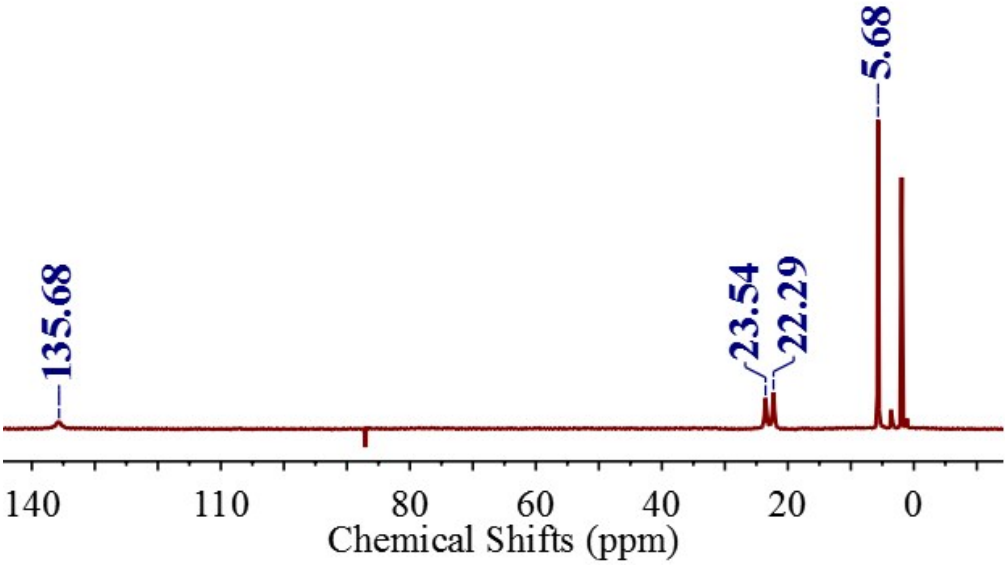


**Figure S4.** $^{1}$H NMR (500 MHz) spectrum of **4-$(CoCp_2)_2V_5FeNO$** ($CD_3CN$, 21 °C).

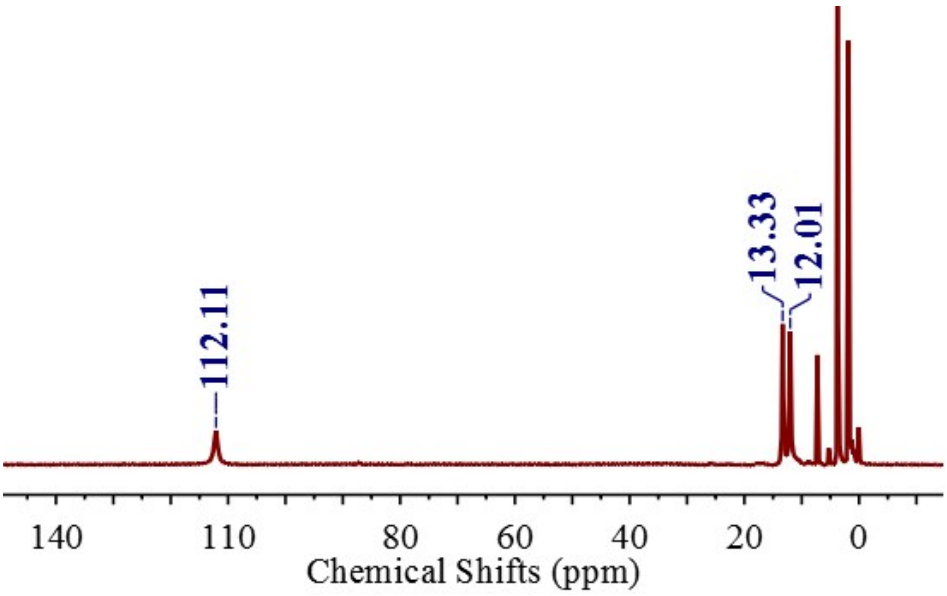


**Figure S5.** $^{1}$H NMR (500 MHz) spectrum of **5-$V_5$FeNOClO$_4$** ($CDCl_3$, 21 °C).

**Figure S6**. 10 K EPR spectrum of complex **3-$V_5$FeNO$^-$** measured in acetonitrile.

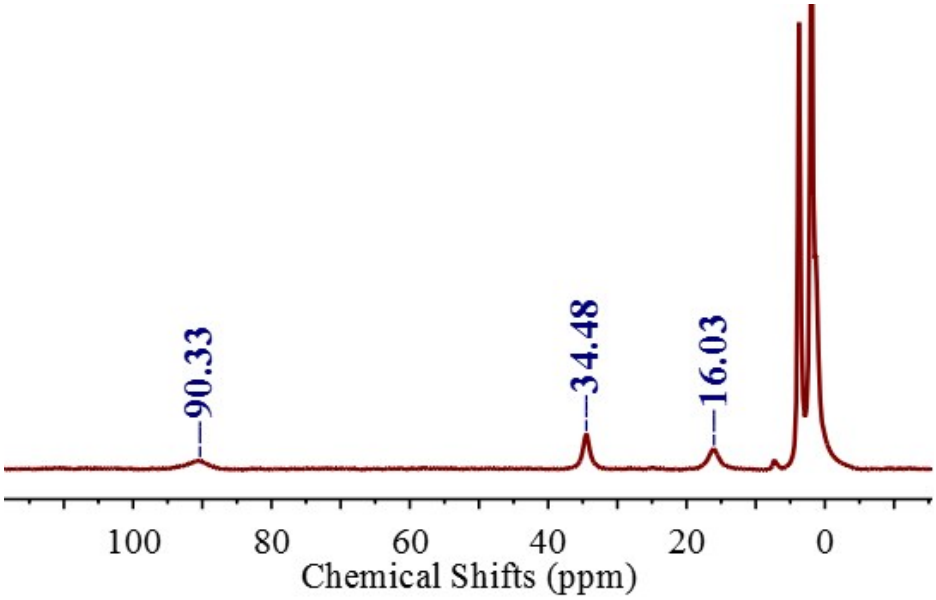


**Figure S7.** $^{1}$H NMR (500 MHz) spectrum of **6- $Na_3V_5FeNO$** ($CD_3CN$, 21 °C).

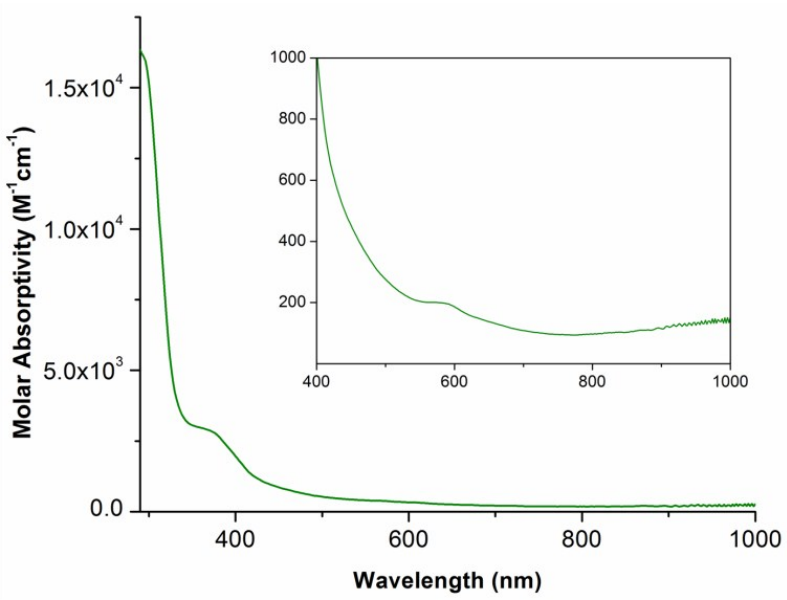


**Figure S8.** Electronic absorption spectrum of **6-$Na_3V_5FeNO$** collected in $CH_3CN$ at 21 °C (the inset shows the low-energy region of the spectrum).

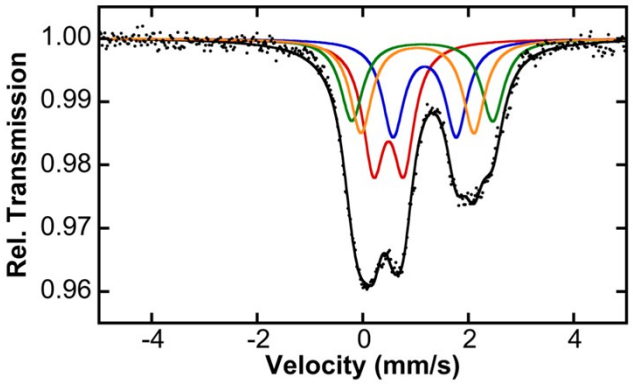


**Figure S9.** 80 K Mössbauer spectrum of the reduction of complex **2-$V_5$FeNO** with sodium napthalanide. Spectrum reveals decomposition of the fully reduced cluster.

**Table S1.** $^{57}$Fe Mössbauer spectroscopic parameters of the decomposition of the product of the reduction of **2-$V_5$FeNO** with sodium napthalanide.

| **Compound** | **Percentage of Sample** | **$\delta$ (mm s$^{-1}$)** | **$\Delta E_Q$ (mm s$^{-1}$)** |
|---|---|---|---|
| Blue Trace | 24% | 1.17 | 1.20 |
| Green Trace | 22% | 1.13 | 2.67 |
| Orange Trace | 24% | 1.04 | 2.14 |
| Red Trace (**[$V_5O_6(OCH_3)_{12}Fe]^-$**) *Inorg. Chem.* **2017**, *56*, 7065-7080 | 30% | 0.49 | 0.57 |